CO₂ REMOVAL IN POWER SYSTEMS USING CALCIUM-BASED SORBENTS

by

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ABSTRACT

Bench scale studies were carried out, focusing on the application of calcium-based sorbents in fossil-fuel-fired combustion and gasification systems, with conditions ranging from atmospheric to elevated pressures and at practical combustion and gasification temperatures.

In the kinetic study of CaO carbonation, the reaction order changed abruptly from first- to zero-order when the CO₂ partial pressure exceeded the equilibrium value by more than ~10 kPa. A Langmuir mechanism successfully explained the experimental information, with the intermediate complex CaO•CO₂ postulated to saturate CaO sites immediately at high CO₂ partial pressure. The activation energies for rate constants were found to be 29±4 kJ/mol and 24±6 kJ/mol for Strassburg limestone and Arctic dolomite, respectively. A discrete-pore-size-distribution-based model was formulated, with the aid of which the kinetic study was extended to obtain diffusivities through the solid product layer formed during carbonation, with activation energies of 215 and 187 kJ/mol for the limestone and dolomite, respectively.

Sorbent cyclic CO₂ removal ability was investigated based on pore size distribution measurements. Several important features observed from measurements could be predicted by a mechanistic model which included simultaneous sintering and calcination in the fixed bed. It was found that the decay in the reversibility of limestone capture/regeneration was insensitive to operating conditions; the achievable carbonation extent of each cycle depends on the <~220 nm pore volume that decreases monotonically during cycling.

Co-capture of SO₂ and CO₂ was attempted at fluidized bed combustion temperatures. Parametric studies with Strassburg limestone and Arctic dolomite found that the presence of SO₂ impeded carbonation even at low concentrations of SO₂ relative to CO₂ concentrations. This finding is significant for the application of calcium-based sorbents in fluidized-bed combustors.
(FBCs), given the initial assumption that sulphur should not be problematic given the low sulfur/carbon ratio in fuels. The mechanism of the impeding effect of SO$_2$ was investigated for seven sorbents at both atmospheric and elevated pressures. It was found that direct sulphation becomes dominant after completion of an initial fast stage of carbonation, enveloping the sorbents and inhibiting further carbonation. Among the techniques tested, increasing the CO$_2$ partial pressure was found to be the most helpful way to improve sorbent reversibility.

It was also shown that often-cycled sorbents can be reactivated and achieve improved reversibility by the use of low-temperature steam or liquid water. CO is not appropriate as an agent to cyclically regenerate CaO from CaSO$_4$ because of slow regeneration of CaSO$_4$. Among the inert dopants tested, only Al$_2$O$_3$ mixed with CaO at a 1:1 molar ratio, was able to achieve satisfactory CO$_2$ capture reversibility.

As extensions of the applications of calcium-based sorbents, sequential SO$_2$ and CO$_2$ capture were investigated for fluidized bed combustion. Among the four options examined, the best was found to be to apply spent sorbent after cyclic CO$_2$ capture to remove SO$_2$ from atmospheric pressure combustors.

A novel concept of co-capture of CO$_2$ and H$_2$S in a gasifier-based process was also investigated. Unlike the findings for co-capture of SO$_2$ and CO$_2$, no obvious impeding effect of H$_2$S was observed on cyclic CO$_2$ capture. Parametric studies indicated that it should be feasible to co-capture H$_2$S and CO$_2$. With CO$_2$ sorbents in a gasifier, one-step hydrogen production via gasification should be achievable.
# TABLE OF CONTENTS

ABSTRACT ................................................................. ii

TABLE OF CONTENTS .................................................. iv

LIST OF TABLES ......................................................... viii

LIST OF FIGURES ........................................................ xi

ACKNOWLEDGEMENTS ................................................... xx

CO-AUTHORSHIP STATEMENT ......................................... xxi

CHAPTER 1 INTRODUCTION, THERMODYNAMICS AND EQUIPMENT ...... 1

1.1 Background and structure of this thesis: using calcium-based sorbent to removal CO₂ ..... 1

1.2 Thermodynamics underlying this thesis ........................................... 5

1.2.1 Sorbent properties, calcination and carbonation ............................... 5

1.2.2 Sorbent calcination temperature .................................................. 6

1.2.3 CO₂ capture in FBC: Effect of SO₂ on CaO carbonation ...................... 11

1.2.4 CO₂ capture during gasification .................................................. 12

1.2.5 Sorption-enhanced hydrogen production using a calcium-based CO₂ sorbent .......... 14

1.2.6 Effect of H₂O, low-temperature eutectic between CaO-Ca(OH)₂-CaCO₃ ............ 16

1.3 Experimental equipment and materials ........................................... 17

1.3.1 Apparatus ................................................................................ 17

1.3.2 Sorbents .................................................................................. 20

1.4 Nomenclature ............................................................................. 21

CHAPTER 2 DETERMINATION OF INTRINSIC RATE CONSTANTS OF THE CaO-
CO₂ REACTION................................................................. 22

2.1 Introduction .............................................................................. 22

2.2 Experimental details ................................................................. 23

2.2.1 Elimination of physical limitations in ATGA tests .............................. 24

2.2.2 PTGA tests .............................................................................. 26

2.3 Results and discussion ............................................................... 27

2.3.1 Direct measurement of carbonation kinetics: use of a gas-solid reaction model ........ 27

2.3.2 High-pressure measurement ..................................................... 31

2.3.3 Carbonation data from equilibrium analyses .................................... 32

2.3.4 Comparison with earlier results ................................................ 33

2.3.5 Mechanistic explanations for the variable order reaction .................... 34

2.3.6 Other issues ............................................................................ 36
### CHAPTER 3 A DISCRETE-PORE-SIZE-DISTRIBUTION BASED GAS-SOLID MODEL AND ITS APPLICATION ON THE CaO+CO\textsubscript{2} REACTION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Introduction</td>
<td>48</td>
</tr>
<tr>
<td>3.2 Experimental details</td>
<td>51</td>
</tr>
<tr>
<td>3.3 Model development</td>
<td>52</td>
</tr>
<tr>
<td>3.3.1 Pore overlap</td>
<td>52</td>
</tr>
<tr>
<td>3.3.2 Model description</td>
<td>53</td>
</tr>
<tr>
<td>3.3.3 Rate expressions</td>
<td>56</td>
</tr>
<tr>
<td>3.3.4 Reaction front, pore evolution and conversions by volume balance</td>
<td>58</td>
</tr>
<tr>
<td>3.3.5 Algorithm</td>
<td>59</td>
</tr>
<tr>
<td>3.4 Results and discussion</td>
<td>60</td>
</tr>
<tr>
<td>3.5 Conclusions</td>
<td>66</td>
</tr>
<tr>
<td>3.6 Nomenclature</td>
<td>68</td>
</tr>
</tbody>
</table>

### CHAPTER 4 INVESTIGATION OF EFFECT OF SINTERING ON CYCLIC CO\textsubscript{2} CAPTURE UNDER FLUIDIZED BED COMBUSTION CONDITIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>81</td>
</tr>
<tr>
<td>4.2 Experimental studies</td>
<td>82</td>
</tr>
<tr>
<td>4.3 Pore size distribution</td>
<td>84</td>
</tr>
<tr>
<td>4.4 Model development</td>
<td>86</td>
</tr>
<tr>
<td>4.4.1 Pore evolution during cyclic calcination/carbonation</td>
<td>86</td>
</tr>
<tr>
<td>4.4.2 Reactor model for calcination</td>
<td>90</td>
</tr>
<tr>
<td>4.4.3 Macroscopic sintering during cyclic calcination/carbonation cycles</td>
<td>93</td>
</tr>
<tr>
<td>4.4.4 Results and discussion</td>
<td>95</td>
</tr>
<tr>
<td>4.5 Conclusions</td>
<td>98</td>
</tr>
<tr>
<td>4.6 Nomenclature</td>
<td>99</td>
</tr>
</tbody>
</table>

### CHAPTER 5 SIMULTANEOUS CO\textsubscript{2} AND SO\textsubscript{2} CAPTURE AT FLUIDIZED BED COMBUSTION TEMPERATURES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>114</td>
</tr>
<tr>
<td>5.2 Experimental details</td>
<td>116</td>
</tr>
<tr>
<td>5.3 Results and Discussion:</td>
<td>117</td>
</tr>
<tr>
<td>5.3.1 Baseline runs: carbonation test with no SO\textsubscript{2} in gas stream</td>
<td>117</td>
</tr>
<tr>
<td>5.3.2 Simultaneous sulphation and carbonation: Effect of SO\textsubscript{2} on CO\textsubscript{2} capture</td>
<td>118</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

Table 1.1 Eutectic formation conditions for the CaO-Ca(OH)$_2$ and CaCO$_3$-Ca(OH)$_2$ system .................................................. 17
Table 1.2 Chemical analyses (% by wt in each case) ................................................................. 20
Table 1.3 Summary of sorbents and reactors in each chapter .................................................. 21
Table 3.1 Comparison of activation energies for effective diffusivity in reactions between CaO or CaCO$_3$ and gases of interest in this work .................................................. 63
Table 4.1 Fitted results for $u_{bed}$ (in equation 4.5) ................................................................. 95
Table 7.1 Regeneration conditions and CaS/CaO test ............................................................... 173
Table 7.2 Test conditions of CaSO$_4$ regeneration by CO ....................................................... 175
Table 7.3 Summary of experiments to test possible additives to improve sorbent reversibility 181
Table 8.1 Gas compositions for the four options examined. All reactions were conducted at 850°C ................................................................. 195
Table 8.2 Sulphation extents after direct sulphation ............................................................... 201
Table A1.1 Fitting results with nonlinear equations. Values in [ ] are values with 95% confidence level. Values in bold are utilized in Chapter 2 .................................................. 267
Table A1.2 Fitting results with linear fit to logarithmic equations. Values in [ ] are values with 95% confidence level; Values in bold are adopted in Chapter 3 .................................................. 268
Table AIX. 1 Proximate and ultimate analysis for the fuels simulated ................................. 307
Table AIX.2 Summary of simulation results for overall mass balance ................................. 308
Table AIX.3 Summary of gas emissions .................................................................................... 308
Table AIX.4 Calculation results for all streams in Figure VIII.1 (with CaO conversion to CaCO$_3$ is assumed as 0.4 in the CARBONER block) .................................................. 314
LIST OF FIGURES

Figure 1.1 Schematic diagram of the process studied in this thesis work to apply calcium-based sorbents .................................................. 4
Figure 1.2 Phase diagram for calcite and aragonite. Adapted from the work of Redfern et al., (1989) .................................................. 6
Figure 1.3 Ellingham plot for the three carbonate decomposition reactions with isobaric lines for partial pressure of CO₂ .................................................. 8
Figure 1.4 Maximum CO₂ removal efficiency as a function of total pressure and molar fraction of CO₂ in the flue gas at the inlet of reactor for a temperature of 850°C .................................................. 10
Figure 1.5 Ellingham plot for CaO and MgO hydration reactions isobaric lines for partial pressure of H₂O .................................................. 11
Figure 1.6 Equilibrium SO₂ concentrations for reaction given in equation (1.8) as the function of reactor temperature and total pressure in the presence of 3%v O₂ .................................................. 12
Figure 1.7 Thermodynamic predictions for gaseous products as a function of temperature for 0.76 MPa total pressure. Gas feed: 1%v H₂S, 20%v CO₂, 12.6%v H₂ and 1.5%v CO with N₂ balance .................................................. 13
Figure 1.8 Effect of CO₂ capture on H₂ production in a simulated gasification system. Feed: 1 kmol carbon, 1.5 kmol steam, 0.01 kmol H₂S, with and without 1 kmol CaO .................................................. 15
Figure 1.9 Schematic of SHIMADZU-based atmospheric thermogravimetric analyzer system (ATGA) .................................................. 18
Figure 1.10 Schematic of pressurized thermogravimetric analyzer (PTGA) system .................................................. 19
Figure 1.11 Schematic of atmospheric thermogravimetric reactor (ATGR) system .................................................. 20
Figure 2.1 High-resolution SEM picture, 38-45 μm Strassburg limestone, calcined under isothermal heating, final temperature 850°C .................................................. 41
Figure 2.2 Slope extraction with the aid of the grain model during early stages of carbonation for 38-45 μm Strassburg limestone particles at 700°C with 15% CO₂ and 85% He .................................................. 41
Figure 2.3 Typical grain model plots. Early stage of carbonation for 38-45 μm Strassburg limestone particles .................................................. 42
Figure 2.4 Reaction order plot (Squares: 850°C; Triangles: 600°C) for fully calcined 38-45 μm Strassburg limestone with varying CO₂ partial pressure, helium making up the balance of the gas stream. RMSE=Root mean square error .................................................. 42
Figure 2.5 Reaction order plot (Squares: at 850°C; Triangles at 600°C) for fully calcined 38-45 μm Arctic dolomite with varying CO₂ partial pressure, helium making up the balance of the gas stream. RMSE= Root mean square error .................................................. 43
Figure 2.6 Arrhenius plot for carbonation reaction with 38-45 μm Strassburg limestone particles .................................................. 43
Figure 2.7 Arrhenius plot for carbonation reaction with 38-45 μm Arctic dolomite particles .................................................. 44
Figure 2.8 Conversion vs time for typical kinetic run showing induction period and how the initial rates were obtained based on the maximum slopes. Strassburg limestone, 38-45 μm, 800 kPa, carbonation with 100% CO₂, 690°C.

Figure 2.9 Conversion vs time for typical kinetic run showing induction period and how the initial rates were obtained based on the maximum slopes. Arctic dolomite, 38-45 μm, 0.8 MPa, carbonation with 100% CO₂ at 764°C.

Figure 2.10 Arrhenius plot comparing PTGA runs (at a total pressure of 0.8 MPa, with 100% CO₂) with ATGA runs for 38-45 μm Strassburg limestone.

Figure 2.11 Arrhenius plot. Comparison of PTGA runs (at total pressure of 0.8 MPa, with 100% CO₂) with ATGA runs for 38-45 μm Arctic dolomite.

Figure 2.12 Arrhenius plot for CaO-CO₂ reaction based on calcination data of Borgwardt (1985).

Figure 2.13 Illustration of energy levels for CaO+CO₂<=>CaCO₃.

Figure 3.1 Schematic of a two-pore system with overlap.

Figure 3.2 Schematic of a two-pore system after evolution.

Figure 3.3 Pore size distribution results for Strassburg limestone calcines. Calcination conditions: isothermal calcination at 850°C in 100% N₂.

Figure 3.4 Pore size distribution results for Arctic dolomite calcines. Calcination conditions: isothermal calcination at 850°C in 100% N₂.

Figure 3.5 Fitting results. Experiments were in ATGA, with 80%v CO₂, 20% N₂ balance and 35-45 μm Strassburg limestone particle. Experiment points.

Figure 3.6 Fitting results. Experiments were in ATGA with 100%v CO₂ and 35-45 μm Arctic dolomite particle.

Figure 3.7 Arrhenius plot for diffusivity, Dₚ, Strassburg limestone. E=215 kJ/mol.

Figure 3.8 Arrhenius plot for diffusivity, Dₚ, Arctic dolomite. E=187 kJ/mol.

Figure 3.9 Experimental carbonation data showing effect of varying CO₂ partial pressure for 38-45 μm Strassburg limestone. Pₐ is calculated from equation (3.19) (a) ATGA at 600°C (b) ATGA at 850°C (c) PTGA at 800 kPa compared with ATGA tests.

Figure 3.10 Experimental carbonation data showing effect of varying CO₂ partial pressure for 35-45 μm Arctic dolomite. Pₐ is calculated from equation (3.19) (a) ATGA at 600°C (b) ATGA at 850°C (c) PTGA at 800 kPa compared with ATGA tests.

Figure 3.11 Predicted effect of varying CO₂ partial pressure for 35-45 μm Strassburg limestone vs experimental data. Pₐ is 48 kPa for 850°C and 0.36 kPa for 600°C, as calculated from equation (3.19).

Figure 3.12 Predicted effect of varying CO₂ partial pressure for 35-45 μm Arctic dolomite vs experimental data. Pₐ is 48 kPa for 850°C and 0.36 kPa for 600°C, as calculated from equation (3.19).

Figure 3.13 Predicted CO₂ concentration at reaction front for Strassburg limestone at 600°C, with varying Pₐ. Pₐ is 0.36 kPa for 600°C, calculated from equation (3.19).
Figure 3.14 Predicted CO₂ concentration at reaction front for Arctic dolomite at 600 °C, with varying P₁CO₂. P₁CO₂,eq is 0.36 kPa for 600°C, calculated from equation (3.19).

Figure 3.15 Pore size distribution evolution for Strassburg calcine carbonation at 600°C and 80 kPa CO₂ partial pressure.

Figure 3.16 Pore size distribution evolution for Arctic dolomite calcine carbonation at 600°C and 100 kPa CO₂ partial pressure.

Figure 4.1 Pore size distribution: effect of carbonation time. Experiments: 850°C for calcination and carbonation in the TGR. 212-250 µm Strassburg particles. Calcination with 100% N₂; carbonation with 100% CO₂, fast stage completed.

Figure 4.2 Pore size distribution: carbonate before and after mild grinding. Same test conditions as in Figure 4.1.

Figure 4.4 Pore size distribution: effect of calcination time or mode. Same test conditions as in Figure 4.1.

Figure 4.5 Pore size distribution: calcines after various number of calcination/carbonation cycle. Test conditions as in Figure 4.1.

Figure 4.6 SEM pictures of cycled Strassburg calcine samples after 15 cycles of 850°C calcination/carbonation cycles. Test conditions as in Figure 4.1.

Figure 4.7 Conversion of CaO to CaCO₃: Experiments vs Predictions with pore volume. Experimental conditions: 850°C for calcination and carbonation in the TGR. 212-250 µm Strassburg particles. Calcination with 100% N₂, carbonation with 100% CO₂, fast stage completed.

Figure 4.8 Specific surface area after each cycle of calcinations: experimental results vs. predictions. The predictions show the sensitivity to S₂. Strassburg limestone, TGR test, 850°C calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast stage of carbonations completed.

Figure 4.9 Schematic of sintering progression during cyclic calcination and carbonation.

Figure 4.10 Reversibility under different test conditions in the TGR or TGA. All with Strassburg limestone, calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast stage of carbonation finished for each cycle of carbonation.

Figure 4.11 CaO conversion profiles for several calcination cycles: experimental results vs. predictions. 212-250 µm Strassburg limestone, TGR test, 850°C calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast Stage of carbonation finished for each cycle of carbonation.

Figure 4.12 Reversibility: experimental results vs. predictions for 212-250 µm Strassburg limestone in the TGR. Calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast Stage of carbonations is allowed to finish for each carbonation cycle.

Figure 4.13 Reversibility: experimental results vs. predictions for 38-45 µm Strassburg limestone in the TGR or TGA. Calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast Stage of carbonations is finished for each carbonation cycle.
Figure 4.14 Calcination time: experimental results vs. prediction. Calcinations: in 100% N₂, carbonation: 850°C, in 100% CO₂. Fast Stage of carbonation is finished for each carbonation step.

Figure 4.15 Predicted CaO utilizations for 1000 cycles. Same calculation conditions as in Figure 4.12 and 4.13 for each case.

Figure 4.16 Effect of carbonation time on cyclic CO₂ capture performance: experimental results. Starting from 850 mg of 212-250 μm fresh Strassburg limestone. Calcinations: in 100% N₂, 850°C; carbonation: 850°C, in 100% CO₂. Carbonation time at each carbonation stage: FSF-Fast stage finished, comparing with 3-minute and 8 minute for each cycle.

Figure 5.1 CO₂ cyclic capture performance. 212-250 μm Arctic dolomite and Strassburg limestone. Calcination: 850°C in 100% N₂; Carbonation 850°C with 80 or 100% CO₂ (no SO₂). Sorption time is 3, 30 min for each sorption stage or FSF.

Figure 5.2 Illustration for turning point selection in a 100% CO₂ capture test with 212-250 μm Strassburg limestone.

Figure 5.3 Test results for 212-250 μm limestone, 850°C calcination and 850°C sorption with 2900 ppm SO₂ and 80% CO₂.

Figure 5.4 Comparison of initial calcination rate of each cycle for the limestone, 850°C calcination/850°C carbonation, 212-250 μm particle.

Figure 5.5 Effect of cumulative reaction time. 850°C calcination/850°C sorption, gas compositions for SO₂/CO₂ sorption: 80% CO₂, 2900 ppm SO₂, 3% O₂, balance N₂. (Baseline, 80% CO₂ 20% N₂).

Figure 5.6 Total calcium utilization change with cycles for 850°C calcination/850°C sorption, gas compositions for sorption: 80% CO₂, 2900 ppm SO₂, 3% O₂, balance N₂.

Figure 5.7 Effect of reaction temperature CO₂ concentration for each cycle, 212-250 μm, 3-minutes sorption time, 850°C calcination, gas compositions for SO₂/CO₂ sorption: 80% CO₂, 2900 ppm SO₂, 3% O₂, balance N₂. (Baseline, 80% CO₂, 20% N₂).

Figure 5.8 Effect of SO₂ concentration for successive cycles for 212-250 μm particle 850°C calcination/850°C sorption, gas compositions for SO₂/CO₂ sorption: 80% CO₂, 3% O₂, balance N₂. (Baseline, 80% CO₂ 20% N₂).

Figure 5.9 Effect of CO₂ concentration for successive cycles with 212-250 μm limestone. 850°C calcination/850°C sorption. Gas compositions for SO₂/CO₂ sorption: 80% CO₂, 2900 ppm SO₂, 3% O₂, balance N₂. (Base lines, 80% CO₂ 20% N₂).

Figure 5.10 Effect of CO₂ on SO₂ capture. 850°C calcination/850°C sorption. Gas compositions or SO₂/CO₂ sorption: 80% CO₂, 2900 ppm SO₂, 3% O₂. (Baseline: 2900 ppm SO₂, 3% O₂).

Figure 6.1. Calcium utilization over 15 cycles for all seven sorbents with 212-250 μm particles and no SO₂ present. ATGR tests. Carbonation: 80% CO₂, 20% N₂, 850°C and 101 kPa, Fast Stage Finished. Calcination: 100% N₂, 850°C and 101 kPa.
Figure 6.2 High-resolution SEM pictures of calcines, with no SO₂ present. Same test conditions as in Figure 6.1. (a) Strassburg limestone, after 15 cycles (b) Kelly Rock limestone, after 15 cycles; (c) Arctic dolomite, after 20 cycles.

Figure 6.3 Evolution of pore size distribution with calcination/carbonation cycling at 850°C. Test conditions: same as in Figure 6.1 for no SO₂ test and in Figure 6.6 for co-capture (a) Strassburg limestone; (b) Kelly Rock limestone; (c) Arctic dolomite.

Figure 6.4 Cyclic performance with no SO₂ present: effect of calcination type. Calcination/carbonation cycling at 850°C with 212-250 μm Strassburg particles.

Figure 6.5 Cyclic performance with no SO₂ present: effect of total pressure. Calcination/carbonation cycling at 850°C PTGA test: 212-250 μm Arctic dolomite.

Figure 6.6 Performance of all seven sorbents for co-capture. ATGR tests, calcination/carbonation cycling at 850°C and 101 kPa with 212-250 μm particles. Sorption: 80% CO₂, 2900 ppmv SO₂, 3%v O₂ and balance N₂, 8 minutes for each cycle. Calcination: 100% N₂. (Lines show corresponding results with no SO₂ present for two of the sorbents.)

Figure 6.7 ATGR once-through tests, at 850°C and 101 kPa with 212-250 μm Strassburg limestone. Top and bottom curves and for limiting case where there was no SO₂ or CO₂ respectively. Points are for co-capture case showing total (squares) calcium utilization, utilization for CO₂ capture (triangles) and utilization for SO₂ capture (circles).

Figure 6.8 Relation between sulfate content and calcination rate for three sorbents. ATGR co-capture tests, same conditions as in Figure 6.

Figure 6.9 Cyclic CO₂ retention performances in 850°C PTGA tests: effect of total pressure. Co-capture with 212-250 μm Strassburg limestone. Sorption: 8%v CO₂, 1125 ppmv SO₂, 3% O₂, and balance N₂, 4 minute for each cycle. Calcination: 101 kPa, 100% N₂.

Figure 6.10 Cyclic CO₂ retention performances in 850°C PTGA tests: effect of total pressure. Co-capture with 212-250 μm Arctic dolomite. Sorption: 8%v CO₂, 1125 ppmv SO₂, 3% O₂, and balance N₂, 4 minute for each cycle. Calcination: 101 kPa, 100% N₂.

Figure 6.11 Sulfur mapping for non-calcined ATGR samples from varied co-capture cycles, same test conditions as in Figure 6.6. (Light points mark sulfur) (a) Strassburg limestone after 12 cycles (b) Kelly Rock limestone after 15 cycles (c) Arctic dolomite, after 7 cycles.

Figure 6.12 High-resolution SEM pictures for calcines after ATGR co-capture tests. (a) Strassburg limestone, after 12th cycle (b) Kelly Rock limestone, after 15th cycle (c) Arctic dolomite, after 7th cycle.

Figure 6.13 Cyclic performances during PTGA co-capture tests: effect of P₇CO₂. 212-250 μm Strassburg limestone. Sorption at 850°C and 1.8 MPa, with 1125 ppmv SO₂, 3%v O₂ and balance N₂, 4 minutes for each cycle and calcination at 850°C and 101 kPa, 100% N₂. (a) For CaO conversion to CaCO₃; (b) For CaO conversion to CaSO₄.

Figure 6.14 Cyclic performance during PTGA co-capture tests: effect of P₇CO₂. 212-250 μm Arctic dolomite particles. Sorption at 850°C, and 1.8 MPa, with 1125 ppmv SO₂, 3%v O₂.
and balance N\(_2\), 4 minutes for each cycle and calcination at 850°C and 101 kPa, 100% N\(_2\).
(a) For CaO conversion to CaCO\(_3\); (b) For CaO conversion to CaSO\(_4\).

Figure 7.1 High-resolution SEM photos of calcines derived from initial calcination of 212-250 \(\mu m\) Strassburg limestone particles; (a) h-CaO (b) c-CaO.

Figure 7.2 Cyclic performance: comparison of c-CaO and h-CaO (no SO\(_2\) present, sorbent derived from 212-250 \(\mu m\) Strassburg limestone). Test conditions: 850°C calcination and carbonation, carbonation in 100% CO\(_2\), calcination in 100% N\(_2\). Fast stage of carbonation finished.

Figure 7.3 Pore size distribution: comparison of c-CaO and h-CaO (no SO\(_2\) present, sorbent derived from Strassburg limestone). Samples are the same as in Figure 7.2.

Figure 7.4 Effect of steam calcination on cyclic capture (No SO\(_2\) present, 212-250 \(\mu m\) Strassburg limestone Strassburg limestone). Test conditions: 850°C calcination and carbonation, Carbonation in 100% CO\(_2\). Calcination in 95% steam, balance N\(_2\). Fast stage of carbonation finished.

Figure 7.5 Pore size distribution: effect of steam calcination (No SO\(_2\) present, Strassburg limestone). Same samples as in Figure 7.4.

Figure 7.6 Calcium utilization for CO\(_2\) capture: effect of varying operating conditions, 212-250 \(\mu m\) particles Test conditions: 850°C calcination and sorption. Sorption in 80% CO\(_2\), 3% O\(_2\), 2900 ppm SO\(_2\) and balance N\(_2\) or with steam. Calcination in 100% N\(_2\). 8 minutes for each sorption.

Figure 7.7 Effect of hydration on co-capture (CO\(_2\)+SO\(_2\)). 212-250 \(\mu m\) Strassburg limestone. Procedure: 1-h co-capture or SO\(_2\) sorption followed by 30 min hydration and 8 min cycles of re-capture: (a) Conversion of CaO to CaCO\(_3\); (b) Conversion of CaO to CaSO\(_4\).

Figure 7.8 Effect of intermediate hydration of carbonates on further carbonation (no SO\(_2\) present) A: 10 min carbonation plus 30 min steam hydration at 300°C plus 30 min carbonation; B: 60 min carbonation plus 30 min steam hydration at 300°C plus 30 min carbonation; C: 60 min carbonation plus 10 min liquid water steam hydration at room temperature plus 30 min carbonation. 850°C for both calcination (100% N\(_2\)) and carbonation (100% CO\(_2\)).

Figure 7.9 Effect of intermediate steam (95%v) or water (100%) hydration at various temperatures of sintered calcines on cycling (no SO\(_2\) present). 850°C for both calcination (100% N\(_2\)) and carbonation (100% CO\(_2\)).

Figure 7.10 Variation of mass increase due to sorption divided by total initial mass of CaO with cycling. Test conditions are provided in Table 7.3.

Figure 7.11 Effect of various dopants on CaO reversibility in cyclic calcination/carbonation. Cycling conditions: 850°C for calcination (in 100% N\(_2\)) and carbonation (in 100% CO\(_2\)): (a) \(\gamma\)-Al\(_2\)O\(_3\); (b) SiO\(_2\) and Kaolinite; (c) ZrO\(_2\); (d) MgO; (e) dolomite, TiO\(_2\), precipitated calcium carbonate; (f) other dopants as identified in Table 7.4.

Figure 8.1 Candidate processes for CO\(_2\) and SO\(_2\) removal with calcium-based sorbents; Options A and C: sulphation before calcination/carbonation; Options B and D: calcination/carbonation before sulphation; Options C and D involve pressurized fluidized-bed combustion (PFBC).
Figure 8.2 Sorbent performance: conversion history based on option A. 212-250 μm Strassburg limestone. Sulphated first for 10 minutes at 850°C and 0.1 MPa. 850°C calcination/carbonation cycles. Baseline conditions for fresh limestone: see Table 8.1 for CO₂ sorption stage.

Figure 8.3. SEM photos for calcines from different runs; for (b), (c) and (d), see Table 8.2, for test conditions. (a) CaO sulphation, followed by 4 calcination/carbonation (c/c) cycles, 12% calcium utilization for sulphation (on molar base). Test conditions: as for solid points in Figure 8.2. Option A. (b) Co-capture for 600 s followed by 4 c/c cycles, Option C. (c) Direct sulphation, 5000 ppm SO₂, for 600 s followed by 4 c/c cycles, Option C. (d) Direct sulphation, 5000 ppm SO₂, for 2400 s followed by 4 c/c cycles, Option C.

Figure 8.4 Sulphation of cycled sorbents after different number of calcination/carbonation cycles. 212-250 μm Strassburg limestone. (Option B)

Figure 8.5 EDX sulfur-mapping of calcines for 212-250 μm Strassburg limestone. Test conditions as in Figure 8.4. (a) Sulphation of Strassburg limestone for 2400 s (Fresh sorbent) (b) Sulphation of Strassburg sorbent after 15 calcination/carbonation cycles.

Figure 8.6 Sulphation of cycled sorbents after different number of calcination/carbonation cycles. 212-250 μm Arctic dolomite (Option B). For conditions, see Table 8.1

Figure 8.7 Mass change profiles during typical runs for Option C with 212-250 μm Strassburg limestone. (a). Direct sulphation for 600 s. (b) Simultaneous sulphation and carbonation for 10 minutes. Test conditions: Both direct sulphation and simultaneous sulphation and carbonation: 5000 ppm SO₂, 15% CO₂, 3% O₂, N₂ balance before calcination/carbonation cycling, 1.82 MPa, 850°C.

Figure 8.8 Cyclic calcination/carbonation performance of 212-250 μm Strassburg limestone after direct sulphation (Option C). See Table 8.1 for calcination/carbonation cycling conditions.

Figure 8.9 Cyclic performance of 212-250 μm Strassburg limestone after simultaneous sulphation and carbonation, and a complete calcination. Option C with 212-250 μm Strassburg limestone. See Table 8.1 for calcination/carbonation cycling conditions.

Figure 8.10 Cyclic performance of 212-250 μm Arctic dolomite after simultaneous sulphation and carbonation, and calcination. Option C. Baseline conditions for fresh sorbent: See Table 8.1 for calcination/carbonation cycling conditions.

Figure 8.11 Cyclic performance of 212-250 μm Arctic dolomite after direct sulphation and calcination. Option C. Baseline test conditions for fresh sorbent: See Table 8.1 for calcination/carbonation cycling conditions.

Figure 8.12 Surface texture of cycled 212-250 μm Arctic particles different sulphation history (a) Same test conditions as in Figure 8.10 (b) Same test conditions as in Figure 8.11.

Figure 8.13 Mass change profiles with simultaneous carbonation and sulphation after 7 cycles of carbonation and calcination. Option D with 212-250 μm Strassburg particles.

Figure 8.14 Sulphation and carbonation extents during co-capture with cycled 212-250 μm Strassburg limestone particles. Option D vs. Option B. See Table 8.1 for conditions.
Figure 8.15 Sulphation and carbonation extents during co-capture with cycled 212-250 μm Arctic dolomite particles. Option D vs. Option B. See Table 8.1 for conditions

Figure 8.16 Effect of small residual $S_0_2$ on calcination/carbonation cycling. 212-250 μm Strassburg limestone particles. Points: Sorption with 14% $C_0_2$, 100 ppmv $S_0_2$, 3% $O_2$ and balance $N_2$ at 850°C and 1.82 MPa. Calcination in 100% $N_2$ at 850°C and atmospheric pressure. Cycling conditions for fresh sorbent with no $S_0_2$ present: see Table 8.1 for carbonation conditions

Figure 9.1 Illustration of operating procedure and masses used to calculate of calcium utilization for $C_0_2$ and $H_2S$ capture. Co-capture at 850°C and 0.76 MPa. Calcination: in 100% $N_2$. Sorption: 1%v $H_2S$, 20%v $C_0_2$, 12.6%v $H_2$ and 1.5%v CO with the balance $N_2$. Calcination in 100% $N_2$. 3 minutes for each sorption stage

Figure 9.2 Once-through tests with 212-250 μm Strassburg limestone. Initial calcination at 850°C and 101 kPa with 100% $N_2$. Co-capture at 850°C and 0.76 MPa with 1%v $H_2S$, 20%v $C_0_2$, 12.6%v $H_2$ and 1.5%v CO, balance $N_2$. Calcination with no $H_2S$: same as for co-capture tests except with no $H_2S$. Sulfidation with no $C_0_2$: same as co-capture tests except with no $C_0_2$

Figure 9.3 Cyclic capture performance for $H_2S$ and $C_0_2$ with 212-250 μm Strassburg limestone at 850°C and 0.76 MPa for sorption, 850°C and 101 kPa for calcination. 3-minute sorption for each cycle. Sorption gas compositions except specified $H_2S$ and $C_0_2$ concentrations in legends: 12.6%v $H_2$, 1%v CO, balance $N_2$. Calcination: 100% $N_2$

Figure 9.4 High-resolution SEM photos of co-capture 212-250 μm Strassburg limestone calcines: (a) $H_2S$ and $C_0_2$ capture in 1%v $H_2S$, 12.6%v $H_2$, 1%v CO, balance $N_2$ (no $C_0_2$). (b) $C_0_2$ and $C_0_2$ capture in 1125 ppmv $S_0_2$, 8%v $C_0_2$, 3%v $O_2$ and balance $N_2$ at 1.8 MPa, 4 min of sorption for each cycle. Sorption and calcination temperatures for both cases were 850°C. All calcinations in 100% $N_2$.

Figure 9.5 EDX sulfur mapping for 212-250 μm reacted Strassburg limestone. (a) Calcine from 1 h continuous sulfidation at 850°C, 0.76 MPa with 1%v $H_2S$, 12.6%v $H_2$, 1.5%v $C_0_2$, balance $N_2$. (b) Calcine from cyclic $H_2S/C_0_2$ sorption for 15 cycles at 850°C, 0.76 MPa with 1%v $H_2S$, 20%v $C_0_2$, 12.6%v $H_2$, 1.5%v CO, balance $N_2$. Calcination at 850°C and 101 kPa with 100% $N_2$. 3 minutes for each sorption stage

Figure 9.6 Mass changes during first and fifth cycles of $H_2S/C_0_2$ capture tests. 212-250 μm Strassburg limestone. Tests conditions except where specified: sorption at 850°C and 0.76 MPa with 20% $C_0_2$, 1%$H_2S$, 12.6%v $H_2$, 1%v CO, balance $N_2$. Calcination at 850°C and 101 kPa with 100% $N_2$. 3 minutes for each sorption stage

Figure 9.7 Effect of changing temperature on cyclic capture of $H_2S$ and $C_0_2$. 212-250 μm Strassburg limestone. Sorption at 0.76 MPa, all with 20% $C_0_2$, 1%$H_2S$, 12.6%v $H_2$, 1%v CO, balance $N_2$. Calcination at 850°C and 101 kPa with 100% $N_2$. 3 minutes for each sorption stage

Figure 9.8 Effect of particle size on cyclic capture of $H_2S$ and $C_0_2$. 212-250 μm Strassburg limestone. Sorption at 850°C and 0.76 MPa, with 20% $C_0_2$, 1%$H_2S$, 12.6%v $H_2$, 1%v CO, balance $N_2$. Calcination at 850°C and 101 kPa with 100% $N_2$. 3 minutes for each sorption stage

Figure 9.9 Effect of cyclic sorption time on cyclic capture of $H_2S$ and $C_0_2$. 212-250 μm Strassburg limestone. Sorption at 850°C and 0.76 MPa, with 20% $C_0_2$, 1% $H_2S$, 12.6%v $H_2$, 1%v CO, balance $N_2$. Calcination at 850°C and 101 kPa with 100% $N_2$. 3 minutes for each sorption stage
H₂, 1%v CO, balance N₂. Calcination at 850°C and 101 kPa with 100% N₂ 3 min for each sorption stage...

Figure 9.10 Effect of total pressure on cyclic capture of H₂S and CO₂. 212-250 μm Strassburg limestone. Sorption at 850°C, with 20% CO₂, 1% H₂S, 12.6%v H₂, 1%v CO, balance N₂. Calcination at 850°C and 101 kPa with 100% N₂ 3 min for each sorption stage...

Figure 9.11 Effect of sorbent type on cyclic capture of H₂S and CO₂. 212-250 μm. Sorption at 850°C and 0.76 MPa, with 20% CO₂, 1% H₂S, 12.6%v H₂, 1%v CO, balance N₂. Calcination at 850°C and 101 kPa with 100% N₂ 3 min for each sorption stage...

Figure 9.12 SEM photos for different sorbents after 15 co-capture cycles. Same test conditions as for Figure 9.10. (a) Arctic dolomite (b) Kelly Rock limestone

Figure 9.13 Sulfur mapping for calcines of different sorbents after co-capture. Same test conditions as for Figure 9.10. (a) Arctic dolomite after 15 cycles. (b) Kelly Rock after 15 cycles.

Figure A1.1 Comparison of experimental and fitting results (Dataset 1)

Figure A1.2 Comparison of experimental and fitting results (Dataset 1). Same as above but in Arrhenius plot

Figure A1.3 Comparison of experimental and fitting results (Dataset 2)

Figure A1.4 Comparison of experimental and fitting equation (Dataset 2) Same as above but in Arrhenius plot

Figure A1.5 Comparison of experimental and fitting equation (Dataset 3) in Arrhenius plot (Data predicted by the nonlinear fitted equation is off this chart)

Figure A1.6 Comparison of experimental and fitting equation (Dataset 4) in Arrhenius plot (Data predicted by the nonlinear fitted equation is off this chart)

Figure AV7.1 Illustration of the relation between initial pore radii based on measured pore volume data

Figure AV7.2 (Comparing with other runs in Figure 6.2) High-resolution SEM pictures of calcines, with no SO₂ present. Same test conditions as in Figure 6.1. Danyang limestone.

Figure AV7.3 (Comparing with other runs in Figure 6.11) Sulfur mapping for non-calcined ATGR samples. 850°C for both tests. SO₂ only test: 2900 ppm SO₂, 3% O₂ and balance N₂ for 2 hours; Co-capture test conditions as in Figure 6.6, 15 cycles. (Light points mark sulfur). Danyang limestone.

Figure AV7.4 (Comparing with other runs in Figure 6.3) Evolution of pore size distribution with calcination/carbonation cycling at 850°C. Test conditions: same as in Figure 6.1 for SO₂ test and in Figure 6.6 for co-captures. Danyang limestone.

Figure AV7.5 (Comparing with other runs in Figure 6.3) Evolution of pore size distribution with calcination/carbonation cycling at 850°C. Test conditions: same as in Figure 6.1 for no SO₂ test and in Figure 6.6 for co-captures. Havelock limestone.

Figure AV7.6 (This is for conversion of CaO to CaSO₄, comparing that for CaO to CaCO₃ shown in Figure 6.9) Cyclic CO₂ retention performances in 850°C PTGA tests: effect of
total pressure. Co-capture with 212-250 μm Strassburg limestone. Sorption: 8 %v CO₂, 1125 ppmv SO₂, 3% O₂, and balance N₂, 4 minute for each cycle. Calcination: 101 kPa, 100% N₂. .................................................................................................................. 296

Figure AVI.6 (This is for conversion of CaO to CaSO₄, comparing that for CaO to CaCO₃ shown in Figure 6.10) Cyclic CO₂ retention performances in 850°C PTGA tests: effect total pressure. Co-capture with 212-250 μm Arctic dolomite. Sorption: 8 %v CO₂, 1125 ppmv SO₂, 3% O₂, and balance N₂, 4 minute for each cycle. Calcination: 101 kPa, 100% 8%v CO₂, 850°C .................................................................................................................. 296

Figure AVII.7 Cyclic performances in no SO₂ only tests: effect of total pressure. Atmospheric calcination. 850°C, 8% CO₂ balanced by N₂, 212-250 μm Straussburg limestone .................................................................................................. 297

Figure AVII.8 Cyclic performances in no SO₂ only tests: effect of temperature. 8%v CO₂ balanced by N₂, 212-250 μm, and Straussburg limestone .................................................................................................. 297

Figure AVII.9 Cyclic performances in no SO₂ only tests: effect of P_CO₂. Pt=18.2 bars CO₂ only, Straussburg, 212-250 μm .................................................................................................................. 298

Figure AVIII.1 Performance of c-CaO and h-CaO (no SO₂ present, sorbent derived from 212-250 μm Arctic dolomite). Same test conditions as specified in Figure 7.2 ........................................................................................................ 299

Figure AVIII.2 Pore size distribution: comparison of c-CaO and h-CaO. (no SO₂ present, sorbent derived from Arctic dolomite) ........................................................................................................ 299

Figure AVIII.3 Effect of steam on cyclic capture (No SO₂ present, 212-250 μm Strassburg limestone). Test conditions: 850°C calcination and carbonation; Carbonation in 86% CO₂ and 14% steam; Calcination in 100% N₂ ........................................................................................................ 300

Figure AVIII.4 Effect of steam on cyclic capture (No SO₂ present, 212-250 μm Arctic dolomite). Test conditions: 850°C calcination and carbonation; Carbonation in 86% CO₂ and 14% steam; Calcination in 100% N₂ ........................................................................................................ 300

Figure AVIII.5 Calcium utilization for SO₂ capture: effect of varying operating conditions. Comparing with Figure 7.6 Calcium utilization for SO₂ capture: effect of varying operating conditions, 212-250 μm particles Test conditions: 850 °C calcination and sorption, Sorption in 80% CO₂, 3% O₂, 2900 ppm SO₂ and balance N₂ or with steam. Calcination in 100% N₂, 8 minutes for each sorption ........................................................................................................ 301

Figure AVIII.6 Close-up view of one cycle of SO₂/CO₂ sorption followed by a CaCO₃ calcination in N₂ and then a slow reduction of CaSO₄ at cycle 9. Test conditions are described in Table 7.3 ........................................................................................................ 302

Figure AVIII.7 EDX element mapping for modified sorbents with the light color points marking the element of the dopants ........................................................................................................ 303

Figure AVIX.1 Case study flowsheet for FBC-based SO₂/CO₂ sequential capture process (based on Option B in Chapter 8) ........................................................................................................ 306

Figure AVIX.2 Sensitivity of CaCO₃ feed to average CaO utilization in carbonator for a 262 MW fossil-fuel-fired conventional FBC unit ........................................................................................................ 310

Figure AVIX.3 Sensitivity of energy production to average CaO conversion in the carbonator for of a 262 MW fossil-fuel-fired conventional FBC unit ........................................................................................................ 311
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CO-AUTHORSHIP STATEMENT

This is a manuscript-based thesis. Chapters 2-9 are independent manuscripts with no overlaps. They are either published papers in peer-reviewed journals/international conference proceedings or manuscripts prepared for publication in peer-reviewed journals. I declare that my contributions to these manuscripts lie in the following areas:

- Proposing research work and designing research plan.
- Performing experiments, modeling and data analyses.
- Preparing manuscript drafts and working with co-authors in revising the drafts.

The use of these manuscripts in this thesis is under the permission of all the co-authors.
CHAPTER 1 INTRODUCTION, THERMODYNAMICS AND EQUIPMENT

1.1 Background and structure of this thesis: using calcium-based sorbent to removal CO₂

CO₂ emissions, as the major source of greenhouse gases, are receiving increasing attention due to the impact of greenhouse gases on global climate change. Affordable CO₂ control technology has become the focus of worldwide research. Among all the point sources of CO₂ emissions, power/thermal plants firing fossil fuels account for the principal anthropogenic source (about 6 gigatonnes carbon/year). Power plants implementing CO₂ capture from power system and storage could become effective net sinks of CO₂ from the atmosphere (Obersteiner et al. 2001).

To capture and dispose of CO₂ safely before it is released into the atmosphere, three major steps are involved (FETC, 1999): capture, storage/transportation and permanent disposal. Among these, capture is the most costly step (Wallance, 2000). This thesis work is dedicated to CO₂ capture.

CO₂ capture technologies under development can be classified into post-combustion capture, pre-combustion technology and oxy-fired technologies (Davison and Thambimuthu, 2004). Among the post-combustion technologies, amine-based CO₂ wet scrubbing is believed to be the most technologically mature (Rao and Rubin, 2002), but it requires high capital and operational costs. Another technology, similar to the approach studied in this work, is to use a sodium-based sorbent to cyclically capture CO₂, with a calciner to drive off a high-purity CO₂ stream for storage (Liang et al., 2004).
Chapter 1 Introduction, thermodynamics and equipment

Pre-combustion technology removes CO₂ during syngas reforming. Syngas comes from natural gas or from fossil fuels gasification. CO₂ removal can be realized by chemical absorption, e.g. based on CaO (Ortiz and Harrison, 2001), chemical adsorption, e.g. using hydrotalcite (Hufton and Sircar, 2001) or membrane separation. The CO₂-free syngas after further treatment can then be burnt for power generation, or converted to other products such as methanol. The Zero-Emission-Coal concept (Ziock et al., 2004a; 2004b) is an example of a pre-combustion process with limestone as CO₂ sorbent. In the pre-combustion processes, capture of CO₂ can also enhance the water-gas-shift (WGS) reaction to produce more hydrogen according to the Le Chatelie' principle. Furthermore, the exothermic carbonation reaction reduces the energy requirement in the reformer or gasifier. Oxy-fired combustion has been studied intensively, including in a small demonstration unit (e.g. Crosiet and Thambimuthu, 2000).

Recently a relatively new combustion concept, chemical looping combustion has been developed (Lyngfelt et al., 2001). In the combustor, gaseous hydrocarbon is oxidized by contacting solid oxidizing agents (instead of air), and the reduced solid species is then transferred to a separate chamber where it is oxidized by reacting with air. As a result, the only gases produced from the combustion system are CO₂ and H₂O. The latter can then be condensed and separated, leaving a relatively pure CO₂ stream, suitable for storage by various sequestration methods.

Reaction 1.1 has recently received renewed research interest (Shimizu et al. 1999; Abanades et al. 2003) as a means of removing CO₂ between a CO₂-lean fluidized bed combustor (FBC) and a calciner where nearly pure CO₂ is driven off for storage. In the combustion temperature range, CaO is also reactive to another air pollutant, SO₂. If co-capture of SO₂ and CO₂ could be realized, the CaO looping system could be readily retrofitted to existing FBC.
Chapter I Introduction, thermodynamics and equipment

plants. This concept does not belong to any of the above categories, instead being an in situ process.

\[ \text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 \quad \Delta H_{298K} = -178 \text{ kJ/mol} \quad (1.1) \]

This thesis focuses on the application of reaction (1.1) in a variety of energy systems, from steam reformers of hydrocarbons, to combustors of fossil fuels and gasifiers of fossil fuels. A schematic diagram of process in which such carriers could be applied is shown in Figure 1.1, with calcium-based sorbents (limestones or dolomites) serving as CO$_2$ carriers between a carbonator and a calciner. Heat must be supplied to the calciner to regenerate the sorbent. Petroleum coke (Wang et al., 2004), natural gas (Abanades et al., 2005), steam (Abanades et al., 2005), solid heat carriers (Abanades et al., 2005), waste heat from fuel cell plants (Ziock et al., 2004a; b) and pure CO$_2$ (Ortiz and Harrison, 2001) have all been proposed as heating sources or carriers. When relatively pure CO$_2$ is generated from the calciner, the task of capturing CO$_2$ is completed. The relatively pure CO$_2$ stream is then further transported for ultimate safe disposal (sequestration).
Chapter 1 Introduction, thermodynamics and equipment

Figure 1.1 Schematic diagram of the process studied in this thesis work to apply calcium-based sorbents

The thesis starts from fundamental topics, such as kinetics of the CaO-CO$_2$ reaction, and extends to a series of practical topics, including the application of calcium-based sorbents (mainly limestones and dolomites) in FBC-based processes and other energy systems. The cyclic reactivity of the calcium-based sorbent is the key unifying subject throughout this thesis.

This thesis is organized as a series of manuscript-based chapters (from Chapter 2 to 9), each dealing with an independent topic and having an independent structure. Content relevant, but not included in the manuscripts, because of its supplemental nature, is relegated to Appendices.

This thesis consists of ten chapters. After this introductory chapter, it includes kinetic study of the CaO-CO$_2$ reaction (Chapter 2), modeling of the gas-solid reaction (Chapter 3), a mechanistic study of sorbent sintering (Chapter 4), application of calcium-based sorbents in a FBC-based process for simultaneous capture of CO$_2$ and SO$_2$ (Chapter 5, 6, 7), consideration of
sequential capture of CO₂ and SO₂ (Chapter 8) and work relevant to simultaneous capture of CO₂ and H₂S in coal-fueled gasification (Chapter 9). Chapter 10 presents overall conclusions and recommendations.

1.2 Thermodynamics underlying this thesis

As the basis of the following chapters, several thermodynamic issues need to be first addressed:

1.2.1 Sorbent properties, calcination and carbonation

Naturally occurring limestones and dolomites are the major sorbents considered throughout this thesis. Boynton (1979) gave a detailed introduction to the properties of limestones, dolomites and limes. Limestones usually contain calcium carbonate and other impurities. Calcite and aragonite are the two major polymorphs of calcium carbonate, with calcite being the more common. As seen in the phase diagram in Figure 1.2, adapted from the work of Redfern et al., (1989), an extremely high pressure is needed for aragonite to form by carbonation (Note: in the original figure the pressures were kbar): Given the test conditions employed in this work and given that all of the limestones tested were initially calcitic, only calcite is dealt with in this work. Dolomites contain calcium carbonate and magnesium carbonate, as well as some impurities. Usually a dolomite contains a solid solution of calcium carbonate and magnesium carbonate, as well as a small portion of free magnesium carbonate. During calcination of dolomites, the breakdown of the chemical bonds between the two carbonates has been investigated using in situ XRD measurements (Engler et al., 1988). It was also found that after full calcination, the mixture consists only of a mechanical mixture of calcium oxide and magnesium oxide.
1.2.2 Sorbent calcination temperature

The temperature required for calcination is predicted using a thermodynamics database. In this work, HSC Chemistry 4.0 (Ronie, 1997) is used to make the equilibrium predictions. In this database, equilibrium concentrations are calculated based on non-stoichiometric Gibbs free energy minimization. In these methods, no details about reaction mechanism or kinetics are
Chapter 1 Introduction, thermodynamics and equipment

required in the numerical solution. In this thesis, the ideal gas model was also applied in the calculations. All solid phases involved were assumed to be pure condensed phases with activities of unity. More details about the non-stoichiometric Gibbs free energy minimization method is included in the monograph of Smith and Missen (1982).

The Figure 1.3 shows plots of standard free energy change versus temperature, sometimes called Ellingham diagrams (Gaskell, 1995) for the calcination reactions,

\[
\begin{align*}
\text{CaCO}_3 & \rightleftharpoons \text{CaO} + \text{CO}_2 \quad \Delta H_{298K} = 178 \text{ kJ/mol} \quad (1.2) \\
\text{MgCO}_3 & \rightleftharpoons \text{MgO} + \text{CO}_2 \quad \Delta H_{298K} = 100.9 \text{ kJ/mol} \quad (1.3) \\
\text{CaMg(CO}_3\text{)}_2 & \rightleftharpoons \text{MgO} + \text{CO}_2 + \text{CaCO}_3 \quad \Delta H_{298K} = 124.5 \text{ kJ/mol} \quad (1.4)
\end{align*}
\]

Standard state refers to 101 kPa pressure and any temperature of interest. The tie-lines (broken lines) show the change in Gibbs free energy when the partial pressure of CO\(_2\) is varied from the standard state to the CO\(_2\) partial pressure level of interest. The incipient calcination temperatures correspond to the intersection of the two lines. Figure 1.3 shows that when the temperature increases at a constant CO\(_2\) partial pressure, the free MgCO\(_3\) part of a dolomite decomposes first, followed by the half-calcination of CaMg(CO\(_3\))\(_2\) into a calcite, and finally by calcite calcination.

While calcite calcination is seen to be more favourable at high temperatures than at low temperatures in the absence of CO\(_2\), calcination of a limestone in a pure N\(_2\) environment does not occur in practice until temperatures of at least 650°C. This probably occurs because calcination kinetics are very slow at lower temperatures. For calcination in vacuum, an equation cited by Dennis and Hayhurst (1987) gives

\[
r_{\text{calcination}} = k_{\text{calcination}} (P_{\text{CO}_2,eq} - P_{\text{CO}_2,\text{true}} - P_o)
\]

(1.5)

This shows that even when the true CO\(_2\) partial pressure is zero, the temperature has to be high enough to overcome the \(P_o\) term. This term is, only important when the driving force is very low.
(e.g. less than ~6 kPa depending on temperature level). For decomposition of both limestones and dolomites, it was found that the incipient decomposition temperature is also related to particle size and crystalline properties (Boynton, 1979).

Figure 1.3 Ellingham plot for the three carbonate decomposition reactions with isobaric lines for partial pressure of CO₂.

It should also be pointed out that Figure 1.3 assumes ideal gas behaviour. The compressibility factors (Perry et al., 1997) for all relevant gases H₂O, O₂, SO₂, CO₂, CO₂, H₂ and N₂ are all close to unity for the test conditions of this work (150-400°C for steam and 500-950°C for all other gases, 101-2000 kPa), so that ideality is a good assumption.
Chapter 1 Introduction, thermodynamics and equipment

The equilibrium partial pressure of CO₂ for CaO carbonation can also be predicted by the correlation (Baker, 1962),

\[ P_{\text{CO}_2,\text{eq}} \text{ (in kPa)} = 10^{-8208/T + 9.079} \text{ (T in K)} \] (1.6)

Figure 1.3 also indicates that for MgO to carbonate at temperatures of interests for FBC, e.g., 850°C, extremely high P_{CO₂} (>50 MPa) would have to be maintained, well beyond the pressures of interest in this thesis. Therefore carbonation of MgO is neglected here.

Equation (1.6) can also be used to estimate the CO₂ removal efficiency. In a pressurized reactor, assuming that the inlet CO₂ molar fraction is \( f_{\text{CO}_2} \) and the total pressure is \( P_T \), the maximum achievable CO₂ removal efficiency is,

\[ \eta_{\text{CO}_2} = \frac{P_T f_{\text{CO}_2} - P_{\text{CO}_2,\text{eq}}}{P_T f_{\text{CO}_2}} \] (1.7)

The removal efficiency is seen to be a function of the overall pressure and the molar fraction of CO₂ at the reactor inlet. Figure 1.4 illustrates how the maximum CO₂ removal efficiency varies with total pressure and inlet molar fraction of CO₂ at 850°C.

Because of possible hydration when using CaO to capture CO₂ in a reformer or gasifier where there is a high steam partial pressure, the conditions for CaO hydration are shown in Figure 1.5, constructed in the same manner as Figure 1.3. It is seen that, MgO needs a higher H₂O partial pressure to be hydrated than CaO.
Figure 1.4 Maximum CO$_2$ removal efficiency as a function of total pressure and molar fraction of CO$_2$ in the flue gas at the inlet of reactor for a temperature of 850°C.
Chapter 1 Introduction, thermodynamics and equipment

Figure 1.5 Ellingham plot for CaO and MgO hydration reactions isobaric lines for partial pressure of H$_2$O.

1.2.3 CO$_2$ capture in FBC: Effect of SO$_2$ on CaO carbonation

When dolomites are employed as CO$_2$ sorbents in FBC-based processes, the MgO part, although inert to CO$_2$, might not be inert to SO$_2$. For the reaction

$$
\text{MgO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{MgSO}_4
$$

$$
\Delta H_{298K} = -386.5 \text{ kJ/mol} \quad (1.8)
$$
Chapter 1 Introduction, thermodynamics and equipment

HSC 4.0 was employed to the equilibrium SO$_2$ concentration in the presence of 3% O$_2$ at varying temperatures and total pressures. The results appear in Figure 1.6. They show that 2250 ppm SO$_2$ are needed for MgO sulphation at 1 atm and 850°C. The equilibrium SO$_2$ concentration decreases with increasing total pressure in good agreement with experimental data of Dewing and Richardson (1959) summarized by Hartman and Svoboda (1985).

![Equilibrium SO$_2$ concentrations](image)

Figure 1.6 Equilibrium SO$_2$ concentrations for reaction given in equation (1.8) as the function of reactor temperature and total pressure in the presence of 3%v O$_2$.

1.2.4 CO$_2$ capture during gasification

Chapter 9 deals with CO$_2$ and SO$_2$ removal for two limestones and a dolomite under simulated gasification conditions. With a simulated syngas, gas phase reactions need to be taken into account. The typical gas feed in the experiment, i.e. 1%v H$_2$S, 20%v CO$_2$, 12.6%v H$_2$ and 1.5%v CO with the balance N$_2$, was analyzed with HSC 4.0. The predicted results are shown in Figure 1.7 as a function of reactor temperature for a total pressure of 0.76 MPa.
Figure 1.7 Thermodynamic predictions for gaseous products as a function of temperature for 0.76 MPa total pressure. Gas feed: 1%v H$_2$S, 20%v CO$_2$, 12.6%v H$_2$ and 1.5%v CO with N$_2$ balance.

Figure 1.7 shows that for the specified gas feed, the water gas-shift reaction favours production of H$_2$O and CO, and consumption of CO$_2$, causing the actual CO$_2$ concentration to be a few percentage points lower than in the inlet gas stream. Gaseous sulfur is retained in the form of H$_2$S, with negligible H$_2$S decomposition, as revealed by the low concentration of S$_2$. The concentrations of NH$_3$ and COS are also very low. The calculation also shows negligible carbon deposition and negligible reaction of CaS with CO$_2$. In the experiments described in Chapter 9, relatively high concentrations of hydrogen and CO were maintained, as suggested in the literature (Fenouli and Lynn, 1995a) to avoid H$_2$S decomposition and CaS oxidization by CO$_2$. 
Chapter 1 Introduction, thermodynamics and equipment

Based on the equilibrium CO₂ and H₂O concentrations with the given feed shown in Figure 1.7, the equilibrium H₂S concentration can be predicted for the other two reversible reactions studied in Chapter 9, i.e., CaO sulfidation (reaction 1.6) and CaCO₃ direct sulfidation:

\[ \text{CaO} + \text{H}_2\text{S(g)} \rightleftharpoons \text{CaS} + \text{H}_2\text{O(g)} \quad \Delta H_{298K} = -59.4 \text{ kJ/mol} \quad (1.9) \]

\[ \text{CaCO}_3 + \text{H}_2\text{S(g)} \rightleftharpoons \text{CaS} + \text{H}_2\text{O(g)} + \text{CO}_2(g) \quad \Delta H_{298K} = 118.7 \text{ kJ/mol} \quad (1.10) \]

For a typical operating conditions, such as 850°C and 0.76 MPa, the equilibrium H₂S concentration was predicted to be 114 ppm and 235 ppm for these two reactions, respectively, using the equilibrium partial pressures P_{CO₂} ≈ 14%v and P_{H₂O} ≈ 8%v, predicted from Figure 1.7.

1.2.5 Sorption-enhanced hydrogen production using a calcium-based CO₂ sorbent

Enhancement of hydrogen production with CO₂ capture with CaO during steam reforming of methane has been investigated by Ortiz and Harrison (2001). They showed that CaO removal could shift the chemical equilibrium to produce relatively pure hydrogen. Sorption-enhanced hydrogen production in a bubbling fluidized-bed reformer was recently demonstrated experimentally by Johnsen et al. (2006). The thermodynamic predictions of Ortiz and Harrison (2001) show that when CaO hydration is favoured, the maximum achievable hydrogen purity is lower than under non-hydration conditions.
Figure 1.8 Effect of CO₂ capture on H₂ production in a simulated gasification system. Feed: 1 kmol carbon, 1.5 kmol steam, 0.01 kmol H₂S, with and without 1 kmol CaO.
Chapter I Introduction, thermodynamics and equipment

As discussed in Chapter 9, calcium-based sorbents are also applicable to CO$_2$ and H$_2$S removal in fossil-fuel gasifiers. Removal of CO$_2$ could also enhance the water-gas shift reaction to produce hydrogen of higher concentration. HSC 4.0 was used to simulate the effect of CO$_2$ removal by CaO gasification for a feedstock of 1 kmol C, 0.01 kmol H$_2$S and 1.5 kmol steam. Illustrative results are shown in Figure 1.8 as a function of reactor temperature and pressure.

Figure 1.8 clearly shows that when the conditions are favourable for CO$_2$ capture by CaO, e.g., for T<900°C at P=1 MPa or for P>0.3 MPa and T=850°C, H$_2$ production can be appreciably enhanced. This finding is similar to that for sorption-enhanced steam methane reforming.

1.2.6 Effect of H$_2$O, low-temperature eutectic between CaO-Ca(OH)$_2$-CaCO$_3$

The operation of a steam reformer or gasifier using a calcium-based CO$_2$ sorbent should also consider the possible formation of a low-melting-point eutectic. It is commonly believed that the CaO-Ca(OH)$_2$-CaCO$_3$ system likely produces a low-temperature eutectic (Curren et al., 1967; Fuerstenau et al., 1981). Curran et al. (1967) calculated the eutectic temperature for the binary systems: CaO-Ca(OH)$_2$ and CaCO$_3$-Ca(OH)$_2$ by equilibrium analyses. The results are summarized in Table 1.1, where the equilibrium steam pressures to maintain solid-phase Ca(OH)$_2$ are also shown for the CaO hydration reaction,

\[
\text{CaO} + \text{H}_2\text{O} (g) \rightarrow \text{Ca(OH)}_2 (s) \quad \Delta H_{298 K} = -109.1 \text{ kJ/mol (1.11)}
\]

However, there are some limitations in this prediction because the predicted H$_2$O equilibrium partial pressures differ from those predicted by HSC 4.0 database (see Figure 1.5), i.e., 4200 kPa for 790°C and 690 kPa for 638°C. The phase diagram for such a binary system could be more rigorously constructed by the method introduced by Gaskell (1995). However, the specific heat data needed for imaginary materials such as CaO (l), Ca(OH)$_2$ (l) and Ca(OH)$_2$ (l) are mostly

16
absent from the literature. Other eutectics, as reviewed by Fuerstenau et al. (1981) for the binary system CaCO\textsubscript{3}-Ca(OH)\textsubscript{2}, are also shown in Table 1.1.

### Table 1.1 Eutectic formation conditions for the CaO-Ca(OH)\textsubscript{2} and CaCO\textsubscript{3}-Ca(OH)\textsubscript{2} system

<table>
<thead>
<tr>
<th>System</th>
<th>Ca(OH)\textsubscript{2}-CaO</th>
<th>Ca(OH)\textsubscript{2}-CaCO\textsubscript{3}</th>
<th>Ca(OH)\textsubscript{2}-CaCO\textsubscript{3}</th>
<th>Ca(OH)\textsubscript{2}-CaCO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Min. Eutectic formation</strong></td>
<td>790 °C (Steam pressure 5400 kPa)</td>
<td>638°C (Steam pressure 880 kPa)</td>
<td>675°C</td>
<td>645°C (1, 100 MPa total pressure)</td>
</tr>
<tr>
<td>temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Molar fraction</strong></td>
<td>69% CaO</td>
<td>41% Ca(OH)\textsubscript{2}</td>
<td>37% CaCO\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>where eutectic forms</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reference</strong></td>
<td>Curran et al. 1976</td>
<td>Curran et al. 1976</td>
<td>Originally from Wyllie and Tuttle (1960),</td>
<td>Originally from Wyllie and Raynor (1965),</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Reviewed by Fuerstenau et al. (1981)</td>
<td>Reviewed by Fuerstenau et al. (1981)</td>
</tr>
</tbody>
</table>

Fuerstenau et al. (1981) determined the composition of the ternary eutectic system CaO-Ca(OH)\textsubscript{2}-CaCO\textsubscript{3} using DSC techniques. They found eutectics to form in the temperature range 640-789°C and at pressures of 1.7 to 7.0 MPa, with CaO accounting for 2.3%-5.0% and CaCO\textsubscript{3} 9.5 to 64.5% molar fraction.

### 1.3 Experimental equipment and materials

#### 1.3.1 Apparatus

The experimental work carried out in this project was all conducted in bench-scale equipment. Three thermogravimetric reactors were utilized, as portrayed in Figures 1.9, 1.10 and 1.11.
Chapter 1 Introduction, thermodynamics and equipment

Figures 1.9 shows the atmospheric pressure thermogravimetric analyzer SHIMADZU TA60 based system (ATGA). The balance has a precision of 1 µg. The sample mass is usually <30 mg. This apparatus was mainly used for kinetic studies with CO₂ partial pressures from 0 to 101 kPa. Gases flow from top to bottom. All gas flows were controlled by mass flow controllers. More details can be found in the chapters where the ATGA system was employed.

![Figure 1.9 Schematic of SHIMADZU-based atmospheric thermogravimetric analyzer system (ATGA).](image)

Figure 1.10 provides a schematic of the pressurized TGA (PTGA) system, with operating pressures up to 2.4 MPa. It was primarily employed to test kinetics at relatively high pressures. This unit includes a Cahn 100 balance with 1 µg sensitivity. The reactor itself is made of Inconel 600 alloy. A pressure regulator adjusted the pressure to the desired level. The mass detection range is adjustable, usually between 0-100 mg. All gas flows were controlled by mass flow controllers. More details are provided in later chapters where the PTGA system was employed.
Chapter 1 Introduction, thermodynamics and equipment

Figure 1.10 Schematic of pressurized thermogravimetric analyzer (PTGA) system

The atmospheric TG reactor (ATGR) is shown in Figures 1.11. This was utilized in a variety of experiments involving sulphation, carbonation, calcination and hydration. It was especially useful for cyclic calcination/carbonation tests. A load cell at the top of the reactor chamber allows much larger sample sizes, i.e., 0-10 grams of total suspension mass (samples plus basket and wire). The advantage is that enough samples can be produced for topology analyses. The TGR allows operation with SO2, CO2, CO, air, steam etc. The flows of gases except steam were controlled by mass flow controllers, whereas the flow rate of steam was controlled by a water pump (powered by a AC motor). Most sample basket were made from stainless wire mesh. Stainless steel wire experienced some oxidization under high-temperature operation, but the mass change was usually less than a few milligrams, negligible for samples of mass 400 mg. More details can be found in Laursen et al. (2000, 2001).
Chapter 1 Introduction, thermodynamics and equipment

Needle Mass flow valve controller

Figure 1.11 Schematic of atmospheric thermogravimetric reactor (ATGR) system

1.3.2 Sorbents

Seven commercially available sorbents were tested: Strassburg limestone (US), Danyang limestone (Korea), Havelock limestone (Canada), Kelly Rock limestone (Canada), Cadomin limestone (Canada), Arctic dolomite (Norway) and GS dolomite (US). Table 1.2 gives their chemical analyses.

Table 1.2 Chemical analyses (% by wt in each case)

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strassburg</td>
<td>0.94</td>
<td>0.19</td>
<td>0.94</td>
<td>1.25</td>
<td>53.7</td>
<td>0.02</td>
<td>0.08</td>
<td>42.9</td>
</tr>
<tr>
<td>Danyang</td>
<td>1.55</td>
<td>0.9</td>
<td>0.29</td>
<td>1.03</td>
<td>52.94</td>
<td>0.01</td>
<td>0.32</td>
<td>42.9</td>
</tr>
<tr>
<td>Havelock</td>
<td>1.5</td>
<td>&lt;0.38</td>
<td>&lt;0.55</td>
<td>0.59</td>
<td>53.99</td>
<td>&lt;0.17</td>
<td>&lt;0.08</td>
<td>43.34</td>
</tr>
<tr>
<td>Cadomin</td>
<td>1.5</td>
<td>&lt;0.38</td>
<td>&lt;0.55</td>
<td>2.25</td>
<td>55.12</td>
<td>&lt;0.17</td>
<td>0.21</td>
<td>42.77</td>
</tr>
<tr>
<td>Kelly Rock</td>
<td>5.31</td>
<td>1.54</td>
<td>0.36</td>
<td>0.58</td>
<td>51.74</td>
<td>0.07</td>
<td>0.36</td>
<td>43.14</td>
</tr>
<tr>
<td>Arctic Dolomite</td>
<td>2.12</td>
<td>0.17</td>
<td>1.3</td>
<td>21.25</td>
<td>30.51</td>
<td>0.15</td>
<td>0.04</td>
<td>44.4</td>
</tr>
<tr>
<td>GS Dolomite</td>
<td>0.87</td>
<td>0.16</td>
<td>0.15</td>
<td>18.69</td>
<td>33.41</td>
<td>0.04</td>
<td>0.08</td>
<td>46.5</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction, thermodynamics and equipment

The apparatus and sorbents used in the major chapters are summarized in Table 1.3.

Table 1.3 Summary of sorbents and reactors in each chapter.

<table>
<thead>
<tr>
<th>Applications and chapter</th>
<th>Reactor used</th>
<th>Sorbent used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic study (Chapters 2, 3)</td>
<td>ATGA, Pressurized TGA, ATGR</td>
<td>Strassburg limestone, Arctic dolomite</td>
</tr>
<tr>
<td>Sintering modeling (Chapter 4)</td>
<td>ATGR</td>
<td>Strassburg limestone</td>
</tr>
<tr>
<td>Co-capture of SO2 and CO2 (Chapters 5, 6)</td>
<td>ATGR, PTGA</td>
<td>Limestones: Strassburg, Danyang, Havelock, Kelly Rock, Cadomin, Dolomites: Arctic, GS</td>
</tr>
<tr>
<td>Effect of steam, sorbent modification etc. (Chapter 7)</td>
<td>ATGR</td>
<td>Strassburg limestone, Arctic dolomite</td>
</tr>
<tr>
<td>Sequential capture of SO2 and CO2 (Chapter 8)</td>
<td>PTGA</td>
<td>Strassburg limestone, Arctic dolomite</td>
</tr>
<tr>
<td>Co-capture of H2S and CO2 (Chapter 9)</td>
<td>PTGA</td>
<td>Strassburg and Kelly Rock limestone, Arctic dolomite</td>
</tr>
</tbody>
</table>

1.4 Nomenclature

Symbols

\( r_{\text{calcination}} \) Calcination rate \( \text{mol/m}^2/\text{s} \)

\( k_{\text{calcination}} \) Calcination rate constant \( \text{mol} \cdot 1 \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot (\text{kPa})^{-1} \)

\( f_{\text{CO}_2} \) Inlet CO2 molar fraction -

\( P_{\text{CO}_2, \text{true}} \) True partial pressure of CO2 kPa

\( P_{\text{CO}_2, \text{eq}} \) Equilibrium partial pressure of CO2 kPa

\( P_T \) Total reactor pressure kPa

\( P_o \) Constant in Equation (1.5) kPa

Greek letters

\( \eta_{\text{CO}_2} \) Maximum achievable CO2 removal efficiency -
CHAPTER 2 DETERMINATION OF INTRINSIC RATE CONSTANTS OF THE CaO-CO$_2$ REACTION

A version of this chapter was prepared for publication in Chemical Engineering Science. Authors: Sun, P., Grace, J. R., Lim, C. J. and Anthony, E. J. This manuscript will be submitted soon.

2.1 Introduction

Extensive research recently has been devoted to CO$_2$ capture techniques because of growing concerns over greenhouse gas emissions. Calcium-based materials have attracted particular attention (Silaban and Harrison, 1995; Silaban et al. 1996; Shimizu et al., 1999; Abanades et al. 2003) as potential sorbents for cyclic CO$_2$-capture processes because of their potential for regeneration. Among the possible applications of calcium-based sorbents for CO$_2$ removal are steam reformers (Han and Harrison, 1994; Balasubramanian et al., 1999; Ortiz and Harrison, 2001; Johnsen et al., 2006), gasifiers of fossil fuels (Lin et al. 2001; Jukkola et al., 2005) to enhance water-gas-shift reaction giving higher hydrogen yields, and fluidized bed combustors with in-situ CO$_2$ capture (Shimizu et al., 1999; Abanades et al., 2003; Abanades et al., 2004a). These applications all involve sorbent cycling between calcination and carbonation. However, the kinetics of the carbonation reaction have been studied much less than its reverse reaction, calcination.

As a typical gas-solid reaction producing a solid product, carbonation is initially fast, followed by a much slower stage. In the absence of pore diffusion, it is controlled jointly by surface reaction and product layer diffusion. However, among the limited number of kinetic studies, only a handful have focused on the intrinsic surface reaction kinetics. Nitsch (1970)
observed a zero-activation energy for an initial growth stage over a narrow temperature range, 800-850°C. Bhatia and Perlmutter (1983) studied the kinetics via a random pore model to fit the early portion of the experimental data. Their experiments, carried out in an atmospheric TGA with 0-10%v CO$_2$, suggested a zero-activation energy. The zero activation energy was further supported by Dennis and Hayhurst (1987) based on an equilibrium analysis of their calcination data. However, a zero-activation-energy is rare. More likely, the activation energy for the carbonation is actually small, i.e. near zero. Based on tests in an atmospheric TGA, Kyaw et al. (1996) reported activation energies of 78 kJ/mol for a limestone and 35 kJ/mol for a dolomite.

Another issue with respect to carbonation kinetics is the uncertainty with respect to intrinsic reaction order. Bhatia and Perlmutter (1983) claimed a first order reaction for P$_{CO2}$ from 0-10 kPa, whereas Kyaw et al. (1996) measured a close-to-zero order for a much higher CO$_2$ partial pressure. Work is needed to cover a wider range of P$_{CO2}$.

This chapter focuses on an intrinsic kinetic study for the CaO-CO$_2$ reaction with two commercial calcium-based sorbents, one a limestone and the other a dolomite. A wide range of CO$_2$ partial pressures was tested using both atmospheric and pressurized TGA equipment.

2.2 Experimental details

Two fixed-bed thermogravimetric analyzers were used in this study, one operated at atmospheric pressure and the other under pressurized conditions. The atmospheric SHIMADZU TA60 system (ATGA) was used for most tests to measure rate constants, with CO$_2$ partial pressures varying from zero to 0.1 MPa. Gases flow from top to bottom. A schematic is provided in Figure 1.9. The inner diameter of the reactor is ~0.02 m, whereas the diameter of sorbent pan is 0.004 m. The pressurized TGA (PTGA) was used to test kinetics at much higher CO$_2$ partial pressures. This unit includes a Cahn 100 balance of 1 μg sensitivity and a reactor column made
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

of Inconel 600 alloy. A pressure regulator adjusted the overall pressure to the desired level. When the required pressure was achieved, the reactant gas stream flowed upwards, passing the suspension sample basket and then leaving through the outlet of the reactor at the middle of column. A schematic of the PTGA system appears in Figure 1.10.

Ultra-pure grade CO$_2$, N$_2$ and He were mixed at the inlet of both reactors. Mass flow controllers accurately controlled the gas flow rates to obtain the desired CO$_2$ concentrations.

To minimize the influence of calcination heating rates, pure CO$_2$ was fed initially to both reactors, preventing CaCO$_3$ decomposition during heating to 850°C at 50°C/min in the ATGA or at 20°C/min in the PTGA. In both cases, the calcination was carried out at atmospheric pressure. When 850°C was reached, the CO$_2$ was replaced by He or N$_2$ to initiate calcination. After completion of calcination, a pre-determined carbonation temperature was then approached while maintaining the flow of inert gas. For PTGA tests, the desired pressure was achieved by rapidly injecting inert gas from the top of the vessel. After adjusting the control valves to establish an inert gas flow rate which would provide the desired CO$_2$ concentration, carbonation was initiated by opening the CO$_2$ control valve.

Strassburg limestone and Arctic dolomite were selected for these tests. Chemical analyses of these two sorbents are provided in Table 1.2

2.2.1 Elimination of physical limitations in ATGA tests

Preparatory runs were conducted with Strassburg limestones to eliminate physical constraints in the ATGA measurements. It has been shown that, after a fast initial stage, the CaO-CO$_2$ reaction becomes an extremely slow product-layer-controlled reaction (Bhatia and Perlmutter, 1983; Abanades et al., 2003). Kinetic control in the initial stage was achieved by careful control of the operating conditions.
Chapter 2 Determination of intrinsic rate constants of the CaO-CO\textsubscript{2} reaction

In the ATGA tests, CO\textsubscript{2} was introduced after no appreciable further calcination was observed during exposure to helium at a pre-determined flow rate. After initiating the CO\textsubscript{2} flow, before significant reaction-related mass change, there was a small step increase of apparent mass due to drag, as confirmed by both drag force calculation and a blank test. This had to be accounted for. The calcium utilization was calculated on a molar basis,

\[
X = \frac{\text{reacted Ca moles}}{\text{total Ca moles}} = \frac{m_{\text{CaO}}(t) - m_{\text{CaO}}(0)}{44} / \frac{m_{\text{CaCO}_3}(0) \times \text{purity}}{100}
\]  

(2.1)

where 44 and 100 are the CO\textsubscript{2} and CaCO\textsubscript{3} molar weights, in g/mol.

Reducing sample size and dispersing particles as well as possible can minimize the “packing” effect causing inter-particle mass transfer resistance. External mass transfer limitations can be minimized by using high gas flow rates. Experiments using varying sample size showed that starting with 2.9 mg fresh limestone gave no difference in mass breakthrough profile compared with 4 mg. Thus in this study, all runs started with samples smaller than 2.9 mg.

Tests at 600°C with P_{CO_2}=50 kPa and the balance He and with varying gas flow rates showed no difference in mass breakthrough profiles for flow rates from 400 up to 800 ml/min. Therefore, total flow rates around 400 ml/min were selected for the later runs. All flow rates provided here were measured at room temperature at the inlet of the ATGA.

Regarding the mechanism for the elimination of external mass transfer limitations, it should be noted that although the particle Reynolds number (defined as \(\text{Re}_p = \frac{U_o d_p}{\nu}\)) is small (~6×10\textsuperscript{3}) for a typical case: e.g., for a 48 \(\mu\)m particle at 850°C with inlet helium flow rate of 400 ml/min at room temperature, Sherwood number would be ~2 for a single particle (Szekely et al., 1976) and almost independent of gas flow rate. However, in a TGA reactor, the fine particles behave like a fixed-bed with the true gas velocity between the particles much lower than the
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

superficial velocity and the true Sherwood number (for a fixed bed) is much smaller than for a single particle and still a function of Reynolds number (Bird, 2000). Therefore, an increase of gas flow rate in the TGA would effectively increase the true Sherwood number (Bird, 2000), so that the external mass transfer coefficient would change with flow rate. Since changes in flow rate did not appreciably alter the measured rate, it can be inferred that external mass transfer was not limiting.

Similar results with varying particles size showed that using particles smaller than 53-63 μm can eliminate the effect of intraparticle mass transfer. In current studies, 38-45 μm particles were therefore employed. Finally changing the balance inert gas from N$_2$ to He did not result in any change in carbonation history, indicating that heat transfer limitations are negligible. In this study, helium was used in all ATGA tests, whereas N$_2$ was used in the PTGA tests.

2.2.2 PTGA tests

The sample pan in the PTGA has a cross-sectional area about 4 times larger than in the ATGA. In each PTGA test, 8-11 mg of sample were used, resulting in a well-dispersed thin-layer sorbent bed.

The PTGA tests provided supplemental data for P$_{CO_2}$ > 101 kPa. Two groups of tests were performed with the Strassburg limestone, one at 101 kPa total pressure to compare with the ATGA run results, and the other at a total pressure of 800 kPa. For Arctic dolomite, all tests were performed at 800 kPa.

After calcination, 100% CO$_2$ replaced 100% N$_2$ to initiate carbonation. Carbonation was detected 0.5 to 1 minute after fully opening the valve for CO$_2$ introduction and fully closing the N$_2$ valve at the same time. Although full openness would give a maximum of 500 ml/min flow rate for the atmospheric reactor vessel, the actual flow rate was only about half this value at 800
Chapter 2 Determination of intrinsic rate constants of the CaO-CO₂ reaction

kPa total pressure. No appreciable decrease in reaction rate at a gas flowrate of 250 ml/min as seen below, confirmed that the gas film is not rate-limiting. A blank test confirmed that no appreciable buoyancy force was caused by changing the gas from N₂ to CO₂.

2.3 Results and discussion

2.3.1 Direct measurement of carbonation kinetics: use of a gas-solid reaction model

SEM photos of the Strassburg calcines (e.g. Figure 2.1) show that grain shapes are almost spherical, but with some evidence of initial grain-neck growth due to the early stage of sintering. Arctic calcines (not shown here) did not show clear grain boundaries, probably due to much smaller grain size. This indicates that the grain model should be a good descriptive model, although the grains are not perfectly spherical due to earlier sintering for limestone calcines. Therefore a grain model with kinetic control was chosen to determine the kinetic-controlled region.

The grain model under kinetic control gives (Szekely et al., 1976)

\[
\frac{dX}{dt(1-X)^{2/3}} = 3r
\]

(2.2)

In integral form,

\[
[1-(1-X)^{1/3}] = r \times t
\]

(2.3)

Equation (2.3) shows that when the reaction is under kinetic control, a plot of \((1-(1-X)^{1/3})\) vs \(t\) should give a straight line of slope \(r\).

Figure 2.2 obtained from mass vs time profiles illustrates how the kinetic control region is identified with the help of the grain model. At the start of the reaction, there was usually a short induction period featuring a lower slope. Following this and starting from a point with maximum slope, several seconds of mass breakthrough led to a nearly linear stage (shown in Figure 2.2)
followed by an obvious slow-down. The short linear stage identifies the kinetic control region with the slope of this stage giving the intrinsic surface reaction rate, defined as \( r \) in equation (2.3). The starting points of the linear stage, featuring the maximum slope, usually resides at low conversions, i.e. 5%. Following the kinetic control region, the slow-down stage is controlled by both surface reaction and product-layer diffusion, showing much slower slopes. As the carbonation reaction proceeds further, product-layer diffusion becomes more and more important, resulting in much slower carbonation. In the kinetic control region, the slope (also the maximum slope) is constant and gives the value of \( r \) in equation (2.3). It should be noted that the initial induction period right before the linear kinetic-controlled stage should also belong to the kinetic control region, in spite of its slower slope as found for typical gas-solid reactions. Therefore the constant value of \( r \) in the kinetic controlled region obtained from the linear plot slope can also be extended to represent the true rate of \( r \) at the zero conversion point, i.e.,

\[
\begin{align*}
    r_0 &= r \\
    (2.4)
\end{align*}
\]

Some other typical plots obtained by applying the grain model are shown in Figure 2.3.

The reaction rate for a gas-solid reaction, is usually defined as a specific rate,

\[
R = \frac{dX}{dt(1-X)} \quad (1/s)
\]

When the reaction is under kinetic control, the specific rate can be further expressed in power law form,

\[
R = \frac{dX}{dt(1-X)} = 56k_s(P_{CO_2} - P_{CO_2,eq})^n S = 3r(1-X)^{-1/3}
\]

where 56 is the molar weight of CaO, in g/mol.

Equations (2.3) and (2.5) lead to,
Chapter 2 Determination of intrinsic rate constants of the CaO-CO\textsubscript{2} reaction

\[ R = \frac{dX}{dt(1 - X)} = 3r(1 - X)^{-1/3} = 56k_s(P_{\text{CO}_2} - P_{\text{CO}_2, eq})^n S \]  \hspace{1cm} (2.7)

At the initial time 0, when the surface area is \( S_0 \), equation (2.7) becomes,

\[ R_0 = \frac{dX}{dt} \bigg|_{t=0} = 3r_0 = 56k_s(P_{\text{CO}_2} - P_{\text{CO}_2, eq})^n S_0 \]  \hspace{1cm} (2.8)

In a logarithmic form, equation (2.8) becomes,

\[ \ln r_0 = \ln(56k_s / 3) + n \ln(P_{\text{CO}_2} - P_{\text{CO}_2, eq}) + \ln S_0 \]  \hspace{1cm} (2.9)

Hence, the slope of \( \ln r_0 \) versus \( \ln(P_{\text{CO}_2} - P_{\text{CO}_2, eq}) \) plot gives the order of the CaO-CO\textsubscript{2} reaction with respect to the CO\textsubscript{2} partial pressure. Such plots are shown in Figures 2.4 and 2.5. They show that at low CO\textsubscript{2} partial pressure driving force or \( P_{\text{CO}_2} - P_{\text{CO}_2, eq} \), the CaO-CO\textsubscript{2} reaction is 1st order. However at higher \( P_{\text{CO}_2} - P_{\text{CO}_2, eq} \), e.g. for about \( P_{\text{CO}_2} - P_{\text{CO}_2, eq} = 6 \) kPa or higher for 850\degree C tests and at about 8 kPa or higher for 600\degree C runs, an obvious transition of the reaction order occurs. The order then quickly approaches zero or close-to-zero order at higher CO\textsubscript{2} partial pressure. The transition, if present, as shown in both Figures 2.4 and 2.5, appears to be sharp, suggesting an abrupt shift in control mechanism. For both sorbents at both temperatures, the driving force in the transition region generally lies between 6 and 12 kPa. Driving force \( (P_{\text{CO}_2} - P_{\text{CO}_2, eq}) \) at \( \sim10 \) kPa is taken as a reasonable approximation of the turning point hereafter.

With \( k_s = k_0 \exp(-E / R / T) \) at the n=0 region, equation (2.9) can be rewritten as,

\[ \ln r_0 = \ln(56k_0 S_0 / 3) - \frac{E}{R} \frac{1}{T} \]  \hspace{1cm} (2.10)

The two parameters, activation energy \( E \) and pre-exponential factor \( k_0 \) for both sorbents were obtained by nonlinearly fitting the Arrhenius equation (2.10) with experimental data. Note that a comparison has been made between nonlinear fitting and linear fitting using the logarithmic form of equation (2.10). The results are summarized in Appendix I, showing that
better results were obtained through nonlinear fitting. The initial specific surface areas \( S_0 \) for both sorbents were measured by N\(_2\) adsorption, giving 29 m\(^2\)/g for Strassburg calcines and 49 m\(^2\)/g for fully calcined Arctic dolomite. The Arctic calcines contain both MgO and CaO, but the surface area for carbonation is only the CaO part. It is reasonable to assume that the surface area ratio of the CaO part to the MgO part is the same as their volumetric ratio. For a fully calcined dolomite, both CaO and MgO crystals should be cubic, with the cube edge length being 0.48 nm for CaO and 0.42 nm for MgO (Boynton, 1979). In the Arctic dolomite, the molar ratio of CaO to MgO is 1.1, so the molar volume ratio of CaO to MgO should be \( \frac{0.48^3}{0.42^3} \times 1.1 = 1.64 \). Thus the CaO surface is of Arctic dolomite is estimated to be 31 m\(^2\)/g. The data in these figures are extracted from runs with 80\%, 50\% and 15\% inlet \( \text{CO}_2 \) volumetric fractions for Strassburg limestone and 100\% for Arctic dolomite. All correspond to the zero-order regions as discussed above. Arrhenius plots using the fitted parameters \( E \) and \( k_0 \) are shown in Figures 2.6 and 2.7.

The resulting parameters are,

for limestones, \( k_s = 1.67 \times 10^{-3} \exp\left(-\frac{E}{R,T}\right) \frac{\text{mol}}{m^2s}; \quad E = 29 \pm 4 \text{kJ/mol}; \quad P_{\text{CO}_2} - P_{\text{CO}_2,\text{eq}} > 10 \text{kPa} \)

\[(2.11)\]

for dolomites, \( k_s = 1.04 \times 10^{-3} \exp\left(-\frac{E}{R,T}\right) \frac{\text{mol}}{m^2s}; \quad E = 24 \pm 6 \text{kJ/mol}; \quad P_{\text{CO}_2} - P_{\text{CO}_2,\text{eq}} > 10 \text{kPa} \)

\[(2.12)\]

where the limits on the activation energy correspond to a 95\% confidence level.

Since at the turning point from the first-order to zero-order reaction, or at \( P_{\text{CO}_2} - P_{\text{CO}_2,\text{eq}} = 10 \text{kPa} \), the specific reaction rate predicted as the zero-order reaction, i.e. \( R_0 = 56k_s(P_{\text{CO}_2} - P_{\text{CO}_2,\text{eq}})S_0 \)
Chapter 2 Determination of intrinsic rate constants of the CaO-CO\textsubscript{2} reaction

\((P_{CO_2} - P_{CO_2,eq} \leq 10 \text{ kPa})\) should equal the one predicted for the first order reaction, it can be derived that for the first order region,

for limestones, \(k_s = 1.67 \times 10^{-4} \exp\left(-\frac{E}{R_T}\right) \frac{mol}{m^2 \cdot s \cdot kPa} ; E = 29 \pm 4 kJ / mol ; P_{CO_2} - P_{CO_2,eq} \leq 10 \text{ kPa} \)

\[(2.13)\]

for dolomites, \(k_s = 1.04 \times 10^{-4} \exp\left(-\frac{E}{R_T}\right) \frac{mol}{m^2 \cdot s \cdot kPa} ; E = 24 \pm 6 kJ / mol ; P_{CO_2} - P_{CO_2,eq} \leq 10 \text{ kPa} \)

\[(2.14)\]

2.3.2 High-pressure measurement

It is been shown above that the driving force \((P_{CO_2} - P_{CO_2,eq})\) has no further effect on the rate of reaction in the ATGA when it exceeds 10 kPa. In the ATGA tests, the highest \(P_{CO_2}\) achievable was 0.1 MPa. To test greater \(P_{CO_2}\), higher total pressure levels are required. The PTGA tests were undertaken for this purpose.

The same methods as described above were applied to the high-pressure data, except that data were smoothed by moving averages to dampen fluctuations probably associated with more significant drag imparted by the higher-density gas.

Typical plots based on the grain model are shown in Figures 2.8 and 2.9, combined with calcium utilization (conversion) curves for Strassburg limestone and Arctic dolomite, respectively. The maximum slopes are also shown in these Figures, in spite of the sparse data points compared to ATGA tests. The Arrhenius plots in Figures 2.10 and 2.11 compare the high-pressure data with previous ATGA data at various temperatures and 0.1 MPa total pressure. These plots indicate that, despite the greater scatter in the PTGA data, the absolute rates at 800 kPa are very similar to those for 101 kPa ATGA runs. Considering the wide difference of
Chapter 2 Determination of intrinsic rate constants of the CaO-CO\textsubscript{2} reaction

absolute P\textsubscript{CO\textsubscript{2}} between the ATGA and PTGA tests, it can be concluded that increasing P\textsubscript{CO\textsubscript{2}} from 0.1 to 800 kPa makes no difference in the intrinsic carbonation kinetics, supporting the above conclusion that for, (P\textsubscript{CO\textsubscript{2}}-P\textsubscript{CO\textsubscript{2}\textsubscript{eq}}) > 10 kPa, the carbonation reaction was of zero order. In view of the PTGA data scatter, the PTGA data were not used for rate constant parameter fitting.

2.3.3 Carbonation data from equilibrium analyses

As a check, rate constants can also be estimated by means of the equilibrium constant and kinetic data of the reverse (calcination) reaction, recognizing that $K=k_{\text{carbonation}}/k_{\text{calcination}}$. The kinetics of calcination have received much more attention in the literature than the kinetics of carbonation. Borgwardt (1985) reviewed important results for calcination and made measurements with ultra-fine particles (1-90 μm) in two different types of reactors (a TGA and an entrained flow reactor). The calcination activation energy from his study, 200±13 kJ/mol, has been widely used in calcination modeling and is adopted here.

The equilibrium constant has been reported (Baker, 1962) to be,

$$K=10^{(8308/T-9.079)}$$

(2.15)

K has units of kPa when the partial pressures are expressed in kPa.

Combining the data utilized by Borgwardt (1985) and equation (2.15), we obtain the rate constants for the carbonation reaction from the slope of Arrhenius plot in Figure 2.12. The activation energy derived from these data is 41.5 kJ/mol, significantly higher than that determined in our ATGA tests for Strassburg limestone. The discrepancy probably arises because at the initial point of carbonation, the assumption of equilibrium is not truly valid, while the lattice structure of the sorbents is also relevant as discussed below. However, the order of magnitude agrees reasonably with the values reported above (24-29 kJ/mol).
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

2.3.4 Comparison with earlier results

Bhatia and Perlmutter (1983) defined a rate as:

$$ \frac{dX}{dt} = k_s' S'C $$

(2.16)

and measured $k_s' = 5.95 \pm 0.18 \times 10^{-10}$ m$^4$/mol/s for a limestone, where C is the driving force in mol/m$^3$. The CaO true density is $3.34 \times 10^6$ g/m$^3$ (Barin, 1989). As noted above, the initial surface area for Strassburg limestone is 29 m$^2$/g from N$_2$ adsorption measurement, while the porosity is $3.5 \times 10^{-4}$ m$^3$/kg from mercury intrusion measurements. So at 615°C, 10 kPa P$_{CO_2}$ with total pressure 0.1 MPa and at the initial point (X=1),

$$ \frac{dX}{dt} = 3r = 3 \times 1.67 \times 10^{-3} \times 56/3 \times 29 \times \exp \left( \frac{-29}{R_s(615+273)} \right) = 0.054 \text{ s}^{-1} \text{ for this work} $$

whereas,

$$ \frac{dX}{dt} = k_s' S'C = 0.041 \text{ s}^{-1} \text{ from Bhatia and Perlmutter (1983).} $$

These two values are of similar magnitude. However, both are smaller than the value of $\sim 0.5$ s$^{-1}$ obtained in the work of Kyaw et al. (1996).

The activation energy derived in this work differs significantly from the results of Bhatia and Perlmutter (1983) who, based on specific rate law analyses, reported that the CaO-CO$_2$ reaction has a zero activation energy in the kinetic-controlled region. This result was supported by Dennis and Hayhurst (1987) based on equilibrium analyses and calcination data. On the other hand, our activation energy is lower than values reported by Kyaw et al. (1996) who found 78 kJ/mol for limestone and 35 kJ/mol for dolomite.

The first order agrees well with results of Bhatia and Perlmutter (1983) who investigated P$_{CO_2}$ only up to 10 kPa at 615°C. The zero order agrees well with the work of Kyaw et al. (1996)
who observed a zero-order reaction for both a limestone and a dolomite based on initial rate analyses with $P_{CO_2} > 20kPa$ and a total pressure of 0.1 MPa. Our results show that there is a shift in reaction order, with neither of the former studies covering the entire $P_{CO_2}$ range.

2.3.5 Mechanistic explanations for the variable order reaction

In an attempt to explain the variable order based on a Langmuir mechanism, a series of elementary steps is assumed to be possible, with CaO•CO$_2$ as the intermediate complex. Similar to Allen and Hayhurst (1991) in the case of the CaO-H$_2$S reaction, several assumptions are made before applying the Langmuir mechanism. The first is that under the steady-state hypothesis, a fraction $\theta$ of CaO sites is covered by short-lived intermediate CaO•CO$_2$, while a fraction of $(1-\theta)$ is available for CO$_2$ adsorption. The second assumption is that the intermediate forms CaCO$_3$ quickly and that the formation of CaCO$_3$ is not the rate-limiting step. Similar to the sketch of Allen and Hayhurst (1991), the intermediate lies between CaO and CaCO$_3$. It is assumed that CaCO$_3$ does not provide any diffusion resistance to CO$_2$ within the kinetic control region.

The shift in apparent reaction order suggests that the CaO-CO$_2$ reaction might follow a series of elementary steps

\[
\begin{align*}
&k_1, \\
&CaO + CO_2 \leftrightarrow CaO\cdot CO_2 \quad \text{step 1} \\
k_2 &
\end{align*}
\]

\[
\begin{align*}
&k_3, \\
&CaO\cdot CO_2 \leftrightarrow CaCO_3 \quad \text{step 2} \\
k_4 &
\end{align*}
\]

Step 1 involves a reversible process with CO$_2$ molecules colliding with CaO sites to produce CaO•CO$_2$ intermediate complexes. Step 2 involves adsorption to produce solid product.
Chapter 2 Determination of intrinsic rate constants of the CaO-CO\textsubscript{2} reaction

Because of the assumption that step 2 is at equilibrium, so that step 1 is rate-controlling and,

\[ k_3 \times \theta - k_4 = 0 \] \hspace{1cm} (2.17)

or \[ \theta = \frac{k_4}{k_3} \] \hspace{1cm} (2.18)

Then,

\[ R = k_1 \times (1 - \theta) \times P_{\text{CO}_2} - k_2 \times \theta \] \hspace{1cm} (2.19)

Re-arrangement of equations (2.18) and (2.19) leads to,

\[ R = k_1\left[\left(1 - \frac{k_4}{k_3}\right)P_{\text{CO}_2} - \frac{k_2k_4}{k_1k_3}\right] \] \hspace{1cm} (2.20)

Overall equilibrium gives \[ \frac{k_2k_4}{k_1k_3} = \frac{1}{K} = P_{\text{CO}_2,eq} \] so that

\[ R = k_1\left[\left(1 - \frac{k_4}{k_3}\right)P_{\text{CO}_2} - \frac{1}{K}\right] \] \hspace{1cm} (2.21)

Since step 2 is assumed to be fast, site coverage of CaO•CO\textsubscript{2} complexes is very low, so that \( \theta = k_4/k_3 << 1 \). Equation (2.21) then becomes,

\[ R = k_1(P_{\text{CO}_2} - P_{\text{CO}_2,eq}) \] \hspace{1cm} (2.22)

This equation indicates the rate dependence through the Langmuir mechanism. However, from measurements at initial points we found that the apparent first order dependence only holds for \( P_{\text{CO}_2} - P_{\text{CO}_2,eq} \leq 10 \) kPa above which a zero-order dependence was observed. Based on this observation, it can be concluded that there must be a shift in reaction mechanism when \( P_{\text{CO}_2} - P_{\text{CO}_2,eq} \) exceeds this critical value, such as \( \sim 10 \) kPa. When the driving force \( (P_{\text{CO}_2} - P_{\text{CO}_2,eq}) \) is greater than the critical value, the concentration of transition complex CaO•CO\textsubscript{2} is high enough that the CaO sites are mostly saturated so that \( \theta \) approaches 1. The assumption of low
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

site-coverage of complex CaO•CO$_2$ is no longer valid. At this stage, step 2 becomes rate-limiting instead. Thus, $R = k_3 \times \theta - k_4 = k_3 \times 1 - k_4 = k_3 - k_4$.

At the critical value of $P_{CO_2} - P_{CO_2,eq}$ (~10 kPa), the rate determined from equation (2.22) reaches its maximum value, numerically equal to the rate determined as $R = k_3 - k_4$, independent of $(P_{CO_2} - P_{CO_2,eq})$.

Based on above analyses, the derived rate law is further written as,

\[
R = k_1(P_{CO_2} - P_{CO_2,eq}) \quad (k_1 \text{ is in } \frac{1}{s \cdot kPa}) \quad \text{for } P_{CO_2} - P_{CO_2,eq} \leq 10 \text{ kPa} \quad (2.23)
\]

\[
R = k_3 - k_4 = (P_{CO_2} - P_{CO_2,eq}) k_1 = 10k_1 \quad (k_1 \text{ is in } \frac{1}{s \cdot kPa}; \ k_3, k_4 \text{ are in } \frac{1}{s})
\quad \text{for } P_{CO_2} - P_{CO_2,eq} > 10 \text{ kPa} \quad (2.24)
\]

The equations (2.23) and (2.24) defining rate constants are equivalent to equations (2.11) and (2.13) for a limestone or (2.12) and (2.14) for a dolomite. In equation (2.24), $(P_{CO_2} - P_{CO_2,eq}) = 10$ kPa, so that the units of $R$ are $1/s$.

2.3.6 Other issues

Our tests indicated a somewhat higher activation energy for limestones than for dolomites, consistent with the results of Kyaw et al. (1996). The difference is probably due to the structure-related difference during nucleation or formation of the solid product. For the CaO-CO$_2$ reaction with swelling solid product, the rate of reaction is not only related to chemical energy change, but also to mechanical energy, such as strain energy between different grains. Young (1966) illustrated that during the nucleation stage, the solid structure might influence the overall free energy change, with
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

\[ \Delta G = b_1 c n^{2/3} + b_2 n (\Delta G + E_n) \tag{2.25} \]

Equation (2.25) indicates that to make the reaction occur, the energy barrier involves not only chemical energy barriers, but also a structure-related mechanical barrier. Dolomite-derived calcines, with a mixture of CaO and MgO, are likely to have relatively low strain energies, resulting in lower apparent activation energy than limestones. Other factors, involving surface energy and nucleation properties, may also be significant.

Secondly, dolomites differ from limestones in their large proportion of magnesium, causing dislocations at full calcination. These dislocations could play several roles in re-crystallization or nucleation. Young (1966) pointed out that during the incipient nucleation stage, the germ nucleus is "situated at regions of disorders, such as points of emergence of dislocations, vacancies, interstitial or impurity clusters", so that the reactant at these points must re-crystallize more readily than on a normal surface, because fewer bonds per ion need to be broken. This could also result in a lower energy barrier for dolomites.

Energy levels between calcination and carbonation are shown schematically in Figure 2.13. Both activation energies obtained from Strassburg limestone and Arctic dolomite, when taking into account the standard deviations of the fitting, are seen to be nearly consistent with thermodynamic analysis, further supporting the experimental results of this study.

2.4 Conclusions

Based on a grain model, it appears that kinetic control applies only briefly in the initial stage of carbonation. The rate constant of the CaO-CO$_2$ reaction was mainly studied using an atmospheric thermogravimetric analyzer (ATGA). Tests with two calcium-based sorbents gave similar results, showing a variable intrinsic rate dependence on CO$_2$ partial pressure. The carbonation reaction was first order only for CO$_2$ partial pressures driving force less than 10 kPa,
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

... abruptly changing to 0-order for higher CO$_2$ partial pressures. Tests in a pressurized TGA showed that further increases in CO$_2$ partial pressures could not enhance the intrinsic rate, thereby confirming the zero-order dependence above 10 kPa. Based on a Langmuir mechanism, it is plausible that saturation of CaO sites with intermediate complex CaO•CO$_2$ above a critical CO$_2$ partial pressure driving force is responsible for the shift in reaction order. The activation energies are $29 \pm 4$ kJ/mol for limestones and $24 \pm 6$ kJ/mol for dolomites, reasonably consistent with those based on equilibrium analysis. Structural differences between the two sorbents are believed to be responsible for their different activation energies.

2.5 Nomenclature

Symbols

- \(a\): Activity
- \(b_1, b_2\): Constants in equation (2.25)
- \(C\): CO$_2$ concentration, mol/m$^3$
- \(d_p\): Particle diameter, m
- \(E\): Activation energy, kJ/mol
- \(E_{st}\): Strain energy, kJ/mol
- \(k_0\): Pre-exponential factor in equation (2.10), mol/(m$^3$·s)
- \(k_1\): Rate constant in equations (2.19) (2.20) etc., 1/(s·kPa)
- \(k_2, k_3, k_4\): Rate constant in equations (2.17) (2.18) (2.20) etc., 1/s
- \(k_s\): Rate constant in equation (2.6), [mol/(s·m$^2$·(kPa)$^n$)]
Chapter 2 Determination of intrinsic rate constants of the CaO-CO\textsubscript{2} reaction

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_s^*$</td>
<td>Rate constant used by Bhatia and Perlmutter (1983)</td>
<td>m\textsuperscript{4}/mol/s</td>
</tr>
<tr>
<td>K</td>
<td>Concentration equilibrium constant</td>
<td>m\textsuperscript{3}/mol</td>
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<tr>
<td>$m_{\text{cao}}(0)$</td>
<td>Mass of calcine at time zero</td>
<td>g</td>
</tr>
<tr>
<td>$m_{\text{cao}}(t)$</td>
<td>Mass of calcine at time t</td>
<td>g</td>
</tr>
<tr>
<td>$m_{\text{CaCO}_3}(0)$</td>
<td>Mass of fresh sorbent at start of run</td>
<td>g</td>
</tr>
<tr>
<td>$n$</td>
<td>Reaction order defined in equation (2.6)</td>
<td>-</td>
</tr>
<tr>
<td>$n_n$</td>
<td>Number of molecules in nucleus in equation (2.25)</td>
<td>-</td>
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<tr>
<td>$P_{\text{CO}_2}$</td>
<td>Partial pressure of CO\textsubscript{2}</td>
<td>kPa</td>
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<tr>
<td>$P_{\text{CO}_2,eq}$</td>
<td>Equilibrium partial pressure of CO\textsubscript{2}</td>
<td>kPa</td>
</tr>
<tr>
<td>Purity</td>
<td>Purity of CaCO\textsubscript{3} in fresh sorbents</td>
<td>-</td>
</tr>
<tr>
<td>$r_0$</td>
<td>Reaction rate at time zero</td>
<td>s\textsuperscript{-1}</td>
</tr>
<tr>
<td>$r$</td>
<td>Reaction rate in grain model</td>
<td>s\textsuperscript{-1}</td>
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<td>R</td>
<td>Specific reaction rate $R = \frac{dX}{dt(1 - X)}$</td>
<td>s\textsuperscript{-1}</td>
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<td>$R_0$</td>
<td>Specific reaction rate at time zero</td>
<td>s\textsuperscript{-1}</td>
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<tr>
<td>$R_t$</td>
<td>Gas constant, 8.314x10\textsuperscript{-3}</td>
<td>kJ/mol/K</td>
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<td>S</td>
<td>Specific surface area</td>
<td>m\textsuperscript{2}/g</td>
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<tr>
<td>$S_0$</td>
<td>Specific surface area at time zero</td>
<td>m\textsuperscript{2}/g</td>
</tr>
<tr>
<td>$S'$</td>
<td>Specific surface area per unit volume of total bulk space, used by Bhatia and Perlmutter (1983)</td>
<td>m\textsuperscript{2}/m\textsuperscript{3}</td>
</tr>
<tr>
<td>T</td>
<td>Reaction time</td>
<td>s</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>K</td>
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Chapter 2 Determination of intrinsic rate constants of the CaO-CO\textsubscript{2} reaction

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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<td>( U_0 )</td>
<td>Superficial velocity in the ATGA reactor</td>
<td>m/s</td>
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<tr>
<td>( \chi )</td>
<td>Conversion of CaO</td>
<td>-</td>
</tr>
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Greek letters

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<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>Fraction of site occupied by CaO•CO\textsubscript{2} complexes</td>
<td>-</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Kinematic viscosity</td>
<td>m\textsuperscript{2}/s</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Surface free energy</td>
<td>kJ/mol</td>
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<tr>
<td>( \Delta G )</td>
<td>Overall free energy</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>( \Delta G_c )</td>
<td>Chemical free energy</td>
<td>kJ/mol</td>
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</table>
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

Figure 2.1 High-resolution SEM picture, 38-45 μm Strassburg limestone, calcined under isothermal heating, final temperature 850°C

Figure 2.2 Slope extraction with the aid of the grain model during early stages of carbonation for 38-45 μm Strassburg limestone particles at 700°C with 15% CO$_2$ and 85% He.
Chapter 2 Determination of intrinsic rate constants of the CaO-CO₂ reaction

Figure 2.3 Typical grain model plots. Early stage of carbonation for 38-45 μm Strassburg limestone particles.

Figure 2.4 Reaction order plot (Squares: 850°C; Triangles: 600°C) for fully calcined 38-45 μm Strassburg limestone with varying CO₂ partial pressure, helium making up the balance of the gas stream. RMSE=Root mean square error.
Chapter 2 Determination of intrinsic rate constants of the CaO-CO₂ reaction

Figure 2.5 Reaction order plot (Squares: at 850°C; Triangles at 600°C) for fully calcined 38-45 μm Arctic dolomite with varying CO₂ partial pressure, helium making up the balance of the gas stream. RMSE= Root mean square error.

Figure 2.6 Arrhenius plot for carbonation reaction with 38-45 μm Strassburg limestone particles.
Figure 2.7 Arrhenius plot for carbonation reaction with 38-45 μm Arctic dolomite particles.

Figure 2.8 Conversion vs time for typical kinetic run showing induction period and how the initial rates were obtained based on the maximum slopes. Strassburg limestone, 38-45 μm, 800 kPa, carbonation with 100% CO₂, 690°C.
Chapter 2 Determination of intrinsic rate constants of the CaO-CO₂ reaction

Figure 2.9 Conversion vs time for typical kinetic run showing induction period and how the initial rates were obtained based on the maximum slopes. Arctic dolomite, 38-45 μm, 0.8 MPa, carbonation with 100% CO₂ at 764°C.

Figure 2.10 Arrhenius plot comparing PTGA runs (at a total pressure of 0.8 MPa, with 100% CO₂) with ATGA runs for 38-45 μm Strassburg limestone.
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

Figure 2.11 Arrhenius plot. Comparison of PTGA runs (at total pressure of 0.8 MPa, with 100% CO$_2$) with ATGA runs for 38-45 μm Arctic dolomite.

Figure 2.12 Arrhenius plot for CaO-CO$_2$ reaction based on calcination data of Borgwardt (1985).
Chapter 2 Determination of intrinsic rate constants of the CaO-CO$_2$ reaction

For calcination:
200±13 kJ/mol (Borgwardt (1985))

For carbonation:
29 ± 4 kJ/mol for limestone
24 ± 6 kJ/mol for dolomite

1 mole CaO + 1 mole CO$_2$

1 mole CaCO$_3$

Reaction heat: 168 kJ/mol by thermodynamic analysis

Figure 2.13 Illustration of energy levels for CaO+CO$_2$<=>CaCO$_3$.
CHAPTER 3 A DISCRETE-PORE-SIZE-DISTRIBUTION BASED GAS-SOLID MODEL AND ITS APPLICATION ON THE CaO+CO₂ REACTION

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3.1 Introduction

The CaO-CO₂ (carbonation) reaction is of growing interest because of its potential usefulness in CO₂ removal in such industrial systems as steam reformers, gasifiers and fluidized bed combustors (Shimizu et al. 1999; Ortiz, A. L.; Harrison, 2001; Lin et al., 2002; Abanades et al., 2003; Johnsen et al. 2006).

In a study of intrinsic kinetics for this reaction, Chapter 2 concluded that the carbonation reaction is first order when the CO₂ partial pressure driving force is less than a critical value, 10 kPa. Above this value, it becomes a zero-order reaction. The activation energies are 29 ± 4 kJ/mol and 24 ± 6 kJ/mol for surface reaction for the limestone and dolomite investigated.

The CaO-CO₂ reaction has been found to consist of two stages, a fast stage followed by an extremely slow stage (Barker, 1973; Bhatia and Perlmutter, 1983; Abanades and Alvarez, 2003; Alvarez and Abanades, 2005a; Alvarez and Abanades, 2005b). As the reaction produces an expanded solid product, the slow stage is believed to be controlled by product-layer diffusion. The sudden change from a fast to a slow stage of reaction is of interest with respect to lime-based sorbents for CO₂ removal. Barker (1973) and Alvarez and Abanades (2005b) attributed the sharp transition to a critical thickness of product layer.

Findings in Chapter 4 and Abanades and coworkers (Abanades, 2002; Abanades and Alvarez, 2003) suggest that pore size distribution plays a crucial role for the CaO-CO₂ reaction.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

When the pore size distribution changes during calcination/carbonation cycles, the reactivity of the sorbent is altered accordingly. In this chapter we consider a mechanistic model based on distributed pore size to describe the CaO-CO\textsubscript{2} reaction with pore structural evolution.

Examples of applications of a descriptive gas-solid model to the CaO-CO\textsubscript{2} reaction are rare in the literature. Bhatia and Perlmutter (1983) employed a random pore model to obtain kinetic data to fit their experimental data at initial points and during the slow stage of reaction. However the ability of the model to describe the reaction history was not reported.

The current work formulates a new gas-solid model based on discrete pore size distribution measurement in order to obtain the effective internal diffusivity, to fit experimental data and to explain some important issues concerning the reaction. We apply intrinsic kinetic data from Chapter 2. Before formulating the model, a brief review of previous gas-solid models and their applicability to the carbonation reaction is in order.

The grain model, initiated by Szekely et al. (1976), has been applied widely and successfully, especially in modeling CaO sulphation. Some major subsequent improvements have been made, e.g. the introduction of various grain size distributions by Szekely and Proposter (1975), the expanding grain model proposed by Georgakis et al. (1979) and separation of micropores from macropores by incorporating sub-grains by Dam-Johansen et al. (1991). However, grain models have several disadvantages (Gavalas, 1980; Bhatia and Perlmutter, 1980; Sahimi et al. 1990): For example, the total internal surface area monotonically increases even when the porosity approaches zero. For this study, it is preferable to use a pore model to directly deal with pore evolution.

Pore models were initiated by Peterson (1957). His model for the first time considered two dimensional overlapping of pores, but was later superseded by 3-dimensional random pore models. Hoshimoto and Silveston (1976) also proposed a pore model with overlapping and
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

distributed pores. However, they introduced a number of fitting parameters, restricting its applicability. Christman and Edgar (1983) proposed a distributed pore size model, which showed a reasonably good ability to predict reactions with expanding product. However, they ignored pore overlapping. Simons and co-workers (Simons and Filson, 1979; Simons and Garman, 1986; Simons et al. 1987) assumed that pores in a particle are distributed such that the widest pores are at the particle surface, while the interior pores decrease in diameter. This model, called a “pore trees model”, started with a good concept of distributed pores, but has been criticized as being oversimplified with respect to the pore geometry evolution (Sahimi et al., 1990).

In pore models, the issue of overlapping of random pores is important. Detailed analyses have been independently discussed by Bhatia and Perlmutter (1980, 1981a) and Gavalas (1980). Bhatia and Perlmutter (1980) applied the overlap theory originally proposed by Avrami (1940), whereas Gavalas formulated his model statistically using a Poisson pore distribution. Later Bhatia and Perlmutter (1985) pointed out a defect resulting from the thin-product-layer assumption and made appropriate corrections, but at the cost of adding further complexity. Bhatia (1985) further extended the random pore model by incorporating distributed pore sizes. Although the random pore model has been improved based on rigorous derivations, the disadvantages of its complexity and the necessity to obtain information on the structural parameters are obvious when simultaneously considering distributed pore sizes and the build-up of product layer.

In this chapter, we develop a simple mechanistic pore model based on distributed-pores with the aid of existing pore overlapping theory. Pore size distribution data based on the mercury intrusion method are applied as input to the model.
3.2 Experimental details

Strassburg limestone and Arctic dolomite particles of diameter 38-45 μm were used for this study. Their chemical analyses are provided in Table 1.2.

Three fixed-bed thermogravimetric analyzers were used in this study, two operating at atmospheric pressures and one at pressurized conditions.

An atmospheric SHIMADZU TA60 system (ATGA) was used for kinetic study purposes with the CO₂ partial pressure, P_{CO₂}, varying from zero to 101 kPa. A pressurized thermogravimetric analyser (PTGA) was used to provide additional high-pressure data to test the effect of high P_{CO₂} on the reaction. Details and test descriptions are provided in Chapter 2. The third apparatus was an atmospheric pressure thermogravimetric reactor (ATGR), which allows operation with larger sample sizes. It was used to generate samples for pore size distribution measurement. Details of this apparatus are given by Laursen et al. (2001).

Heating from room temperature to the pre-set calcination temperature (850°C) in all three reactors was in pure CO₂ to prevent CaCO₃ decomposition. As all calcinations were conducted isothermally, heating rates of the reactors have no effect of the pore structure of calcines. Thus the thermal history of the calcines from the ATGR and the other reactors were the same so that the pore size distribution of the samples from the ATGR are the same as for samples from the other two TGAs.

Pore size distribution of samples were determined by a Micromeritics 9300 Poresizer with maximum pressure ~197 MPa, corresponding to a 5.8 nm pore size according to the Washburn equation (Lowell and Shields, 1991). Specific surface area was measured by the multiple point BET method in a Micromeritics ASPS 2010 analyser.
3.3 Model development

3.3.1 Pore overlap

Figure 3.1 illustrates a simplified two-dimensional two-pore system. The two pores, with radii $R_i$ and $R_j$, and finite length $l_i$ and $l_j$ normal to the plane, overlap as indicated. The difference of the total volume from the summation of pore volume for the two circular pores $\pi R_i^2 l_i + \pi R_j^2 l_j$ lies in the overlapped part.

In a real system, the relation between total pore volume and summation of pore volume for all cylindrical pores needs to be considered through probability analysis. Both reactant and product surfaces are developing at any time, all evolving from a group with the same initial pore radius $R_{i,0}$ ($i = 1, N$). The volumes enclosed by either the reactant surface or the product surfaces are not necessarily parallel and can spatially overlap.

For pore overlappings, both Gavalas (1980) and Bhatia and Perlmutter (1980) used the same correlation, i.e., in 1 m$^3$ of total space, the increment in the volume enclosed by the overlapped pore system is only the fraction of the growth in the non-overlapped system,

$$dV = (1-V)dV_E$$

so that, after integration,

$$V = 1 - \exp(-V_E)$$

where $V$ is the true pore volume per unit particle space (m$^3$/m$^3$), whereas $V_E$ is the pore volume (m$^3$/m$^3$) obtained by adding the volumes of all the independently developing voids, with no consideration of overlap, e.g. $V_i = \pi R_i^2 l_i$ for a pore of radius $R_i$. 

52
3.3.2 Model description

The basic assumptions for the current model are as follows.

1. The reaction proceeds isothermally.

2. Diffusion in pores and external mass transfer are not limiting factors compared to surface reaction and solid-state diffusion in product layers.

3. The product layer CaCO₃ is non-porous once formed. Therefore the reaction proceeds through solid-state diffusion crossing the product layer.

4. Pores are circular cylindrical with a total length \( L_i \) (m/m³).

5. All intraparticle pores are available for carbonation. There is no premature pore-mouth blocking.

Figure 3.2 shows the evolution of pore structure for a reaction with swelling solid product for two representative pores of initial \( R_i,0 \) and \( R_j,0 \). In a real pore system the assembly of pores is represented by a set of discrete pores with initial pore radii \( R_{i,0} \) (i=1 to N). As the reaction proceeds, the reaction fronts migrate outwards, whereas product boundaries move inwards. Initially, the reaction front is the same as the product surface because there is no product. For cell i, during reaction, the pore of initial radius \( R_{i,0} \) evolves concentrically. After time \( t \), the pore of initial radius \( R_{i,0} \) has developed into one of reactant radius \( R_{i,r} \) and product radius \( R_{i,p} \), as illustrated in Figure 2. Cylindrical voids enclosed by the product surface form the new pore volume available for further reaction. As the reaction proceeds, the overlap between adjacent surfaces grows. Although the solid product migrates inwards, the reaction fronts may also overlap with each other, especially in a 3-dimensional randomly distributed pore system. As the volume enclosed by product shrinks, \( V_E \) becomes smaller, and \( V \) closely approaches \( V_E \).
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Equation (3.2) generally applies both to the volume enclosed by the reaction front, and to that enclosed by the solid product surface, or pore volume, e.g., in Figure 3.2, the volume enclosed by the reaction front is that enclosed by $R_i,r$ or $R_j,r$, and pore volume by $R_i,p$ or $R_j,p$.

The total non-overlapping specific volume enclosed by reactant surface denoted by $V_{i,r,E}$ is obtained by adding all pores enclosed by reactant surface, i.e.

$$V_{r,E} = \sum_{i=1}^{N} V_{i,r,E} = \sum_{i=1}^{N} \pi R_{i,r}^2 I_i$$

(3.3)

Similarly the total pore volume by product surface is given by,

$$V_{p,E} = \sum_{i=1}^{N} V_{i,p,E} = \sum_{i=1}^{N} \pi R_{i,p}^2 I_i$$

(3.4)

The total length can be determined from the fractional pore volume, i.e.

$$I_i = V_{i,0,E} / (\pi R_{i,r,0}^2)$$

(3.5)

On the other hand, the counterpart variables with consideration of overlap are $V_r = \sum_{i=1}^{N} V_{i,r} =$ total volume enclosed by the reactant surface, and $V_p = \sum_{i=1}^{N} V_{i,p} =$ total volume enclosed by the product surface.

Applying equation (3.2) leads to,

$$V_r = 1 - \exp(-V_{r,E})$$

so that $\sum_{i=1}^{N} V_{i,r} = 1 - \exp(-\sum_{i=1}^{N} V_{i,r,E})$

(3.6)

$$V_p = 1 - \exp(-V_{p,E})$$

so that $\sum_{i=1}^{N} V_{i,p} = 1 - \exp(-\sum_{i=1}^{N} V_{i,p,E})$

(3.7)
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

It needs to be noted that, equations (3.6) and (3.7) are applicable to both total volumes enclosed by reactant and product surface. However, this is not exactly true for each discrete pore, i.e., for pore $R_i$,

$$V_{i,r} \neq 1 - \exp(-V_{i,r,E}) \quad (3.8)$$

$$V_{i,p} \neq 1 - \exp(-V_{i,p,E}) \quad (3.9)$$

However, equation (3.1) is applicable to discrete pores,

$$dV_r = (1 - V_r) dV_{r,E} \quad \text{so that} \quad d\left(\sum_{i=1}^{N} V_{i,r}\right) = (1 - V_r) d\sum_{i=1}^{N} V_{i,r,E} \quad (3.10)$$

$$dV_p = (1 - V_p) dV_{p,E} \quad \text{so that} \quad d\left(\sum_{i=1}^{N} V_{i,p}\right) = (1 - V_p) d\sum_{i=1}^{N} V_{i,p,E} \quad (3.11)$$

Considering that each group of pores randomly overlaps with others, it is reasonable to assume that the ratio of the overlapped volume to the non-overlapped one, as stipulated in equations (3.10) and (3.11), is applicable to each discrete pore, i.e.

$$dV_{i,r} = (1 - V_r) dV_{i,r,E} \quad (3.12)$$

$$dV_{i,p} = (1 - V_p) dV_{i,p,E} \quad (3.13)$$

Note that the discrete variables $V_{i,r,E}, V_{i,p,E}$ relate to the radii by equation (3.3) and (3.4), or

$$V_{i,r,E} = \pi R_{i,r}^2 l_i \quad (3.14)$$

$$V_{i,p,E} = \pi R_{i,p}^2 l_i \quad (3.15)$$

The specific surface areas with overlap is given by

$$s_{i,r} = dV_{i,r} / dR_{i,r} \quad (3.16)$$

for the reactant front. The area for the product surface, or the true pore surface area, can be estimated in a similar manner, leading to,
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

\[ s_{i,p} = \frac{dV_{i,p}}{dR_{i,p}} \]  \hspace{1cm} (3.17)

The current model is intended to trace the evolution of the radii of both reactant surface and pore surface. Although cylindrical pores overlap with one another according to equations (3.12) and (3.13), the radii are only determined by the non-overlapping volumes \( V_{i,r,E} \) and \( V_{i,p,E} \) using equations (3.14) and (3.15).

### 3.3.3 Rate expressions

The material balance for the solid reactant is

\[ \frac{d(n_{CO2})}{dt} = \frac{\rho_x}{M} \frac{d(V_{i,r})}{dt} = k_s (P_{CO2} - P_{CO2,eq})^{n_{r,i,s,r}} \]  \hspace{1cm} (3.18)

From Baker (1962),

\[ P_{CO2,eq} = 10^{(-8308/T+9.099)} \text{ (kPa)} \]  \hspace{1cm} (3.19)

Applying equation (3.16) into equation (3.18) leads to

\[ \frac{\rho_x}{M} \frac{d(R_{i,r})}{dt} = k_s (P_{CO2} - P_{CO2,eq})^{n_{r,i,r}} \]  \hspace{1cm} (3.20)

The gaseous reactant concentration driving force at the reaction front is determined by applying a pseudo-steady state mass balance across the product layer, i.e.

\[ \frac{\partial}{R_p \partial R_i} [D_{p,i} R_i \frac{\partial C_{CO2}}{\partial R_i}] = 0 \]  \hspace{1cm} (3.21)

The psuedo-steady-state assumption has been critically examined by Bischoff (1963). The significance of this assumption is that the interface remains stationary at any time \( t \), so that equation (3.21) can be integrated as an ordinary differential equation. The boundary conditions are:

At product surface \( R=R_{i,p}, C_{CO2} = C_{CO2,0} \)  \hspace{1cm} (3.22)
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

At reactant surface $R=R_{i,r}$, $k_s (P_{CO_2} - P_{CO_2,eq})^n = -D_p \frac{\partial C_{CO_2}}{\partial R_i}$ \hspace{1cm} (3.23)

At $t=0$ $R_{i,p} = R_{i,r} = R_{i,0}$ and $C_{CO_2} - C_{CO_2,eq} = C_{CO_2,0} - C_{CO_2,eq}$ \hspace{1cm} (3.24)

The partial pressure of $CO_2$ is related to the $CO_2$ concentration by

$$C_{CO_2} = \frac{P_{CO_2}}{R_i T}$$ \hspace{1cm} (3.25)

For limestones, kinetic results from Chapter 2 apply to equation (3.20) and (3.23),

For $n=0$, $k_s = 1.67 \times 10^{-3} \exp \left( -\frac{E}{R_i T} \right) \frac{mol}{m^2 \cdot s}$, $E = 29 \pm 4 kJ$ with $P_{CO_2} - P_{CO_2,eq} > 10 kPa$ \hspace{1cm} (3.26)

For $n=1$, $k_s = 1.67 \times 10^{-4} \exp \left( -\frac{E}{R_i T} \right) \frac{mol}{m^2 \cdot s \cdot kPa}$, $E = 29 \pm 4 kJ$ with $P_{CO_2} - P_{CO_2,eq} < 10 kPa$ \hspace{1cm} (3.27)

In the case of dolomites,

For $n=0$, $k_s = 1.04 \times 10^{-3} \exp \left( -\frac{E}{R_i T} \right) \frac{mol}{m^2 \cdot s}$, $E = 24 \pm 6 kJ$ with $P_{CO_2} - P_{CO_2,eq} > 10 kPa$ \hspace{1cm} (3.28)

For $n=1$, $k_s = 1.04 \times 10^{-4} \exp \left( -\frac{E}{R_i T} \right) \frac{mol}{m^2 \cdot s \cdot kPa}$, $E = 24 \pm 6 kJ$ with $P_{CO_2} - P_{CO_2,eq} < 10 kPa$ \hspace{1cm} (3.29)

Measured specific surface areas $S'_0$ were 29 m$^2$/g for Strassburg calcine and 48 m$^2$/g for Arctic calcine, or 31 m$^2$/g for the CaO part in the dolomite (See Appendix II for further discussion on dolomites).

At reaction front, if $P_{CO_2} - P_{CO_2,eq} < 10$ kPa, when the reaction order is unity, integration of
equations (3.20) and (3.21), together with boundary conditions, leads to

$$C_{r,j} - C_{eq} = \frac{C_0 - C_{eq}}{1 - \frac{k_s R_i T}{D_p} \frac{R_{i,p}}{R_{i,r}} \ln \left( \frac{R_{i,p}}{R_{i,r}} \right)}$$ \hspace{1cm} (3.30)
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

When \( P_{\text{CO}_2} - P_{\text{CO}_2,eq} > 10 \text{kPa} \), the reaction order is zero, and integration gives

\[
C_{r,i} = C_0 - \frac{k_r R_{i,r}}{D_p} \ln \left( \frac{R_{i,r}}{R_{i,p}} \right)
\]  

(3.31)

3.3.4 Reaction front, pore evolution and conversions by volume balance

The relationship between the pore surface and reaction surface can be further related through a volume balance. For the \( i^{th} \) group of pores,

\[
V_{i,p} = ZV_{i,0} - (Z-1) V_{i,r}
\]  

(3.32)

where, \( Z \) is the molar volume ratio of CaCO\(_3\) to CaO, about 2.17. For a dolomite, one must also consider the fraction of MgO. In this case, the molar volume ratio \( Z' \) is adopted, as discussed in Appendix II. To trace the evolution of product radius, equation (3.32) is rearranged to give

\[
dV_{i,p} = (1-Z)dV_{i,r}
\]  

(3.33)

Further applying \( dV_{i,p} = (1-V_p) \, dV_{i,p,E} \) and \( dV_{i,r} = (1-V_r) \, dV_{i,r,E} \) gives

\[
dV_{i,p,E} = \frac{1-V_r}{1-V_p} (1-Z) dV_{i,r,E}
\]  

(3.34)

Note that, for dolomites, \( Z \) needs to be replaced by \( Z' \).

Since \( dV_{i,p,E} = d(\pi l R_{i,p}^2) = 2\pi l R_{i,p} dR_{i,p} \) and \( dV_{i,r,E} = d(\pi l R_{i,r}^2) = 2\pi l R_{i,r} dR_{i,r} \), equation (3.34) leads to

\[
dR_{i,p} = (1-Z) \frac{1-V_r}{1-V_p} \frac{R_{i,r}}{R_{i,p}} dR_{i,r}
\]  

(3.35)

Combining equation (3.20) with equation (3.35) gives

\[
\frac{dR_{i,p}}{dt} = (1-Z) \frac{M}{\rho_s} \frac{1-V_r}{1-V_p} R_{i,p} k_i (P_{\text{CO}_2} - P_{\text{CO}_2,eq})^n
\]  

(3.36)
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Equations (3.20) and (3.36) are integrated to calculate surface positions as a function of reaction time with the initial condition $R_{i,p} = R_{i,r} = R_{i,0}$. When integrating, it should be noted that the reaction order is variable ($1^{st}$ or zero order) depending on the local driving force as shown in equations (3.26)-(3.29).

As the reaction causes a swelling, the radius of product surface monotonically decreases as the reaction proceeds. Once the pore radius becomes zero, there is no space for further reaction, so the reaction stops in that pore, i.e.

$$\frac{d(R_{i,r})}{dt} = 0 \quad \text{when} \quad R_{i,p} = 0$$  \hspace{1cm} (3.37)

The initial pore properties utilized here come directly from experimental measurements. Detailed discussion regarding the relationship between measured values and the initial conditions appears in Appendix III.

Initially,

$$V_{i,r} = V_{i,p} = V_{i,r,E} = V_{i,p,E} = \pi R_{i,r}^2 l_i = V_{i,0,E}$$  \hspace{1cm} (3.38)

The initial specific pore volume, $V_{i,0,E}$ ($m^3/m^3$) relates to measured pore size distribution (see Appendix III).

The overall conversion at any time is expressed as,

$$X = 1 - \frac{1 - V_r}{1 - V_0}$$  \hspace{1cm} (3.39)

where $V_r$ is determined by equation (3.6) and $V_0 = \sum_{i=1}^{K} V_{i,0}$.

3.3.5 Algorithm

The measured pore size distribution data were divided into 29 discrete pore size groups ($i=1$ to 29) for both sorbents. Detailed discussion about initial pore size distribution input can be
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

found in Appendix III. Other input data include measured kinetic data (equations (3.26-29) for the two sorbents), reaction temperature, bulk CO$_2$ concentration, molar volume ratio $Z$ or $Z'$ and time step length.

At each time step for each group of pores, the CO$_2$ concentrations at the reaction front are obtained from equation (3.30). After comparing the converted CO$_2$ concentrations (in kPa) with critical partial pressure (10 kPa), it is decided whether equation (3.31) is needed to recalculate concentrations. The reaction order and kinetic data may then also need to be revised. Equations (3.20) and (3.36) for the reaction front and pore surface are then solved using 4th order Runge-Kutta integration. Once the conditions for equation (3.37) are satisfied for a certain group of pores, the reaction stops inside this group of pores. After finishing a time step for all discrete pores, the volumes enclosed by reactant and product surface, are calculated by means of equations (3.14) and (3.15) for non-overlapped volumes for each discrete pore, equations (3.3) and (3.4) for non-overlapped total volume, and equations (3.6) and (3.7) for total volumes with overlap. Finally the conversion is estimated based on equation (3.39). A Fortran program employed for this calculation is attached in Appendix IV.

In this model, the solid-state diffusivity crossing product layer, $D_p$, is the only fitting parameter. The ATGA conversion data obtained at different temperatures with 80%v CO$_2$ for Strassburg limestone and 100% CO$_2$ for Arctic dolomite were used to fit this parameter. The best fit is found for each case by least square curve regression.

3.4 Results and discussion

The measured pore size distributions for both sorbents are shown in Figures 3.3 and 3.4. Both 38-45 and 212-250 μm particles were used in the measurements. For Strassburg limestone, the larger particles show much larger pore volume for sizes > 610 nm; the major difference
between the samples with different particle size, but with the same thermal history, implies that
the pore volume measured for sizes > 610 nm belongs to interparticle voids. Thus only the pore
volume for pores < 610 nm can be used as input for this model. Similar analysis for Arctic
dolomite calcine in Figure 3.4 shows the actual intraparticle pores reside within 360 nm. The
smaller division line for Arctic dolomite is probably because some finer particles were generated
during calcination due to the weak mechanical strength of dolomitic samples. Comparison of
Figures 3.3 and 3.4 shows that the Strassburg calcines had broader pore distributions of a
bimodal shape. The volume in 300-610 nm range is probably due to sintering during calcination
that shifts the pore volume through a lattice diffusion mechanism (German, 1996).

Fitting results are shown in Figure 3.5 and 3.6 for both sorbents. Wider deviation is found
for lower temperature runs with Arctic dolomite, e.g. 570-700°C, but reasonably good agreement
is achieved for other tests. Compared to Strassburg limestone, the Arctic dolomite generally
achieved higher calcium utilizations as shown by others (Dobner et al. 1977; Silaban et al. 1996).
The reason for the different utilizations of the two sorbents can be reasonably explained by the
current model based on structural difference. As discussed in Appendix II, the different effective
molar volume ratio for Z (for limestones) and Z' (for dolomites) indicates that the enhanced
occurrence of MgO relative to CaO in a dolomite ensures that the sorbent has enough pore
volume to accommodate carbonate product. However, the wider deviation between predictions
and experiments for Arctic dolomite at lower temperatures still indicates a deficiency in
modeling the mixture structure in the product layer of the dolomite. One possibility is that the
product layer zone is not totally non-porous because of the presence of the MgO component.

The fitted diffusivity by taking slopes from Arrhenius plots (or linear fitting) in Figure 3.6
and 3.7 is used to find the activation energy, (see Appendix I for discussions on linear fitting and
nonlinear fitting)
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

\[ D_p = 0.27 \exp\left( -\frac{E}{R_i T} \right) \text{ m}^2/\text{s}, \quad E = 215 \frac{kJ}{mol} \text{ for Strassburg limestone, } 500^\circ\text{C} \leq T \leq 850^\circ\text{C} \quad (3.40) \]

\[ D_p = 0.00083 \exp\left( -\frac{E}{R_i T} \right) \text{ m}^2/\text{s}, \quad E = 187 \frac{kJ}{mol} \text{ for Arctic dolomite, } 570^\circ\text{C} \leq T \leq 850^\circ\text{C} \quad (3.41) \]

The activation energies are found to be 215 kJ/mol for Strassburg limestone and 187 kJ/mol for Arctic dolomite. These values are reasonably close to, or slightly higher than, the 175 kJ/mol for temperatures higher than 515°C reported by Bhatia and Perlmutter (1983). A slightly higher diffusivity 238 kJ/mol was reported by Mess et al. (1999) who operated their TGA in the 550-1200°C range with non-porous CaO. As pointed out by Mess et al. (1999) and Bhatia and Perlmutter (1983), the high magnitude of activation energy is due to the solid-state diffusivity. As lattice defects due to the presence of impurities are known to enhance solid-state diffusion, the value is still lower than lattice diffusivities in single crystals of calcite (352 kJ/mol) (Mess et al., 1999). The discrepancies in measured diffusivities may also relate to lattice defects due to different impurity contents in the sorbents.

It should be noted that the diffusivities obtained in Equations (3.40) and (3.41) should be referred to as effective diffusivity because it presumably combines the diffusivity in both micropores of the product layer and in the solid product lattice. The temperature could also have a variety of effects on solid-state diffusion, i.e. affecting crystal structure or increasing diffusivity by causing lattice defects.

Activation energies obtained for some other typical product-layer-diffusion-controlled gas-solid reactions (sulphation, direct sulphation, sulfidation) are also listed in Table 3.1 for comparisons. Note that all the reactions are similar in that they are controlled by product layer diffusion at the later stage of the reaction and that different type of models have been applied to derive the data reported in this table.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Another feature of the CaO-CO$_2$ reaction is that increasing P$_{CO_2}$ will not greatly change the conversion-vs-time profile when the bulk CO$_2$ concentration is appreciably higher than the equilibrium CO$_2$ concentration. This has also been pointed out by Bhatia and Perlmutter (1983), but no analytical explanation has been given for the lack of dependence on P$_{CO_2}$.

Table 3.1 Comparison of activation energies for effective diffusivity in reactions between CaO or CaCO$_3$ and gases of interest in this work

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation energy (kJ/mol)</th>
<th>Reference</th>
<th>Reaction</th>
<th>Activation energy (kJ/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO carbonation</td>
<td>215 (limestone)</td>
<td>This work</td>
<td>CaO sulphation</td>
<td>153</td>
<td>Borgwardt and Bruce (1986)</td>
</tr>
<tr>
<td>CaO carbonation</td>
<td>175 (&gt;515°C)</td>
<td>Bhatia and Perlmutter (1983)</td>
<td>CaO sulphation</td>
<td>137</td>
<td>Borgwardt et al. (1987)</td>
</tr>
<tr>
<td>CaO carbonation</td>
<td>238 (limestone)</td>
<td>Mess et al. (1999)</td>
<td>CaO sulphation</td>
<td>120</td>
<td>Bhatia and Perlmutter (1981b)</td>
</tr>
<tr>
<td>CaCO$_3$ sulphation</td>
<td>146</td>
<td>Hajaligol et al. (1988)</td>
<td>CaO sulfidation</td>
<td>154</td>
<td>Attar and Dupuis, (1979)</td>
</tr>
</tbody>
</table>

The ATGA and PTGA experimental results are shown in Figure 3.9 and 3.10. Results for two typical temperatures, 600°C and 850°C, with Strassburg limestone are shown in Figures 3.9a and 3.9b. Only runs with CO$_2$ partial pressure driving force <10 kPa show either lower conversions or appreciably slower carbonation. Further increase of P$_{CO_2}$ well beyond P$_{CO_2,eq}$ cannot enhance carbonation rate and final conversions appreciably. Figure 3.9c compares the PTGA results, where there is much higher driving force, with the atmospheric runs at different temperatures. Comparing the PTGA and ATGA runs at 850°C, similar conclusions can be reached, with a lack of dependence on P$_{CO_2}$. Similar plots for Arctic dolomite appear in Figure 3.10. The trends are similar to those for Strassburg limestone, but with higher conversions. PTGA results in Figure 3.10c do not show appreciable improvement in either the carbonation history or final conversions for the carbonation.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

The current model is next used to predict the removal history with varying $P_{CO_2, eq}$. The results are shown in Figure 3.11 for the limestone and Figure 3.12 for the dolomite. The dotted points are used to distinguish close prediction results, with experimental data at 600°C and 850°C also plotted for comparison. The predictions confirm that increasing $P_{CO_2}$ beyond the equilibrium partial pressure has little effect on the capture. Only runs at very low driving force, e.g. driving force of 7 kPa at 600°C, show appreciably slower carbonation.

In Figure 3.13 and 3.14, the $CO_2$ concentrations at the reaction front for pores of initial measured pore size 30 nm are traced in order to explain the lack of dependence of $P_{CO_2}$. Runs with different bulk $CO_2$ concentrations are compared. The dashed horizontal line marks the converted critical $CO_2$ partial pressure driving force for reaction change (10 kPa). The plots show that there are generally two stages of reactions. During the first, $(P_{CO_2} - P_{CO_2, eq})$ at the reaction front is much higher than the critical driving force. At this stage, as shown in Chapter 2 and in equations (3.26)-(3.29) for the two sorbents, the local surface reaction lies in the zero-order reaction zone, so there is no influence of $CO_2$ concentration. With the quick build-up of the product layers, the slower stage of carbonation quickly becomes dominant. The $CO_2$ concentrations at the reaction fronts drop sharply, so the reaction lies in the first-order reaction zone. At this stage, the reaction is very slow compared to the first stage, presumably because of the controlling product-layer-diffusion step in the overall reaction. As seen in Figure 3.13 and 3.14, at this stage the $CO_2$ concentrations at the reaction fronts become very close for runs with different bulk concentrations. During the very early stage of carbonation, the $CO_2$ driving force at the reaction front usually exceeds the critical driving force (10 kPa), but the changing order of the CaO-$CO_2$ reaction makes the reaction less dependent on $P_{CO_2}$. At the later stage the product layer diffusion becomes rate-controlling, the difference in the bulk $CO_2$ concentrations is much reduced causing the $CO_2$ driving force at the reaction front to become very low.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

It is also of interest to investigate the reason for the sudden shift of the carbonation reaction from a fast stage of reaction to a slow stage. Barker (1973) and Alvarez and Abanades (2005b) attribute this sharp turn to a critical product layer thickness. In the current work, typical experimental data clearly indicate a sharp turn at the transition point (Figure 3.5 for the 600°C Strassburg limestone run with 80%v CO₂). This abrupt transition occurred at ~100 s. However, for similar conditions (100%v CO₂) Arctic dolomite shown in Figure 3.6 fails to show a very sharp turn between the initial fast breakthrough and the level-off slow stage.

The pore surface (product surface) represented by $R_{i,p}$ monotonically decreases as shown by equation (3.36) due to the assumption of unchanging total pore length. The invariable total pore length assumption, adopted in most pore models (Gavalas, 1980; Bhatia and Perlmutter, 1980; Sahimi et al., 1990) is convenient for calculating pore volume. In reality, the pore-filling by swelling product might actually occur in a three-dimensional highly overlapped pore network, and the total pore length may also be reduced. Evidence for this can be found in work by Gullett and Bruce (1987) who measured pore size distribution at different stages of the CaO-SO₂ reaction. They found reduced pore volume at each pore size, but did not find a shift in pore diameter to smaller values.

Based on these considerations, pore size distributions estimated (by calculating $V_{i,p,E}$) at different reaction times versus the initial pore sizes, are plotted in Figure 3.15 and 3.16 for both sorbents. Figure 3.15 shows that during carbonation, pore volume shrinks for pores < 250 nm, but no appreciable pore volume change can be observed found for larger pores. At the sharp turn, i.e. ~100 s for Strassburg limestone carbonated at 600°C with 80 kPa CO₂, nearly all the smaller pores were consumed, marking the turning point from the fast stage of carbonation to the slow stage, as smaller pores contribute more surface area. The remaining carbonation must proceed
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

mainly in pores of original size > 250 nm. The reaction proceeds very slowly because of the loss of most surface area. The bimodal pore size distribution of the Strassburg limestone is believed to be responsible for the two-stage pattern of the reaction. The total pore volume for small pores determines what conversions can be achieved for industrial applications where only the fast stage of reaction is of interest. In the case of the Arctic dolomite, the pore volume decreases monotonically as shown in Figure 3.16. After 500 s of reaction, some small pore volume remains, contributing to higher conversions for dolomite than for limestone. The lack of larger pores means that the carbonation of the dolomite does not pass through a sharp turn.

Note that bigger particles with appreciable pore diffusion resistance, or even appreciable external diffusion limitations, can be readily integrated into the current model using an overall mass balance on the particle. Usually a partial differential equation is needed to determine local gaseous reactant concentration at the pore surface that can be further used as an input to the current model to replace the bulk gaseous reactant concentration $C_{CO_2,0}$. Finally, the current model and mechanism are not limited only to the CaO+CO$_2$ reaction, but may be applicable also to other gas-solid reaction.

3.5 Conclusions

The CaO-CO$_2$ reaction is sensitive to the pore size distribution of calcines. A gas-solid model based on measured discrete-pore-size-distribution is formulated. The measured pore size distribution from mercury intrusion data is applied as input. The pore evolution is traced along with reaction. The method is more straightforward than other distributed-pore based pore models. Previous pore overlap theory is employed to deal with the evolution of reactant and product surface. For dolomite calcines, allowance is made for the smaller effective molar ratio of solid product to solid reactant than for limestones.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

The model is fitted to thermogravimetric reactor data from Chapter 2, with effective diffusivity as the only fitting parameter. The results indicate that the limestone and dolomite examined have activation energies of 215 kJ/mol and dolomites 187 kJ/mol, respectively, due to solid-state lattice diffusion.

Experimental data under atmospheric and pressurized conditions demonstrated that showed the reaction is appreciably affected by the CO₂ partial pressure when it is significantly higher than the equilibrium CO₂ partial pressure. The model predictions with varying P_{CO₂} generally confirm the trend and show a lack of dependence on CO₂ partial pressure beyond a critical CO₂ partial pressure of 10 kPa. During the very early stage of carbonation, the surface reaction is mostly in the zero-order zone, whereas product layer diffusion becomes rate-controlling later, but concentrations at the reaction front have little influence for different bulk CO₂ concentrations.

The pore size distribution evolution provides an explanation for the sharp turn of some limestone carbonations. The generally bimodal pore size distribution, probably arising from sintering during calcination, accounts for this pattern. When pores smaller then 300 nm are filled, the reaction turns into a slow reaction because of loss of most surface area and increasingly important product-layer diffusion. For the dolomite investigated, the carbonation is generally more gradual due to the difference in pore volumes and size distributions.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

3.6 Nomenclature

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Measured pore volume</td>
<td>m^3/kg</td>
</tr>
<tr>
<td>C</td>
<td>Concentration of CO₂</td>
<td>mol/m^3</td>
</tr>
<tr>
<td>D_p</td>
<td>Diffusivity of gaseous reactant</td>
<td>m^2/s</td>
</tr>
<tr>
<td>E</td>
<td>Carbonation activation energy</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>k_s</td>
<td>Rate constant defined by equation (3.20)</td>
<td>[mol/ s<em>m^2</em>(kPa)^-1]</td>
</tr>
<tr>
<td>M</td>
<td>Molecular weight of CaO</td>
<td>kg/mol</td>
</tr>
<tr>
<td>l</td>
<td>Total pore length</td>
<td>m/m^3</td>
</tr>
<tr>
<td>n</td>
<td>Reaction order defined in equation (3.20)</td>
<td>-</td>
</tr>
<tr>
<td>n_CaO</td>
<td>Number of molecules of CaO per unit particle volume</td>
<td>mole/m^3</td>
</tr>
<tr>
<td>N</td>
<td>Maximum group size of pores</td>
<td>-</td>
</tr>
<tr>
<td>P_CO₂</td>
<td>Partial pressure of CO₂</td>
<td>kPa</td>
</tr>
<tr>
<td>P_{CO₂,eq}</td>
<td>Equilibrium partial pressure of CO₂</td>
<td>kPa</td>
</tr>
<tr>
<td>P*</td>
<td>Critical partial pressure of CO₂</td>
<td>kPa</td>
</tr>
<tr>
<td>R</td>
<td>Pore radius</td>
<td>m</td>
</tr>
<tr>
<td>R_t</td>
<td>Gas constant, 8.31 x 10^-3 in equation (3.25)</td>
<td>kJ/mol/K</td>
</tr>
<tr>
<td>s</td>
<td>Surface area per unit particle volume</td>
<td>m^2/m^3</td>
</tr>
<tr>
<td>S'</td>
<td>Specific surface area per unit of mass of CaO</td>
<td>m^2/g</td>
</tr>
<tr>
<td>t</td>
<td>Reaction time</td>
<td>s</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>K</td>
</tr>
</tbody>
</table>
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v)</td>
<td>Volume of void</td>
<td>m³/m³</td>
</tr>
<tr>
<td>(V)</td>
<td>Volume enclosed by reactant or product surface per unit particle volume</td>
<td>m³/m³</td>
</tr>
<tr>
<td>(X)</td>
<td>Conversion of CaO</td>
<td>-</td>
</tr>
<tr>
<td>(Z)</td>
<td>Molar volume ratio of product to reactant for limestones</td>
<td>-</td>
</tr>
<tr>
<td>(Z')</td>
<td>Molar volume ratio of product to reactant for dolomites</td>
<td>-</td>
</tr>
</tbody>
</table>

Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Phi)</td>
<td>Dimensionless term containing kinetic rate expressions</td>
<td>-</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Probability density</td>
<td>m/m³</td>
</tr>
<tr>
<td>(\delta)</td>
<td>Molar volume ratio of CaO to MgO in a dolomite</td>
<td>-</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Volume fraction of voids</td>
<td>m³/m³</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Molar ratio of Ca to Mg in a dolomite</td>
<td>-</td>
</tr>
<tr>
<td>(\rho_s)</td>
<td>Density of CaO</td>
<td>kg/m³</td>
</tr>
</tbody>
</table>

Subscripts

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Definition</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i, j)</td>
<td>Index for discrete pore size interval, from 1 to N</td>
<td>-</td>
</tr>
<tr>
<td>(0)</td>
<td>Initial value</td>
<td>-</td>
</tr>
<tr>
<td>(m)</td>
<td>Measured variables, from mercury intrusion data</td>
<td>-</td>
</tr>
<tr>
<td>(E)</td>
<td>No consideration of overlap</td>
<td>-</td>
</tr>
<tr>
<td>(r)</td>
<td>Enclosed by reaction front</td>
<td>-</td>
</tr>
<tr>
<td>(p)</td>
<td>Enclosed by solid product surface</td>
<td>-</td>
</tr>
<tr>
<td>(\text{CaCO}_3)</td>
<td>Calcium carbonate</td>
<td>-</td>
</tr>
<tr>
<td>(\text{CaO})</td>
<td>Lime</td>
<td>-</td>
</tr>
<tr>
<td>(\text{MgO})</td>
<td>Magnesium oxide</td>
<td>-</td>
</tr>
</tbody>
</table>
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Figure 3.1 Schematic of a two-pore system with overlap.

Figure 3.2 Schematic of a two-pore system after evolution.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Figure 3.3 Pore size distribution results for Strassburg limestone calcines. Calcination conditions: isothermal calcination at 850°C in 100% N₂.

Figure 3.4 Pore size distribution results for Arctic dolomite calcines. Calcination conditions: isothermal calcination at 850°C in 100% N₂.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Figure 3.5 Fitting results. Experiments were in ATGA, with 80%\(^\circ\) \(\text{CO}_2\), 20% \(\text{N}_2\) balance and 35-45 \(\mu\)m Strassburg limestone particle.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Figure 3.6 Fitting results. Experiments were in ATGA with 100% CO₂ and 35-45 µm Arctic dolomite particle.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Figure 3.7 Arrhenius plot for diffusivity, $D_p$, Strassburg limestone. $E=215$ kJ/mol.

\[ y = -25980x - 1.2974 \]

$R^2 = 0.951$

Figure 3.8 Arrhenius plot for diffusivity, $D_p$, Arctic dolomite. $E=187$ kJ/mol.

\[ y = -22513x - 7.1335 \]

$R^2 = 0.9081$
Figure 3.9 Experimental carbonation data showing effect of varying CO₂ partial pressure for 38-45 μm Strassburg limestone. $P_{CO₂,eq}$ is calculated from equation (3.19) (a) ATGA at 600°C (b) ATGA at 850°C (c) PTGA at 800 kPa compared with ATGA tests
Figure 3.10 Experimental carbonation data showing effect of varying CO\textsubscript{2} partial pressure for 35-45 μm Arctic dolomite. P\textsubscript{CO\textsubscript{2},eq} is calculated from equation (3.19) (a) ATGA at 600°C (b) ATGA at 850°C (c) PTGA at 800 kPa compared with ATGA tests.
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Figure 3.11 Predicted effect of varying CO₂ partial pressure for 35-45 µm Strassburg limestone vs experimental data. $P_{CO_2, eq}$ is 48 kPa for 850°C and 0.36 kPa for 600°C, as calculated from equation (3.19).
Figure 3.12 Predicted effect of varying CO$_2$ partial pressure for 35-45 μm Arctic dolomite vs experimental data. P$_{CO_2,\text{eq}}$ is 48 kPa for 850°C and 0.36 kPa for 600°C, as calculated from equation (3.19).
Chapter 3 A discrete-pore-size-distribution based gas-solid model and its application

Figure 3.13 Predicted CO$_2$ concentration at reaction front for Strassburg limestone at 600°C, with varying P$_{CO_2}$. P$_{CO_2,eq}$ is 0.36 kPa for 600°C, calculated from equation (3.19).

Figure 3.14 Predicted CO$_2$ concentration at reaction front for Arctic dolomite at 600°C, with varying P$_{CO_2}$. P$_{CO_2,eq}$ is 0.36 kPa for 600°C, calculated from equation (3.19).
Chapter 3  A discrete-pore-size-distribution based gas-solid model and its application

Figure 3.15 Pore size distribution evolution for Strassburg calcine carbonation at 600°C and 80 kPa CO₂ partial pressure. Prediction results.

Figure 3.16 Pore size distribution evolution for Arctic dolomite calcine carbonation at 600°C and 100 kPa CO₂ partial pressure. Prediction results.
CHAPTER 4 INVESTIGATION OF EFFECT OF SINTERING ON CYCLIC CO₂ CAPTURE UNDER FLUIDIZED BED COMBUSTION CONDITIONS

A version of this chapter has been submitted for publication in AIChE J. The authors are P. Sun, J. R. Grace, C. J. Lim and E. J. Anthony.

4.1 Introduction

Calcium-based sorbents have been receiving increasing attention as possible candidates to remove CO₂ in-situ from reactors, such as steam reformers, gasifiers and water-gas shift reactors, where they can also improve hydrogen yields (Han and Harrison, 1994; Ortiz and Harrison 2001; Lin et al. 2001; 2002a; 2002b; Johnsen et al. 2006). Calcium-based sorbents can also provide CO₂ removal from fluidized bed combustors (FBC) (Shimizu et al. 1999; Gupta and Fan, 2002; Abanades et al., 2003; Salvador et al. 2003; Abanades et al. 2004a; Abanades et al. 2005). Sorbent lack of reversibility, i.e., the decline of sorbent capability over multiple cycles, is a key factor affecting process economics for calcium-based CO₂ sorbents (Abanades et al. 2004b). Among calcium-based sorbents, limestones are most appealing because of their high calcium-content, widespread occurrence and competitive prices.

Previous work on cyclic CO₂ removal with natural limestones shows that, the reversibility of limestones decays according to a similar trend for a wide variety of test conditions (Barker, 1973; Silaban and Harrison, 1995; Salvador et al. 2003; Abanades et al. 2004a; Abanades 2002; Abanades and Alvarez, 2003). CaO Sintering is believed to be the major cause of deactivation, as evidenced by the change of sorbent surface texture after multiple cycles (Barker, 1973; Abanades and Alvarez, 2003; Abanades et al. 2004a). The surface textures of cycled limestones usually show growth of macropores, as well as shrinkage of smaller pores (Abanades and...
Chapter 4 Investigation of effect of sintering on cyclic \( \text{CO}_2 \) capture under FBC conditions

Alvarez, 2003). These trends are typical of an intermediate sintering stage, described by sintering theory (German, 1996) in which vacancies (or voids) generated by temperature-and-ion-sensitive lattice defects direct void sites from smaller to larger ones, whereas the mass flow is from larger to smaller pores.

The importance of sintering of calcined limestones or their hydroxides has been studied because of the importance of limestones in high-temperature \( \text{SO}_2 \) capture (Borgwardt, 1989a, Borgwardt, 1989b; Silcox et al. 1989; Milne et al. 1990; Fuertes et al. 1993; Ghosh-dastidar et al. 1995; Mahuli et al. 1999). Ionic compounds, such as CaO mostly sinter due to volume diffusion (or lattice diffusion) mechanism. Borgwardt (1989a) introduced extremely mildly calcined CaO to a high-temperature oven to study sintering kinetics, confirming that the controlling sintering mechanism is through lattice diffusion. \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) have also been reported to enhance CaO sintering (Ewing et al. 1979; Beruto et al. 1984; Borgwardt, 1989b).

Sintering theory has not been previously applied to explain cyclic \( \text{CO}_2 \) capture. The mechanism behind the very similar sorbent performance under a variety of test conditions also needs to be clarified. It is the aim of this work to formulate and relate the sintering mechanism to sorbent cyclic behaviour and to provide better understanding of cyclic \( \text{CO}_2 \) capture.

4.2 Experimental studies

A fixed-bed thermogravimetric reactor (TGR) was used for the cyclic \( \text{CO}_2 \) capture tests. For comparison, one cyclic \( \text{CO}_2 \) capture run was also performed on a SHIMADZU TA60 thermogravimetric analyzer (TGA). All reactors operated at atmospheric pressure.

Further details of the TGR are provided elsewhere (Laursen et al. 2000; Laursen et al. 2001). Mass flow controllers were utilized to achieve desired inlet gas concentrations. A total gas flow of 1600 ml/min was maintained at the reactor inlet for both calcination and carbonation in the
Chapter 4 Investigation of effect of sintering on cyclic CO$_2$ capture under FBC conditions

TGR tests. Calcination temperatures were varied from 720 to 900°C. All carbonation reactions were carried out at 850°C with 100% CO$_2$ for a variety of times in different cycles to allow the fast stage of carbonation to go to completion. The TGA test featured 38-45 μm particles with 300 ml/min N$_2$ flow for calcination and 300 ml/min CO$_2$ for carbonation. Physical limitations were explored by varying operating parameters, e.g. particle and sample size, gas flow rate etc., to make sure surface reaction was the rate-controlling step during calcination. In all the TGR and TGA runs, a 100% CO$_2$ atmosphere was maintained during heating from room temperature to the desired calcination temperature to prevent non-isothermal calcination. When suitable temperatures were reached, calcination was initiated by switching to 100% N$_2$. As both heating and cooling rates of the TGR were fast compared to the calcination process itself, the time needed to change between calcination and carbonation operating temperatures, is considered negligible. Each calcination stage continued until no further mass decrease was observed.

Previous studies have shown that different natural limestones decay very similarly (Abanades 2002; Abanades et al. 2004a). This leads to an assumption that the sintering kinetics for natural limestones are similar, probably due to their similar lattice diffusion behaviour. Therefore, in this study, only one sorbent was used as a representative natural sorbent for the experimental and modeling study. Strassburg limestone particles of size ranges 38-45 μm and 212-250 μm were used for the TGR and TGA tests. Because of different bulk densities, 1 g of 212-250 μm or 0.5 g of 38-45 μm fresh particles was used at the start of TGR tests. In the TGA test, 4 mg 38-45 μm fresh particles were used.

After the TGR tests, the sorbents were collected and stored in a desiccator. Samples were transferred to a Micromeritics 9300 Poresizer for pore size distribution (PSD) measurement. The highest pressure achievable in this instrument is around 197 MPa, corresponding to a pore size of 5.8 nm according to the Washburn equation (Lowell and Shields, 1991).
Chapter 4 Investigation of effect of sintering on cyclic \( \text{CO}_2 \) capture under FBC conditions

A separate PSD result based on \( \text{N}_2 \) adsorption showed that a 212-335 \( \mu \text{m} \) Strassburg calcine after initial calcination had a peak pore volume of \( \sim 30 \text{ nm} \), with very limited pore volume residing at pores \( <6 \text{ nm} \), beyond the range of the mercury intrusion measurement employed in this work. Under these conditions, the specific surface area obtained by mercury intrusion data should approximate the BET values (Lowell and Shields, 1991). As a check, for initial calcines under 850°C, the two repeated specific surface area measurements by mercury intrusion gave 33 and 31 \( \text{m}^2/\text{g} \), respectively, whereas the BET method gave 36 \( \text{m}^2/\text{g} \). The differences are believed to be due to the pores outside the range of mercury porosimetry, which, while low in pore volume still contribute to surface area. Since the measured specific surface area is neither the main modeling objective nor input data in the current study, the specific surface area provided by mercury porosimetry is adequate for our purposes here.

4.3 Pore size distribution

The pore size distributions for calcines after different carbonation times in Figure 4.1 show that changing the carbonation time had negligible effect on the subsequent calcine structure. In these experiments, each carbonation step was allowed to proceed long enough to complete the fast stage. These results imply that lime sintering has no memory of carbonation history for the first cycle, or that carbonation makes no contribution to CaO sintering. It is believed that during calcination the re-crystallization from \( \text{CaCO}_3 \) to CaO eliminates all structural differences caused by carbonation. As discussed below, only extended carbonation (24 h or more) was capable of filling of the intraparticle pores of highly cycled sorbents and hence able to rearrange the CaO to give a single-peaked pore structure. Since in this study, all the carbonation steps were only allowed to finish their fast portion, the calcination step is the sole stage considered for sintering.
Chapter 4 Investigation of effect of sintering on cyclic CO$_2$ capture under FBC conditions

To investigate whether the carbonation process experiences early pore blocking as is usually found for CaO sulphation, a calcined sample was carbonated long enough to allow the fast stage carbonation to be completed. The sample was split into two parts, one of which was then mildly ground into finer powder in order to expose blocked pores. Both carbonate samples were analysed using mercury intrusion. Figure 4.2 compares the pore size distributions for the ground and the non-ground carbonates, as well as their calcines prior to being carbonated. No appreciable pore volume was found to be due to the blocked pores for runs under current test conditions. EDX mapping further indicated uniform carbon distribution over the particle cross-section as shown in Figure 4.3. (Note that the more concentrated carbon layer in the background was due to carbon-rich material used as sample bonders.)

Figure 4.4 shows the pore size distributions for calcines with different calcination holding times at 850°C. Results show that without cycling, longer holding times reduced the pore volume for pores <220 nm, but the pore distributions were all similar, with one major peak below <220 nm. Cycling the sorbent between carbonation and calcination for a cumulative holding time of 80 minutes resulted in a very different pore size distribution compared to the (single) run with initial calcination prolonged to 82 minutes. For the cyclic run, except for reduced volume of pores <220 nm (denoted V$_1$ pores), marked pore volume growth can be observed for pores larger than 220 nm (denoted V$_2$ pores). This indicates that sintering by holding calcines in N$_2$ is very different from that after cyclic calcination/carbonation. The cycled samples with shrinkage of the smaller pores and simultaneous growth in the larger pores are typical of intermediate stage solid-state sintering (German, 1996). Given that the presence of CO$_2$ is able to accelerate sintering (Ewing et al. 1979; Beruto et al. 1984; Borgwardt, 1989b), the cyclically released CO$_2$ during each calcination stage must be responsible for the development of the bimodal pore size distribution.
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

The pore size distribution results for calcines after different numbers of cycles in Figure 4.5 give further clear evidence of the development of bimodal distributions. Generally with an increase in the number of cycles, the $V_1$ pore volume decreased, whereas the $V_2$ volume increased. Similar observations were reported by Abanades et al. (2004a). However, more tests on different limestones are needed to test whether the trend observed in this work applies more generally.

To identify the upper limit of pore sizes in Figure 4.5, a SEM picture of a highly cycled calcine in Figure 4.6 shows that no pores larger than 1 μm can be observed on the surface of the cycled sample. Thus the inflection point (at ~610 nm) in the range of 500-1000 nm in Figure 4.5 should mark the limiting size for the largest intraparticle pores. Pores larger than 610 nm are believed to be interparticle voids. Figure 4.5 also shows that there are clear divisions between the two pore size ranges, i.e. pores <220 nm and larger ones of 220-610 nm. 220 nm functions as a division line in this study, but it can also be applied to the work of Alvarez and Abanades (2005) and Fennell et al. (2007). The smaller pores are presumably due to CO₂ being driving off during calcination, whereas the larger ones are due to sintering shifting vacancies from smaller pores to larger ones, driven by vacancy gradients (German, 1996).

4.4 Model development

4.4.1 Pore evolution during cyclic calcination/carbonation

Based on the above observations, a model for pore evolution during the cyclic operation is constructed. The pore evolution during cycling is believed to be responsible for the apparent decrease in CaO utilization. In the carbonation steps, a much slower reaction occurs when pores smaller than a critical pore diameter (around 220 nm in this work) are filled. This phenomenon has been reported elsewhere (Barker, 1973; Bhatia and Perlmutter, 1983; Abanades, 2002;
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

Abanades and Alvarez, 2003). To help clarify this for cyclic operation, the relationship between CaO utilization and available pore volume is plotted in Figure 4.7, where the conversion of CaO to carbonate is based on the measured pore volume given by,

\[ X = \frac{\varepsilon_0}{(1/Z - 1)(1 - \varepsilon_0)} \]  \hspace{1cm} (4.1)

Both the total pore volume and the pore volume below 220 nm are used in the calculation. When the predictions are compared to the experimental CaO utilization in the TGR, good agreement is found for the \( V_1 \) pores. This further confirms that, on recarbonation, solid CaCO₃ product fills pores of small diameters (<220 nm). Once these pores are filled, the carbonation reaction becomes product-layer-controlled and proceeds at a much slower rate, with the carbonation product then slowly filling the \( V_2 \) pores. In other words, the pore volume of smaller-diameter pores determines the achievable extent of carbonation during the fast stage of carbonation.

The specific surface area of calcines also decreases with increasing cycle number. The specific surface areas after different numbers of cycles are shown in Figure 4.8. In all of these experiments, carbonation and calcination were carried out at 850°C with 212-250 μm Strassburg limestone particles.

Given that carbonation depends strongly on the smaller pores \( (V_1) \) and the monotonic decreasing trend of pore volume of \( V_1 \) pores and specific surface area with cycling, as well as the fact that pores of larger diameter contribute much less to surface area, the relationship between the volume of <220 nm pores and specific surface area is approximated as

\[ dS = AdV_1 \]  \hspace{1cm} (4.2)

with \( S = S_g \) when \( V_1 = V_g \)

and \( S = S_a \) when \( V_1 = V_a \)
where \( S_g \) and \( V_g \) are the initial specific surface area and specific pore volume. Subscript "g" refers to a "green state" (German, 1996), an assumed state for freshly calcined limestones with zero degree of sintering where the grains are ideally spherical. A value of \( S_g = 70 \text{ m}^2/\text{g} \) is taken, the lower limit of the range (70-80 m\(^2\)/g) recommended by Mai and Edgar (1989). As different values are used in different models, sensitivity analyses on this parameter are performed below.

\( V_g \) is estimated from the theoretical maximum porosity \( \varepsilon_g \):

\[
V_g = \frac{\varepsilon_g}{\rho_{CaO}(1-\varepsilon_g)} \tag{4.3}
\]

where \( \varepsilon_g \) is obtained from equation (4.1) with \( X=1 \).

\( S_a \) and \( V_a \) are the asymptotic specific surface area and specific pore volume when the sample is sintered for an extremely long time. Various values, from 2 to 4 m\(^2\)/g, have been suggested for \( S_a \) (Mai and Edgar, 1989; Silcox et al. 1989; Milne et al. 1990; Fuertes et al. 1993; Ghoshdastidar et al. 1995; Mahuli et al. 1999). A value of 1.4 m\(^2\)/g is taken in this study as our separate BET data, using the five-point BET method for a CaO sample overnight-sintered at 1100°C, gave 1.4 m\(^2\)/g. Integration of equation (4.2) gives,

\[
V_1 = \frac{(S - S_g)}{A} + V_a \quad \text{with} \quad A = \frac{(S_g - S_a)(1-\varepsilon_g)}{\varepsilon_g} \rho_{CaO} \tag{4.4}
\]

Based on the above findings for cyclic calcination/carbonation, a pore evolution model is described as follows. It is assumed that after calcination with no sintering, CO\(_2\) released during the calcination produces calcines with voids <220 nm and a single-peaked pore size distribution in the green-state calcine. This is illustrated in Figure 4.9a, where \( V_1 \) pores are <220 nm within a unit volume occupied by the original nonporous limestone. However, in practice, calcination always involves sintering. During the initial calcination, the sintering, under the driving force of
Chapter 4 Investigation of effect of sintering on cyclic CO$_2$ capture under FBC conditions

A surface energy gradient, directs ions to fill inter-granular space or vacancies to transfer from smaller to larger pore space. As sintering is occurring simultaneously with calcination, CO$_2$ mass flow could greatly enhance sintering of CaO along the path of the offgas flow. The net results of the process are shown in Figure 4.9b. The resulting pores consist of two parts: $V_1$ pores (<220 nm) relating to the original calcination and $V_2$ pores (>220 nm) relating to pore growth due to fast CO$_2$-catalyzed vacancy flow.

During subsequent carbonation, as portrayed in Figure 4.9c, the reaction occurs in the smaller pores, and the CaO surface of the larger pores contributes little to the carbonation because of low surface area. After the fast stage of carbonation is complete, all the $V_1$ pores (<220 nm) are filled, whereas $V_2$ pores are largely unfilled, serving as high-effective-diffusivity transport passages for CO$_2$ during the reversible reactions. During carbonation, CaO sintering will not be considered, because the sintering-related mass flow of solid-state ions in $V_1$ is suppressed by the fast carbonation reaction, whereas for $V_2$ the surface energy is too small to permit appreciable sintering during carbonation.

The next sintering occurs during the next calcination stage. This sintering process is similar to the previous cycle, but with $V_1$ pores being partially occupied during the last carbonation. As CO$_2$ is released and transported outward, the resulting pores, which should reproduce all the pore volume of $V_1$ if there were no sintering, could split into pores <220 nm ($V_1$) and those >220 nm ($V_2$) because of the sintering. The net results in Figure 4.9d, show further reduction in $V_1$ and growth in $V_2$ compared to the previous cycle portrayed in Figure 4.9b. The reduced pore volume in $V_1$ is used to accommodate carbonate during the next cycle. The pore volume in $V_2$ is additive during cycling. As $V_1$ continues to decrease, CaO utilization decreases accordingly. Note that the
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

intermediate stage of sintering also involves a decrease in $V_2$ porosity, causing a decrease in total porosity (German, 1996). But equation (4) eliminates the need to model total porosity change, and it is also found that the decrease in total particle porosity is modest (to ~0.46 for samples after 15 calcination/carbonation cycles at 850°C compared to 0.54 for the theoretical maximum porosity). It is believed that particle shrinkage only becomes dominant during the later state of the intermediate and final sintering stages. Therefore shrinkage of particles is neglected when considering calcination below.

4.4.2 Reactor model for calcination

Based on the measurements discussed above, most CaO sintering occurs during calcination. To describe experimental cyclic calcination histories, a fixed bed was used for the thermogravimetric reactor. The superficial velocity in the reactor was 0.1 m/s (850°C), but the actual in-bed gas velocity in the bed should be lower due to bypassing, resulting in very low particle Reynolds numbers in the packed bed. For gas-solid flows at low Reynolds numbers (<1), the Peclet number (based on particle diameter) is small (Szekely et al. 1976), and axial dispersion has to be considered. Radial dispersion is not considered in this work. The control equation is written as,

$$ u_{\text{bed}} \frac{\partial C(t, z)}{\partial z} - D_t \frac{\partial^2 C(t, z)}{\partial z^2} = \rho_{CaCO_3}(n)(1 - \varepsilon_b) \frac{\partial X(t, z)}{\partial t} $$

The final term is related to the calcination rate for CaCO₃. In this equation, the time-derivative of $C(t, z)$ is omitted as it is usually negligible compared to other terms (Szekely et al. 1976). The bed voidage $\varepsilon_b$ was chosen as 0.5 for the randomly packed bed of uniformly sized particles. $u_{\text{bed}}$ is obtained by fitting the calcination time needed for the initial calcination. Once it is determined, it is assumed to apply also to the later cycles. In equation (4.5), time $t$ is calcination
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

time. As discussed above, for each calcination/carbonation cycle sintering accompanies calcination. The time needed to complete each calcination stage is termed the calcination time for that cycle.

The boundary conditions are,

\[ \text{At } z=0, \ C(t, z) = 0 \]  \hspace{1cm} (4.6)

\[ \text{At } z=L, \ \frac{\partial C(t, z)}{\partial z} = 0 \]

In the reactor, the gas flowed downward from the top. At the top inlet, the CO₂ concentration is always zero. In equation (4.5), at a certain vertical position \( z \), \( \frac{dX}{dt} \) describes the solid calcination rate to produce CaO at any bed location. Because calcination of limestones proceeds in a shrinking-core manner (Borgwardt, 1985; Dennis and Hayhurst, 1987), a shrinking core model (SCM) was used to express \( \frac{dX}{dt} \). The SCM model was derived with the following rate law for calcination,

\[ r = k_c [1 - C(t, z)/K_e] \]  \hspace{1cm} (4.7)

where, the equilibrium constant \( K_e \) is based on the correlation of Baker (1962),

\[ K_e = 10^{\frac{8308}{T+2979}} \text{/(R}_1T) \]  \hspace{1cm} (4.8)

The equilibrium constant \( K_e \) has units of mol/m³ when the concentrations are expressed in mol/m³.

Kinetic data for limestone calcination suggested by Borgwardt (1985) were adopted here:

\[ k_c = 3.013 \times 10^7 \times \exp[-200/(R_1T)] \]  \hspace{1cm} (mol/m²·s)  \hspace{1cm} (4.9)

The final expression for the SCM is then, at vertical position \( z \),
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

\[
\frac{dX}{dt} = \frac{1 - C(z)}{K_e} \cdot \frac{\rho_{CaCO_3}(n)R\left(\frac{1}{3k_mK_e} + \frac{(1 - X)^{-2/3}}{k_e} + \frac{R}{3D_eK_e}[(1 - X)^{-1/3} - 1]\right)}{3k_mK_e + \frac{R}{3D_eK_e}[(1 - X)^{-1/3} - 1]}
\]

(4.10)

where \(k_m\) = mass transfer coefficient (= \(ShD_0/R\)), with the Sherwood number \(Sh\) calculated from the correlation suggested by Bird et al. (2002) for creeping flow in packed beds.

\[
Sh = 0.6(Re_p \times Sc)^{1/2}
\]

(4.11)

The effective diffusivity, \(D_e\), for CO₂ inside the porous lime layer is estimated from

\[
D_e = D_0 \times \varepsilon_i^2
\]

(4.12)

The newly formed lime layer has a theoretical local porosity \(\varepsilon_i\), assumed to equal to the theoretical maximum porosity \(\varepsilon_g\). For calcined nonporous limestone, \(\varepsilon_g\) is around 0.54 based on a pore volume balance. As the current TGR calcinations have been found to be mainly controlled by gas-film mass transfer, the intraparticle mass transfer and surface reaction are not rate-limiting. Therefore, the assumption of this constant local porosity does not lead to appreciable errors.

The correlation suggested by Levenspiel (1999) for packed beds was adopted for the axial dispersion coefficient \(D_z\).

The extent of decaying carbonation with cycling is reflected in the skeleton density of carbonate, i.e., if the CaO-CaCO₃ conversion achieved after the nth carbonation is \(X_{\text{carb}}(n)\), during the \((n+1)^{\text{th}}\) calcination, the density is taken as:

\[
\rho_{CaCO_3}(n + 1) = \rho_{CaCO_3,0} X_{\text{carb}}(n)
\]

(4.13)
Chapter 4 Investigation of effect of sintering on cyclic CO\textsubscript{2} capture under FBC conditions

For the initial calcination of fresh limestone, $\rho_{\text{CaCO}_3}(1) = \rho_{\text{CaCO}_3,0}$. Note that the density of CaCO\textsubscript{3} inside a particle obtained from equation (4.13) is no longer the skeletal density, but the CaCO\textsubscript{3} density for a particle with unchanged particle size.

Equation (4.5) was linearized and then solved numerically using a finite difference method. Appendix V shows the linearization method. A downstream scheme was used for all differentiation terms. The bed height was divided into 20 equal intervals. Macroscopic variables, specific surface area and CaO conversions were obtained by averaging over the cells as follows,

$$\Phi = \frac{1}{L} \sum_{i=1}^{N} \Phi_i dl_i$$  \hspace{1cm} (4.14)

4.4.3 Macroscopic sintering during cyclic calcination/carbonation cycles

Sintering occurs simultaneously with calcination. On the macroscopic scale, the CaO surface area evolves as a result of both calcination and sintering. Hence

$$\frac{dS}{dt} = \left( \frac{dS}{dt} \right)_{\text{calcination}} - \left( \frac{dS}{dt} \right)_{\text{sintering}}$$  \hspace{1cm} (4.15)

An empirical correlation was adopted to describe CaO surface evolution in the absence of sintering:

$$S = S_g X_{\text{carb}} (n) X$$  \hspace{1cm} (4.16)

This gives $S = S_g X_{\text{carb}} (n)$ for complete calcination and zero for no calcination. For the $n^{th}$ cycle,

$$\left( \frac{dS}{dt} \right)_{\text{calcination}} = S_g X_{\text{carb}} (n) \frac{dX}{dt}$$  \hspace{1cm} (4.17)

The CaO surface area reduction $\left( \frac{dS}{dt} \right)_{\text{sintering}}$ involves the sintering kinetics.

$$\left( \frac{dS}{dt} \right)_{\text{sintering}} = k_s (S - S_g)^2$$  \hspace{1cm} (4.18)

with
Equation (4.19), based on surface area reduction, has been adopted in studies on CaO sintering during calcination (Mai and Edgar, 1989; Silcox et al. 1989; Milne et al. 1990; Fuertes et al. 1993; Ghosh-dastidar et al. 1995; Mahuli et al. 1999). An obvious disadvantage of this equation is that when the reaction is under kinetic control, $P_{\text{CO}_2}$ at the interface should closely approach the bulk CO$_2$ concentration, zero in the current TGA test. Although calcination was completed more quickly, resulting in a shorter sintering time for each successive cycle, the cyclic performance showed similar decay behaviour as in other TGA tests (Figure 4.10), indicating that sintering is still significant during the TGA test, probably due to accelerated calcination under the TGA test conditions. Therefore, in this work, equation (4.19) is modified to include calcination rate in the sintering rate expression, giving

$$k_s = 2.45(1 + 10.3P_{\text{CO}_2}^{0.67})\exp(-29000/T)$$  \hspace{1cm} (4.19)$$

where the activation energy of equation (4.19) is retained. Once the sintering rate constant was determined by equation (4.20), equation (4.18) was solved by a 4$^{th}$ order Runge-Kutta method with the initial condition that at the start of calcination, the CaO surface area is zero.

At the end of the $n^{th}$ calcination, the $V_1(n)$ pore volume can be estimated by relating it to the specific surface area as described by equation (4.4). $V_1(n)$ is then used to predict CaO conversions for the next carbonation based on a mass balance,

$$X_{\text{carb}}(n) = V_1(n) \times 56 \times \rho_{\text{CaCO}_3} \times (1 - Z)$$ \hspace{1cm} (4.21)$$

where, 56 is the molecular weight of CaO, in g/mole.

A MATLAB 6.5 based program (see Appendix VI) was employed in the overall calculation.
Chapter 4 Investigation of effect of sintering on cyclic CO$_2$ capture under FBC conditions

4.4.4 Results and discussion

Figure 4.10 shows the reversibility under various test conditions. The general trends for different cyclic runs are seen to be very similar. As described above, these tests involve different particle sizes and sample sizes for both the TGR and TGA tests. Figure 4.10 indicates somewhat better reversibility at a lower temperature, e.g. 720°C, and for a small sample size, 4 mg for the TGA run, but the trend is not strong enough to allow clear conclusions. Results from the literature (Salvador et al. 2003; Abanades and Alvarez, 2003) indicate that different natural limestones give similar reversibility.

Table 4.1 summarizes the fitted results for $u_{\text{bed}}$ based on the time needed for the initial calcination. The velocities in Table 4.1 are much smaller than the superficial velocity based on the cross-section area of the reactor (0.1 m/s). As a result, the particle Reynolds number is only about 0.04, and the Peclet number is only ~0.03 for a Schmidt number of ~0.7, justifying the inclusion of axial dispersion in the model.

Table 4.1 Fitted results for $u_{\text{bed}}$ (in equation 4.5)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Test conditions</th>
<th>$u_{\text{bed}}$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TGR, 850°C/212-250µm</td>
<td>0.012</td>
</tr>
<tr>
<td>2</td>
<td>TGR, 900°C/212-250µm</td>
<td>0.013</td>
</tr>
<tr>
<td>3</td>
<td>TGR, 800°C/212-250µm</td>
<td>0.011</td>
</tr>
<tr>
<td>4</td>
<td>TGR, 850°C/38-45µm</td>
<td>0.0105</td>
</tr>
<tr>
<td>5</td>
<td>TGR, 720°C/38-45µm</td>
<td>0.009</td>
</tr>
<tr>
<td>6</td>
<td>TGA, 850°C/38-45µm</td>
<td>Not needed</td>
</tr>
</tbody>
</table>

Once $u_{\text{bed}}$ has been estimated in this manner, it is assumed to be unchanged for the following cycles. The fitted results for calcination history are shown in Figure 4.11 for three typical cycles where 212-250 µm Strassburg limestone was subjected to calcination/carbonation...
Chapter 4 Investigation of effect of sintering on cyclic \( \text{CO}_2 \) capture under FBC conditions

cycles at 850°C in the TGR. Although some deviation can be seen along the calcination history, the predictions of the current model generally fit the experimental data reasonably well. Values of \( a \) and \( b \), determined by least square fitting using all experimental data from the six runs are 1.26 and 0.59, respectively.

Comparisons for all runs with these values of \( a \) and \( b \) are shown in Figures 4.12 and 4.13. The predictions are seen to agree reasonably well with the experimental data. The general decay trend of calcium utilizations is predicted by the current model. As described above, the degree of sintering is affected both by the duration of the calcination stage and by the sintering rate expressed by equation (4.20). These two effects could counterbalance each other to give similar sintering for different tests. For instance, the TGA test involved fast calcination or very brief exposure under sintering conditions, but a much faster rate of \( \text{CO}_2 \) release which should greatly accelerate the sintering rate, resulting in a similar sintering degree as seen in Figure 4.13.

The fitted specific surface area for the run with 212-250 \( \mu \)m particles in the TGR is compared with measured data in Figure 4.8. The predicted specific surface areas are generally higher but with a similar decay trend. Given that the specific surface area by mercury porosimetry is smaller than that obtained by the BET method, as discussed above, the model gives reasonable predictions. Predicted times for completion of the fast stage of calcination were in reasonably good agreement with experimental data as shown in Figure 4.14. When \( S_g \) was varied from 60 to 80 \( \text{m}^2/\text{g} \), the model prediction was not very sensitive to \( S_g \) as shown in Figure 4.14.

In a practical process for cyclic \( \text{CO}_2 \) capture, the sorbent would have to endure many more cycles than the number tested here. Despite losing capacity during cycling, if the highly sintered sorbent could maintain a residual \( \text{CO}_2 \) capture ability, it could be used in an affordable for \( \text{CO}_2 \) removal process. Alvarez and Abanades (2005) showed a \( \approx \)10% residual \( \text{CO}_2 \) capture ability in a
Chapter 4 Investigation of effect of sintering on cyclic CO\textsubscript{2} capture under FBC conditions

100-calcination/carbonation-cycle study. In Figure 4.15, the model is extrapolated to 1000 cycles for three cases, TGR/850°C/231 µm, TGR/900°C/231 µm, TGA/850°C/41 µm, respectively. They generally give CaO conversion, 8.5-14\% after 100 cycles, 4-6\% after 500 cycles and 2.5-4.1\% at 1000 cycles. Given the similarity for limestone reversibility, empirically regressed equations based on the extended prediction data are also shown in Figure 4.15, all with an exponential decay factor ~0.5. Considering that the current model overestimated the TGA/850°C/41 µm run and underestimated the TGR/850°C/231 µm run, the one based on TGR/900°C/231 µm test gives a reasonable estimation for long-term limestone sorbent capture.

\[ X_{\text{carb}}(n) = 1.05n^{-0.49} \]  

(4.22)

The current sintering model provides guidance on optimal \text{CO}_2 removal. As longer sintering time and higher calcination rate jointly control the degree of sintering, better CaO reversibility over long-time cycling may be achieved by adopting a lower degree of carbonation for each cycle. In this way the cumulative sintering time will be greatly shortened. Figure 4.16 shows the effect of carbonation time on the cyclic performance over 20 cycles. Under the given test conditions, 8 minutes is not enough to complete the fast stage of carbonation until after the 5\textsuperscript{th} cycle. On the other hand, for the 3-minute run where all carbonation step lasted 3 minutes, the slower stage of carbonation did not occur over the entire 20 cycles, except for the 18\textsuperscript{th} cycle that was deliberately extended to complete the fast carbonation stage. Given our finding that extent of the carbonation is determined by the pore volume of <220 nm pores, it is clear that for the same number of calcination/carbonation cycles, a shorter carbonation time retains more useful pore volume of <220 nm pores, most likely because of the reduced cumulative calcination time (Recall that each calcination step was terminated when the weight stabilized). More experimental efforts are needed to investigate the performance over >20 cycle.
Another possibility would be to use a very long carbonation time to reactivate highly cycled samples. This is because in most cases during cyclic calcination/carbonation, $V_1$ pore volume monotonically decreases, whereas $V_2$ increases over cycling, since $V_2$ pores are barely involved in the fast portion of carbonation. When the carbonation is allowed to proceed for such a long time that $V_2$ pores are gradually filled through slow product-layer-controlled carbonation, the subsequent calcination will rearrange the pore size distribution as if it were the initial calcination. Barker (1973) demonstrated the effectiveness of one-day long carbonation on cycling, and this has recently been confirmed by Salvador et al. (2003). However, the reactivated sorbents after a long saturated carbonation would again show a normal decay trend when subjected to normal cyclic CO$_2$ capture where the fast stage of carbonation is completed for each cycle.

4.5 Conclusions

Investigation of samples obtained after different numbers of calcination/carbonation cycles showed that carbonation with the fast stage completed for each cycle has no influence on calcine pore size distribution. Cycling gives pore size distributions which differ greatly from those for one-time calcination, even if there is a similar cumulative holding time. All cycled samples showed bimodal pore size distributions, with a clear division between pores <220 nm and 220-610 nm pores. The volume of <220 nm pores decreased monotonically with cycling.

A sintering model formulated based on the experimental observations relates specific surface area to the volume of <220 nm pores. This portion of pores determines the calcium utilization achievable for the next fast stage of carbonation. A packed bed model and shrinking core model were used to predict cyclic calcination history, with a modified sintering kinetic model incorporated to describe specific surface area evolution. The predictions are in reasonably good agreement with experimental data. There is little sensitivity to specific surface area, $S_g$. The
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

model reasonably explains the very similar reversibility of sorbents for the range of conditions tested. The balance between shorter cumulative sintering time and higher calcination rate can explain the similar degree of sintering. Extrapolation of the model suggests that the calcium utilization slowly decreases over cycling, eventually approaching zero, but this needs to be tested experimentally.

### 4.6 Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, b</td>
<td>Coefficients in equation (4.20)</td>
<td>-</td>
</tr>
<tr>
<td>C(t, z)</td>
<td>CO₂ concentration</td>
<td>mol/ m³</td>
</tr>
<tr>
<td>D₀</td>
<td>CO₂ molecular diffusivity in N₂</td>
<td>m²/s</td>
</tr>
<tr>
<td>Dₑ</td>
<td>Effective diffusivity of calcined product layer</td>
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</tr>
<tr>
<td>Dₜ</td>
<td>Axial dispersion coefficient</td>
<td>m²/s</td>
</tr>
<tr>
<td>I</td>
<td>Cell number</td>
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<tr>
<td>kₑ</td>
<td>Calcination rate constant</td>
<td>mol/(s/m³)</td>
</tr>
<tr>
<td>Kₑ</td>
<td>Equilibrium CO₂ concentration</td>
<td>mol/m³</td>
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<tr>
<td>kₘ</td>
<td>Mass transfer coefficient</td>
<td>m/s</td>
</tr>
<tr>
<td>kₛ</td>
<td>Rate constant for sintering</td>
<td>g/s/m²</td>
</tr>
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<td>Total bed height</td>
<td>m</td>
</tr>
<tr>
<td>i</td>
<td>Height of the i-th bed cell</td>
<td>m</td>
</tr>
<tr>
<td>N</td>
<td>Total number of cells</td>
<td>-</td>
</tr>
<tr>
<td>R</td>
<td>Particle radius</td>
<td>m</td>
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</table>
Chapter 4 Investigation of effect of sintering on cyclic \( \text{CO}_2 \) capture under FBC conditions

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
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<tr>
<td>( R_1 )</td>
<td>Gas constant, ( 8.314 \times 10^{-3} ) in equations (4.8), (4.9)</td>
<td>( \text{m}^3 \text{kPa/mol/K} )</td>
</tr>
<tr>
<td>( \text{Re}_p )</td>
<td>Particle Reynolds number, ( \text{Re}<em>p = 2Ru</em>{\text{bed}} / \nu )</td>
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<td>( S )</td>
<td>Specific surface area for CaO</td>
<td>( \text{m}^2/\text{g} )</td>
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<td>( S_a )</td>
<td>Asymptotic specific surface area for CaO, taken as 1.5</td>
<td>( \text{m}^2/\text{g} )</td>
</tr>
<tr>
<td>( Sc )</td>
<td>Schmidt number, ( \nu / D_0 )</td>
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<tr>
<td>( S_g )</td>
<td>Specific surface area for CaO with zero sintering</td>
<td>( \text{m}^2/\text{g} )</td>
</tr>
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<td>( Sh )</td>
<td>Sherwood number, defined in equation (4.11)</td>
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<td>( t )</td>
<td>Calcination or sintering time</td>
<td>( \text{s} )</td>
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<td>( T )</td>
<td>Calcination temperature</td>
<td>( \text{K} )</td>
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<tr>
<td>( u_{\text{bed}} )</td>
<td>Absolute velocity in packed bed</td>
<td>( \text{m/s} )</td>
</tr>
<tr>
<td>( V )</td>
<td>Total specific pore volume</td>
<td>( \text{m}^3/\text{m}^3 )</td>
</tr>
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<td>( V_1 )</td>
<td>Specific pore volume of pores &lt;220 nm</td>
<td>( \text{m}^3/\text{g} )</td>
</tr>
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<td>( V_1(n) )</td>
<td>Specific pore volume of pores &lt;220 nm after ( n )th calcination</td>
<td>( \text{m}^3/\text{g} )</td>
</tr>
<tr>
<td>( V_2 )</td>
<td>Specific pore volume of pores &gt;220 nm</td>
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<tr>
<td>( V_g )</td>
<td>Specific pore volume at green state</td>
<td>( \text{m}^3/\text{g} )</td>
</tr>
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<td>( V_a )</td>
<td>Asymptotic pore volume, 0</td>
<td>( \text{m}^3/\text{g} )</td>
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<td>( X )</td>
<td>Conversion of calcination when CaCO(_3) is calcined, in equation (4.5)</td>
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<tr>
<td>( X_{\text{carb}}(n) )</td>
<td>CaO conversion after ( n )th carbonation</td>
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</tr>
<tr>
<td>( z )</td>
<td>Distance from the top of bed</td>
<td>( \text{m} )</td>
</tr>
<tr>
<td>( Z )</td>
<td>Molar volume ratio of calcine to carbonate for limestones, 0.46</td>
<td>-</td>
</tr>
</tbody>
</table>
Greek letters

\( \Phi \)  
Macroscopic variables  
\( \varepsilon_0 \)  
Pore volume available for carbonation  
\( \varepsilon_b \)  
Bed voidage  
\( \varepsilon_g \)  
Theoretical maximum porosity for complete calcination, 0.54  
\( \varepsilon_l \)  
Theoretical local porosity of product layer  
\( \nu \)  
Kinematic viscosity of CO\(_2\)  
\( \rho_{\text{CaO}} \)  
Skeleton density of CaO, \( 3.34 \times 10^6 \)  
\( \rho_{\text{CaCO}_3(n)} \)  
Molar density of \( \text{CaCO}_3 \) at start of \( n^{th} \) calcination  
\( \rho_{\text{CaCO}_3,0} \)  
Molar density of \( \text{CaCO}_3 \) in original limestone
Chapter 4 Investigation of effect of sintering on cyclic $CO_2$ capture under FBC conditions

![Graph showing pore size distribution](image)

Figure 4.1 Pore size distribution: effect of carbonation time. Experiments: 850°C for calcination and carbonation in the TGR. 212-250 μm Strassburg particles. Calcination with 100% N$_2$; carbonation with 100% CO$_2$, fast stage completed.
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

Figure 4.2 Pore size distribution: carbonate before and after mild grinding. Same test conditions as in Figure 4.1.

Figure 4.3 X-ray carbon mapping for carbonated Strassburg limestone (a) Relative position of particles; (b) Carbon distribution (Light white points represent carbon; the background contains carbon-rich material) Same test conditions as in Figure 4.1.
Chapter 4 Investigation of effect of sintering on cyclic CO$_2$ capture under FBC conditions

Figure 4.4 Pore size distribution: effect of calcination time or mode. Same test conditions as in Figure 4.1.

Figure 4.5 Pore size distribution: calcines after various number of calcination/carbonation cycle. Test conditions as in Figure 4.1.
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

Figure 4.6 SEM pictures of cycled Strassburg calcine samples after 15 cycles of 850°C calcination/carbonation cycles. Test conditions as in Figure 4.1.

Figure 4.7 Conversion of CaO to CaCO₃: Experiments vs Predictions with pore volume. Experimental conditions: 850°C for calcination and carbonation in the TGR. 212-250 μm Strassburg particles. Calcination with 100% N₂, carbonation with 100% CO₂, fast stage completed.
Figure 4.8 Specific surface area after each cycle of calcinations: experimental results vs. predictions. The predictions show the sensitivity to $S_g$. Strassburg limestone, TGR test, 850°C calcination in 100% N$_2$, 850°C carbonation in 100% CO$_2$. Fast stage of carbonations completed.
Chapter 4 Investigation of effect of sintering on cyclic CO$_2$ capture under FBC conditions

Figure 4.9 Schematic of sintering progression during cyclic calcination and carbonation.

- a. 1$^\text{st}$ Calcination with no sintering
- b. After sintering, bimodal PSD
- c. After carbonation, smaller pores filled
- d. After re-calcination and sintering, pores further developed
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

Figure 4.10 Reversibility under different test conditions in the TGR or TGA. All with Strassburg limestone, calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast stage of carbonation finished for each cycle of carbonation.

Figure 4.11 CaO conversion profiles for several calcination cycles: experimental results vs. predictions. 212-250 μm Strassburg limestone, TGR test, 850°C calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast Stage of carbonation finished for each cycle of carbonation.
Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

Figure 4.12 Reversibility: experimental results vs. predictions for 212-250 µm Strassburg limestone in the TGR. Calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast Stage of carbonations is allowed to finish for each carbonation cycle.
Chapter 4 Investigation of effect of sintering on cyclic CO₂ capture under FBC conditions

Figure 4.13 Reversibility: experimental results vs. predictions for 38-45 μm Strassburg limestone in the TGR or TGA. Calcination in 100% N₂, 850°C carbonation in 100% CO₂. Fast Stage of carbonations is finished for each carbonation cycle.
Chapter 4 Investigation of effect of sintering on cyclic CO\textsubscript{2} capture under FBC conditions

Figure 4.14 Calcination time: experimental results vs. prediction. Calcinations: in 100% N\textsubscript{2}, carbonation: 850°C, in 100% CO\textsubscript{2}. Fast Stage of carbonation is finished for each carbonation step.
Figure 4.15 Predicted CaO utilizations for 1000 cycles. Same calculation conditions as in Figure 4.12 and 4.13 for each case.
Chapter 4 Investigation of effect of sintering on cyclic CO$_2$ capture under FBC conditions

Figure 4.16 Effect of carbonation time on cyclic CO$_2$ capture performance: experimental results. Starting from 850 mg of 212-250 μm fresh Strassburg limestone. Calcinations: in 100% N$_2$, 850°C; carbonation: 850°C, in 100% CO$_2$. Carbonation time at each carbonation stage: FSF - Fast stage finished, comparing with 3-minute and 8 minute for each cycle.
5.1 Introduction

Growing concerns with respect to greenhouse gas emissions have encouraged research on CO\textsubscript{2} capture. Calcium-based materials have recently attracted renewed attention (Silaban and Harrison, 1995; Silaban et al., 1996; Shimizu et al., 1999; Abanades et al., 2003; Anthony and Wang, 2003) as possible sorbents for cyclic CO\textsubscript{2}-capture processes due to their potential for regeneration. In the proposed systems, calcium oxide serves as a carbon carrier passing back and forth between the combustor and the regenerator (i.e., calciner). The concept has recently received further impetus as a result of effective CO\textsubscript{2} capture in fluidized bed reactor tests (Salvador et al., 2003; Abanades et al., 2004a; Johnsen et al., 2006).

Given that it is constrained by thermodynamics, the CO\textsubscript{2}-CaO reaction benefits by higher CO\textsubscript{2} partial pressure to achieve a higher extent of CO\textsubscript{2} removal. For a typical flue gas stream (e.g. containing 15\% CO\textsubscript{2} volumetric fraction) from a fossil fuel-fired fluidized bed combustor, Anthony and Wang (2003) showed that a total pressure as high as 1.5\times10^{3} \text{ kPa} is thermodynamically required to capture 80\% or more CO\textsubscript{2} at typical FBC temperatures (e.g. 850°C) using CaO. However, the requirement for high pressure can be relaxed when the combustor is allowed to operate at 800°C or lower when burning low-heating-value feedstocks, e.g. biomass or woodchips.
Chapter 5 Simultaneous CO₂ and SO₂ capture at fluidized-bed combustion temperatures

A pressurized fluidized bed combustor with in-situ CO₂ removal by regenerable calcium-based sorbents (Abanades et al., 2003) could be a competitive fossil-fuel-fired energy system, when CO₂ emissions are regulated in the future. To achieve this goal, several important issues need to be investigated.

To reduce sorbent cost and compete with other CO₂ capture technologies, the reversibility of sorbents during cyclic sorption/calcination must be excellent (Abanades et al., 2004b). Among the candidate sorbents, dolomites have been found to be less subject to loss of effectiveness than limestones (Silaban et al., 1996), likely due to MgO enhancing porosity and reducing sintering.

A key issue in this CO₂ removal concept is to be able to obtain favourable simultaneous CO₂ and SO₂ removal with calcium oxide in the combustor. Abanades et al. (2003) believed that the presence of SO₂ in a gas stream should not be a limiting factor because large quantities of calcium required for the carbonation would result in such high Ca/S ratios that virtually complete SO₂ capture should occur. However, detailed investigation into simultaneous CO₂ and SO₂ capture is required to test this hypothesis and to determine the effect of sulphur on Ca-utilization efficiency for carbonation. Furthermore, in pressurized fluidized bed combustors, there exist regions where calcination occurs (Iisa et al., 1991; Hansen et al., 1993) (with low local CO₂ concentrations). Hence investigation of simultaneous CO₂ and SO₂ capture by calcium oxide is of special interest for PFBC systems.

The objective of this work is to investigate simultaneous SO₂ and CO₂ removal with calcined limestone and dolomite in an ambient pressure reactor, but with augmented CO₂ partial pressures in order to extend the range of applicability of the results.
Chapter 5 Simultaneous CO\textsubscript{2} and SO\textsubscript{2} capture at fluidized-bed combustion temperatures

5.2 Experimental details

An atmospheric pressure thermogravimetric reactor (TGR) was employed in our experiments. Detailed descriptions of the system are provided elsewhere (Laursen et al., 2000; 2001). Ultra-pure CO\textsubscript{2}, 10% SO\textsubscript{2} diluted with balance N\textsubscript{2}, pure N\textsubscript{2}, and medical grade air supplied from gas cylinders were controlled by mass flow controllers to maintain the desired inlet gas concentrations. Two commercially available sorbents were investigated, Arctic dolomite and Strassburg limestone. Their chemical analyses appear in Table 1.2. Two sieve size fractions were employed: 212-250 and 500-600 μm. For the TGR tests, the temperatures were measured by K-type thermocouples located immediately below the sample holder.

To gain information on the reversibility, the two sorbents were first subjected to cyclic carbonation and calcination in pure CO\textsubscript{2} and pure N\textsubscript{2}, respectively, at 850°C. (This test is designated below as the “100% CO\textsubscript{2} test”).

In the tests for simultaneous CO\textsubscript{2} and SO\textsubscript{2} capture, 65% and 80% CO\textsubscript{2} mole fractions, well above those corresponding to AFBC conditions, were used to simulate typical non-calcining conditions in PFBCs. SO\textsubscript{2} concentrations were chosen as 1600, 2900 and 4100 ppm. The oxygen volume fraction was kept at 3%. Baselines were provided by tests with 80% CO\textsubscript{2} balanced by 20% N\textsubscript{2} for the sorption step. Fixed durations of 3, 8 and 30 minutes were employed in the sorption steps. Sulphation and carbonation temperatures were set at 750, 800 and 850°C. Calcinations were conducted in a pure N\textsubscript{2} environment. For all runs, calcinations were deemed to be complete when no further change in mass was observed. 850 mg ± 2 mg of fresh sorbents were used in all tests. The total gas flow rate was maintained at 1600 ml/min for both the calcination and carbonation stages.
Chapter 5 Simultaneous CO$_2$ and SO$_2$ capture at fluidized-bed combustion temperatures

The sorbents were first calcined at 850°C in a pure nitrogen stream. Then the temperature was adjusted by the temperature controller to the desired reaction temperature, and the specified gas stream was then introduced. Sulphation and carbonation proceeded until the calcination was complete. For the cyclic tests, when the carbonation/sulphation lasted for pre-set duration, the temperature controller and gas valves were simultaneously and promptly switched to the calcination conditions: 850°C and pure N$_2$. Cycles were then repeated until the run was complete.

5.3 Results and Discussion:

5.3.1 Baseline runs: carbonation test with no SO$_2$ in gas stream

The performance of both sorbents in cyclic calcination/carbonation tests are shown in Figure 5.1. Temperatures for both the calcination and carbonation were 850°C. In the tests with pure CO$_2$ in the sorption stage, the sorption stage was initiated as soon as the mass change was observed, as illustrated in Figure 5.2, corresponding to the turning point from the fast carbonation to the much slower product-layer-diffusion-controlled stage. Cyclic CO$_2$ capture experiments in 100% CO$_2$ environment were usually conducted with sorption time allowing the completion of each fast stage. This sorption time is designated as Fast Stage Finished or “FSF”. It typically required 3-5 minutes to detect an obvious plateau, with the shorter time for later cycles. It is believed that the micropores are filled when the fast stage carbonation is completed, whereas the slower stage is controlled by diffusion of CO$_2$ through the product-layer (Bhatia and Perlmutter, 1983; Abanades and Alvarez, 2003), so that the turning point from the fast to the slow stage is usually sharp and readily detectable.

This test supports the earlier conclusion (Silaban and Harrison, 1995; Silaban et al., 1996; Abanades and Alvarez, 2003) that for limestone, grain size growth caused by sintering decreases the reversibility of the sorbents when there are multiple cycles of calcination/carbonation. For
dolomites, the presence of MgO significantly reduces the rate of sintering, thus retaining the pore structure and facilitating better reversibility.

The baseline data with carbonation in 80% CO$_2$ and 20% N$_2$, operating for 3- and 30-minute durations are also shown in Figure 5.1 (open symbols). For the 30-minute reaction time, the data for three cycles follow the same trend as for 100% CO$_2$ tests. However, for the 3-minute reaction time, there was no obvious decay in the reversibility for either sorbent, likely due to the low calcium utilization. The reaction rate during the initial stages of carbonation experienced little change with cycling. To find whether a longer period of carbonation could alter this trend, the 18$^{th}$ cycle in the 3-minute reaction time carbonation test was extended to complete its fast stage (extended to 12.5 minutes for this cycle). As shown in Figure 5.1, no unexpected consequences were observed for the following two (19$^{th}$ and 20$^{th}$) cycles.

5.3.2 Simultaneous sulphation and carbonation: Effect of SO$_2$ on CO$_2$ capture

(a) Calcination rate

Typical results for simultaneous sulphation and carbonation are shown in Figure 5.3. Each cycle includes a sorption (sulphation and carbonation) stage and a calcination stage. The sulphate and carbonate contents are obtained from the sorbent mass profiles. During each cycle, the mass gain due to carbonation and sulphation could be separated when the carbonate was subsequently subjected to complete calcination assuming that none of the sulphate was lost. For a sorption time of 30 min, the sorbents usually exhibited a strong decay in calcination rates by the end of the third cycle. On the other hand, the decay in calcination rates for the 8-minute cyclic tests was appreciable only after 7-8 cycles. There was no such decay in calcination rates in the 3-minute tests, even after 15 cycles.
Chapter 5 Simultaneous CO₂ and SO₂ capture at fluidized-bed combustion temperatures

The decay in the initial calcination rate is illustrated in Figure 5.4. The initial calcination rate for the nᵗʰ cycle in min⁻¹ is defined as,

\[ R_{c,0} = \frac{d(\text{Mass of CO}_2 \text{ released})}{d(\text{time})} \text{ at start of } n^{th} \text{ calcination} \]

For comparison, we also show the initial calcination rates in the reversibility tests with pure CO₂ as the gas stream during the sorption stage. For the simultaneous tests with 3-minute sorption time, the decay in calcination rate was much slower. However, for SO₂/CO₂ sorption tests of longer duration, a sharp decrease was observed in the initial calcination rate as the number of cycles increased probably due to the build-up of a sulphate layer which could increase the resistance for CO₂ diffusion into the bulk or impede intra-particle heat transfer driving the calcination. Retardation of calcination due to sulphate shells was also observed in the dolomite tests (not shown here).

(b) Effects of reaction time and effect of particle size

The influence of reaction time on CO₂ capture is shown in Figure 5.5 for both sorbents. Each data point corresponds to one cycle. The reaction time on the abscissa-axis is the cumulative sorption time obtained by summing the duration of each individual sorption time stage. For comparison, we have also plotted the baselines without any SO₂ in the inlet gas stream, but with an identical CO₂ concentration (80% by volume). A major drop in the CO₂ capture ability is observed compared to the baseline. Unlike the results in Figure 5.1, the dolomite performed no better than the limestone, although the limestone decayed more sharply in some cases under comparable conditions.

Under FBC and simulated conditions, there are three possible reactions involving calcium:

\[
\text{Carbonation:} \quad \text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 \quad \Delta H_{298K} = -178 \text{ kJ/mol (5.1)}
\]
Chapter 5 Simultaneous CO₂ and SO₂ capture at fluidized-bed combustion temperatures

Sulphation: \[ \text{CaO} + \frac{1}{2}\text{O}_2 + \text{SO}_2 = \text{CaSO}_4 \quad \Delta H_{298K} = -426.5 \text{ kJ/mol} \quad (5.2) \]

Direct sulphation: \[ \text{CaCO}_3 + \frac{1}{2}\text{O}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2 \quad \Delta H_{298K} = -323.6 \text{ kJ/mol} \quad (5.3) \]

The rates for reactions (5.2) and (5.3) have been found to be comparable (Tullin and Ljungstrom, 1989), provided that the specific surface areas are similar for the two sorbents (CaO and CaCO₃).

Carbonation of CaO is much faster than sulphation in typical PFBC flue gases, with the result that the sulphation of CaO proceeds to a very limited degree when both reactions are occurring (Iisa et al., 1991; Tullin and Ljungstrom, 1989). During the first few minutes of reaction, carbonation dominates, producing a compact product shell of carbonate, thereby greatly retarding both reactions (5.1) and (5.2). Exposure of the carbonate product favours reaction (5.3). Compared to the CaO-SO₂ reaction, reaction (5.3) has been reported to suffer less product-layer-related decay because of the release of gaseous CO₂, causing a more porous product layer and a higher effective diffusivity in the nascent sulphate product (Tullin and Ljungstrom, 1989; Krishnan and Sotirchos, 1993). If enough time were allowed for the carbonation to become product-layer-diffusion controlled, direct sulphation could become dominant.

The cumulative loss of calcium due to sulphur capture with each cycle, reducing the availability of solid reactant and reacting surface, thus partially causes the observed drop in CO₂ capture capability. The reduction of calcium due to sulphur capture cannot account for the entire loss of reversibility as suggested in Figure 5.6, where the ordinate gives the moles of lime determined by subtracting the amount of calcium consumed by sulphation from the total calcium. The calcium utilization due to CO₂ removal is also shown to decrease sharply with each successive cycle. The free-lime-based calcium utilization decays more for longer-sorption-time cycles, with the least decay occurring for the 3-minute-sorption runs. Based on a comparison with the baseline tests shown in Figure 5.6 and also in Figure 5.1 where there was no SO₂
Chapter 5 Simultaneous CO\textsubscript{2} and SO\textsubscript{2} capture at fluidized-bed combustion temperatures

involved, we attribute this to the presence of SO\textsubscript{2} in gas stream in the present circumstance for the sharp decay of the sorbents in their ability to cyclically capture CO\textsubscript{2}. As there might be more engineering interest in carbonation efficiency based on the free-lime-content at different sulphation conditions, the free-lime basis is adopted for the following discussion of CO\textsubscript{2}-related calcium utilization.

The likely explanation for the decrease of CO\textsubscript{2} capture ability is that the sulphated envelope becomes thicker with longer sorption time. The thicker sulphate layer not only reduces the calcination rate, as shown in Figure 5.4, but also adds to the resistance for the subsequent carbonation. For 3-minute runs, this effect is weak, probably due to the thinness of the sulphate layer.

As seen in Figure 5.5, the dependence of the decay in reversibility on the particle size is weak for the dolomite and for shorter sorption times. For the dolomite, almost all runs with larger (500-600 μm) particles experienced an increase of CO\textsubscript{2} uptake during the first two cycles, probably due to a change in pore structure. For the limestone, however, there was little difference between the larger and smaller particles as shown in Figure 5.5(b), with almost the same performance for both sizes of particles in 8-minute tests. These results suggest that pore diffusion resistance is more important for calcined dolomite than for limestone, especially during the first few cycles of sorption in the 8-minute tests.

(c) Effect of reaction temperatures

Higher temperatures give higher sulphation rates; the direct sulphation rate-dependence on temperature shows no obvious maximum compared to sulphation of CaO (Podolski et al., 1995). The dependence of rate of carbonation on temperature is not well-understood, with some researchers (Bhatia and Perlmutter, 1983) concluding that the activation energy of reaction (5.1) is zero. The decrease in reaction temperatures results in an increase in driving force for reaction
Chapter 5 Simultaneous CO₂ and SO₂ capture at fluidized-bed combustion temperatures

(5.1). In our tests, when the temperature decreased from 850 to 800°C and then to 750°C, the driving force, estimated from the correlation of Baker (1962), increased from 32 to 58 kPa and then to 71 kPa with the CO₂ partial pressure maintained constant at 80 kPa.

Figure 5.7 shows a strong effect of temperature for both sorbents, although the dolomite shows slightly less decay. Runs at lower temperature, e.g. 750°C, led to higher CO₂ capture, especially for early cycles, due to the higher absorption rates provided by the higher driving force. However, a sharp decrease is immediately observed, indicating that SO₂, or more precisely the sulphate layer, has a stronger impairing effect on the CaO-CO₂ reaction. Although higher temperatures lead to increased sulphation rates, so that one would expect the effect of SO₂ on CO₂ capture to be more appreciable at higher temperature, the sharpest decreases in sorbent reversibility are observed at lower temperatures, indicating that under the current temperature conditions the effect of changes in sulphation rates is surpassed by the decrease in carbonation rates. These trends are similar for both sorbents.

(d) Effect of SO₂ concentration

Higher SO₂ concentration allows more calcium to be sulphated. The resulting thicker sulphate shell increases the resistance to CO₂ diffusion, causing a sharper decay in the rate of carbonation. This is confirmed in Figure 5.8 for both sorbents and for different durations of sorption. The influence of SO₂ concentration becomes more appreciable for later cycles, consistent with thicker layers of sulphate causing greater decay in the reversibility of carbonation.

(e) Effect of CO₂ concentration

As shown in Figure 5.9, the effect of SO₂ to diminish the carbonation reversibility was appreciably greater for high CO₂ concentrations than for low CO₂ concentrations. Although the
higher driving force for the same temperatures should lead to greater CaO utilization, this was only true for the early cycles, with the advantage being greatly reduced for later cycles, presumably because of the presence of a compact sulphate layer which exerts more influence on the CaO-CO\textsubscript{2} reaction for higher CO\textsubscript{2} concentration and longer sorption times.

5.3.3 Simultaneous sulphation and carbonation: Effect of CO\textsubscript{2} on SO\textsubscript{2} capture

Figure 5.10 shows that the presence of CO\textsubscript{2} in the gas stream enhances SO\textsubscript{2} capture. Direct sulphation of the carbonates could proceed more quickly than sulphation of CaO because of the porous nature of the sulphate product (Tullin and Ljungstrom, 1989; Krishnan and Sotirchos, 1993). However, this phenomenon only became appreciable at higher conversions, e.g. calcium utilization higher than 30-40\%, because at lower conversions kinetics tend to be the limiting step, and the CaO-SO\textsubscript{2} reaction was probably faster than the CaCO\textsubscript{3}-SO\textsubscript{2} reaction due to CaO having a higher surface area than CaCO\textsubscript{3}. In Figure 5.10, however, enhancement is observed even at the very low conversions in all cases, especially for runs of shorter duration. In other words, although CaCO\textsubscript{3} is usually lower in surface area than CaO and is supposed to be slower than CaO when reacting with SO\textsubscript{2} at low conversions, it actually exhibits more reactivity when cyclic carbonation(calcination proceeds in parallel with sulphation, as shown in Figure 5.10. This suggests that cyclic sorption could enhance sulphation by producing more reactive CaCO\textsubscript{3} compared to the CaO-SO\textsubscript{2} reaction. Cycles of shorter duration show the greatest enhancement effect.

By comparing the performance of different sorbents and particle sizes, we find that the dolomite shows a significantly greater ability to capture SO\textsubscript{2} than limestone. Particle size seems to have little effect on the rate of SO\textsubscript{2} capture or on the enhancement effect of CO\textsubscript{2}. 

123
Chapter 5 Simultaneous CO$_2$ and SO$_2$ capture at fluidized-bed combustion temperatures

5.4 Conclusions

Simultaneous carbonation and sulphation were investigated under simulated FBC conditions in an atmospheric-pressure thermogravimetric reactor (TGR). SO$_2$ was found to impede CO$_2$ capture, with calcination rates diminished by the sulphate outer shells enveloping the sorbent particles. The decrease in rate was less for shorter sorption durations, but these led to less CO$_2$ capture. Higher temperatures resulted in less decay, but also in reduced CO$_2$ capture. Total calcium utilization decreased with multiple cycles, especially for longer sorption times. Higher SO$_2$ concentrations led to a sharper decay in reversibility. Sharper decays in reversibility occurred at higher CO$_2$ conditions. CO$_2$ enhanced the capture of SO$_2$, especially for runs of brief sorption duration.

Due to the high molar ratio of CO$_2$ to SO$_2$, Abanades et al. (2003) believed that the high Ca/S molar ratio for cyclic carbonation/calcination would enable efficient SO$_2$ capture in a proposed PFBC-based CO$_2$ removal process (Abanades et al., 2003; 2004a) such that CO$_2$ removal would not be influenced significantly by calcium loss due to reaction with SO$_2$. However, the results of this work show that the presence of SO$_2$ in the gas stream greatly impedes the reversibility of even potentially good sorbents such as dolomite. This may lead to difficulties for practical CO$_2$ capture based on limestone cycles. We recognize, however, that the current results are only based on simulated non-calcining conditions and bench scale tests. Further tests under more realistic conditions and with macro-scale reactors are required. If the adverse effect of SO$_2$ on CO$_2$ capture is confirmed, revisions of the present concept, such as separate removal of SO$_2$ and CO$_2$ or steam reactivation would need to be tested in the search for a practical process.
Chapter 5 Simultaneous CO\textsubscript{2} and SO\textsubscript{2} capture at fluidized-bed combustion temperatures

Figure 5.1 CO\textsubscript{2} cyclic capture performance. 212-250 μm Arctic dolomite and Strassburg limestone. Calcination: 850°C in 100% N\textsubscript{2}; Carbonation 850°C with 80 or 100% CO\textsubscript{2} (no SO\textsubscript{2}). Sorption time is 3, 30 min for each sorption stage or FSF.

Figure 5.2 Illustration for turning point selection in a 100% CO\textsubscript{2} capture test with 212-250 μm Strassburg limestone.
Chapter 5 Simultaneous CO$_2$ and SO$_2$ capture at fluidized-bed combustion temperatures

Figure 5.3 Test results for 212-250 µm limestone, 850°C calcination and 850°C sorption with 2900 ppm SO$_2$ and 80% CO$_2$. 
Figure 5.4 Comparison of initial calcination rate of each cycle for the limestone, 850°C calcination/850°C carbonation, 212-250 μm particle.
Chapter 5 Simultaneous CO$_2$ and SO$_2$ capture at fluidized-bed combustion temperatures

Figure 5.5 Effect of cumulative reaction time. 850°C calcination/850°C sorption, gas compositions for SO$_2$/CO$_2$ sorption: 80% CO$_2$, 2900 ppm SO$_2$, 3% O$_2$, balance N$_2$. (Baseline, 80% CO$_2$, 20% N$_2$).
Figure 5.6 Total calcium utilization change with cycles for 850°C calcination/850°C sorption, gas compositions for sorption: 80% CO$_2$, 2900 ppm SO$_2$, 3% O$_2$, balance N$_2$. 
Figure 5.7 Effect of reaction temperature CO$_2$ concentration for each cycle, 212-250 μm, 3-minutes sorption time, 850°C calcination, gas compositions for SO$_2$/CO$_2$ sorption:

80% CO$_2$, 2900 ppm SO$_2$, 3% O$_2$, balance N$_2$. (Base lines, 80% CO$_2$, 20% N$_2$).
Chapter 5 Simultaneous CO\textsubscript{2} and SO\textsubscript{2} capture at fluidized-bed combustion temperatures

Figure 5.8 Effect of SO\textsubscript{2} concentration for successive cycles for 212-250 \(\mu\)m particle 850°C calcination/850°C sorption, gas compositions for SO\textsubscript{2}/CO\textsubscript{2} sorption: 80% CO\textsubscript{2}, 3% O\textsubscript{2}, balance N\textsubscript{2}. (Baseline, 80% CO\textsubscript{2} 20% N\textsubscript{2}).
Figure 5.9 Effect of CO₂ concentration for successive cycles with 212-250 μm limestone. 850°C calcination/850°C sorption. Gas compositions for SO₂/CO₂ sorption: 80% CO₂, 2900 ppm SO₂, 3% O₂, balance N₂ (Base lines, 80% CO₂ 20% N₂).
Chapter 5 Simultaneous $\text{CO}_2$ and $\text{SO}_2$ capture at fluidized-bed combustion temperatures

(a) 212-250 µm Arctic dolomite

(b) 212-250 µm Strassburg limestone
Figure 5.10 Effect of CO$_2$ on SO$_2$ capture. 850°C calcination/850°C sorption. Gas compositions or SO$_2$/CO$_2$ sorption: 80% CO$_2$, 2900 ppm SO$_2$, 3% O$_2$ (Base lines: 2900 ppm SO$_2$, 3% O$_2$).
CHAPTER 6 REMOVAL OF CO₂ BY CALCIUM-BASED SORBENTS IN THE PRESENCE OF SO₂

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6.1 Introduction

The use of calcium-based sorbents as candidates to remove CO₂ in-situ from reactors has been receiving increasing attention, not only for steam reformers, steam gasifiers and water-gas shift reactors to improve hydrogen yields (Han and Harrison, 1994; Lin et al. 2001; 2002; Ortiz and Harrison, 2001; Johnsen et al., 2006), but also for CO₂ removal from fluidized bed combustors (FBC) (Shimizu et al., 1999; Gupta and Fan, 2002; Hughes et al., 2004; Abanades et al., 2003, 2004a; 2005; Salvador et al., 2003).

The decline in sorbent capability in multiple cycles, i.e. reversibility, is a key factor affecting process economics for calcium-based CO₂ sorbents (Abanades et al., 2004b). It has been reported that dolomites are generally more reversible than limestones in such cycles (Silaban et al., 1996). Natural limestones usually follow similar decay trends when exposed to cyclic capture conditions (Abanades, 2002). Sintering of unreacted CaO is believed to be the major cause of deactivation, as evidenced by the change of sorbent surface texture after multiple cycles (Abanades, 2002; Abanades and Alvarez, 2003; Alvarez and Abanades, 2005). In Chapter 5, it was found that the SO₂, a common pollutant in coal-fired fluidized bed combustors, appreciably decreases the CO₂ capture capacity for multiple cycles, despite the fact that SO₂ concentrations are several orders of magnitude lower than CO₂ concentrations. This adverse
Chapter 6 Removal of CO₂ by calcium-based sorbents in the presence of SO₂

Effect of SO₂ was recently confirmed by Ryu et al. (2006) in a bubbling fluidized bed with batches of sorbent. However, the mechanism of deactivation by low levels of SO₂ is still unclear.

The objective of this work was to investigate cyclic co-capture of SO₂ and CO₂ in greater detail in order to clarify the mechanism of deactivation, to test the effect of sorbent type, and to test possible ways to improve the reversibility of calcium-based sorbents.

6.2 Experimental details

Seven commercially available sorbents were tested: Strassburg limestone (US), Danyang limestone (Korea), Havelock limestone (Canada), Kelly Rock limestone (Canada), Cadomin limestone (Canada), Arctic dolomite (Norway) and GS dolomite (US). Table 1.2 gives chemical analyses. For all tests in this study, the particle size range was screened to 212-250 μm. Two fixed-bed thermogravimetric reactors were used for the experiments, one operating at atmospheric pressure and the other under pressurized conditions up to 2.4 MPa. Details of the atmospheric pressure thermogravimetric reactor (ATGR) are provided elsewhere (Laursen et al., 2000; 2001). Mass flow controllers were utilized to achieve desired inlet gas concentrations. A total gas flow of 1600 ml/min was maintained for both calcination and carbonation. A typical FBC combustor temperature, 850°C, was chosen for all runs. During the sorption stage, 80% CO₂ was typically used at 850°C. The inlet concentrations of SO₂ and O₂ were maintained at 2900 ppm and 3% by volume respectively. Fresh samples weighing approximately 850 mg were loaded into the basket for each ATGR run so that enough sorbents were generated for pore size analyses, chemical analyses or SEM studies. Under such conditions, both interparticle and intraparticle mass transfer can be significant.

The sorption time for each cycle has been found to be important in previous work (Barker, 1973; Alvarez and Abanades, 2005). Each cycle includes one step of calcination followed by a
Chapter 6 Removal of CO\textsubscript{2} by calcium-based sorbents in the presence of SO\textsubscript{2}

sorption (carbonation w/o sulphation) step. Two durations for the sorption step were employed for ATGR tests. The turning point from an initial fast stage of carbonation to a slower stage, easily detected under the current test conditions (see Chapter 5), was used to determine the stopping point for each cycle. This duration, denoted “fast stage finished” (FSF), is predominantly used in tests with no SO\textsubscript{2} present. Alternatively, a fixed duration of 8 minutes was selected, primarily for co-capture tests in the atmospheric TGR. During the first few cycles, a time of 8 minutes was not long enough to complete the fast stage of carbonation. However, this duration was sufficient for later cycles.

The pressurized thermogravimetric analyser (PTGA), consisting of a Cahn 100 balance of 1 \( \mu \)g sensitivity and a reactor column made of Inconel 600 alloy, was used to simulate pressurized fluidized bed combustion (PFBC) conditions. Restricted by the operating temperatures utilized in FBC combustors, high removal efficiencies could only be achieved at high CO\textsubscript{2} partial pressures. A PFBC is therefore ideal for capture of CO\textsubscript{2} by calcium-based sorbents. The PTGA was used to test the effects of total pressure and partial pressure of CO\textsubscript{2} and SO\textsubscript{2}. Strassburg limestone and Arctic dolomite were selected for these tests. A pressure regulator adjusted the pressure level. Mass flow controllers allowed desired mixtures of reactant gases to be delivered. A CO\textsubscript{2} concentration of 8% by volume was selected as the base condition. As shown below, varying the CO\textsubscript{2} concentration from 14%\textsubscript{v} to 20%\textsubscript{v} had negligible effect on the reversibility of sorbents when CO\textsubscript{2} was the only reactant gas. In PTGA runs, 50±2 mg of fresh sorbents screened to a 212 to 250 \( \mu \)m size range were introduced to the reactor at the start of each run. For the PTGA runs, the sorption time was 4 minutes for tests with and without SO\textsubscript{2}, enough for the fast stage of carbonation to be completed for each cycle. Each sorption stage was conducted under high-
pressure conditions, whereas calcination could be conducted under either atmospheric or pressurized conditions.

For the tests in both reactors, temperatures for calcination and carbonation were maintained at 850°C except where specified. Only the initial calcination was operated non-isothermally, increasing the temperature from room temperature, whereas all subsequent cycles shifted between calcination and carbonation by switching gas compositions while maintaining the temperature. After switching, the gas took around 1 minute to reach the sample surface, making no difference to the cycling time given the cyclic operational manner. All calcinations were performed in an atmosphere of pure N₂.

The collected samples were analysed by several techniques. SEM/EDX was carried out using HITACHI S-3000. For sulfur mappings, samples were first embedded in epoxy and then carefully ground and polished to expose cross-sections. For high-resolution SEM measurements, all samples were gold-coated to make them conductive. A Micromeritics 9300 Poresizer determined the pore size distributions of sorbents. A Siemens Diffraktometer D5000 provided phase detection for some samples.

6.3 Results and Discussion

6.3.1 Tests with no SO₂ among the gaseous reactants, referred to hereafter as “no SO₂” tests

The cyclic performance of the seven sorbents during the 850°C sorption/calcination cycles, based on total calcium utilization, is shown in Figure 6.1. The tests were performed at ATGR. 80% CO₂, 20% N₂ were used for the sorption stage and 100% N₂ for the calcination stage. Calcium utilization is calculated on a molar basis.
Chapter 6 Removal of CO$_2$ by calcium-based sorbents in the presence of SO$_2$

The dolomites showed both higher calcium utilizations and better reversibility than the limestones. The superior reversibility of the dolomites is probably due to a lack of sintering-related CaO crystal coarsening, presumably due to the MgO part resisting the mass flow of sintering-stress-driven ions and vacancies in this ionic compound. For limestones, the Ca utilization decreased to 20-30% of the original value after 15 cycles, with relatively minor differences among the five limestones investigated.

High-resolution SEM images for calcines of Strassburg limestone, Arctic dolomite and Kelly Rock limestone after cycling are shown in Figure 6.2 (that of Danyang limestone is shown in Figure AVII.1 in Appendix VII). Strassburg and Kelly Rock limestones showed similar decay trends, probably related to structural changes during the sintering cycles. The microstructures for their calcines, however, differed significantly. Strassburg limestone showed a typical intermediate sintering pattern (German, 1996), characteristic of shrinking small pores and growing larger pores, leaving behind clusters when some parts of CaO coarsen. Kelly Rock limestone, showed a more grainy structure with clear neck development between grains, but with more pore volume between grains. Despite differences in their microstructures, the pore size distributions of Strassburg and Kelly Rock limestones in Figures 6.3a and 6.3b showed similar sintering patterns, reducing pore volume in the $<$~200 nm range in favour of pores of 200 nm or larger. This caused the previous mono-modal pore distribution to undergo a transition to a bimodal distribution, with the degree of reversibility appearing to be very similar for these two limestones.

In Figure 6.2c, cycled Arctic dolomite calcines did not contain visible pores from the SEM photo, and the grain size could not be viewed clearly. The extent of sintering was much lower than for the limestones. Given that dolomites may have higher surface-area-related sintering stresses, the reduction in sintering was likely due to retarded sintering kinetics or to interspersed
MgO reducing diffusion of CaO ions. Figure 6.3c compares the evolution of pore size distribution from initial calcines and cycled samples. The unique pores resided in the 10-100 nm ranges with a peak at 15.8 nm, smaller than for most of the limestones, but with lower volume. After 20 cycles the pores were not appreciably retained as one might expect based on the excellent cyclic performance for this sorbent. However, there were no signs of larger pores being generated. Silaban et al. (1996) and Silaban and Harrison (1995) also found that the porosity of their dolomite decreased, even after the first cycle. Given that Arctic dolomite performed relatively well, as shown in Figure 6.1, it can be deduced that dolomite indeed sinters, but at much reduced rates.

In FBC where temperatures of 850-900°C are preferred, high CO₂ removal efficiency can only be achieved under pressurized conditions, given the thermodynamics of the CaO-CO₂ reaction. In the present work, Strassburg limestone and Arctic dolomite were selected for the PTGA tests.

Two sets of results for cyclic performance of Strassburg limestone are compared with the ATGR result in Figure 6.4. It can be seen that the PTGA and the ATGR generated similar decay behaviour for this sorbent. For calcination at elevated pressures, augmented sintering or further decay was expected based on reported (Borgwardt, 1989) enhanced CaO sintering in higher concentrations of CO₂. However, the reversibility actually improved slightly as shown in Figure 6.4. Because under pressurized calcinations, the actual N₂ mass flow and superficial velocity were much lower, actual carbonation duration was longer than the prescribed 4 minutes, responsible for the extra CaO conversions observed. It is notable that pressurized calcination under 100% N₂ conditions did not accelerate sorbent deterioration. This was confirmed by SEM investigation, which revealed no difference in sorbent surface microstructure. This evidence indicates that a pressurized calciner is a possible option for practical applications. Further PTGA
Chapter 6 Removal of CO\textsubscript{2} by calcium-based sorbents in the presence of SO\textsubscript{2}

tests (not plotted here) show that changes of total pressure up to 2.4 MPa or varying the CO\textsubscript{2} partial pressures from 8\% to 14\%v and 20\%v did not appreciably change sorbent reversibility.

Contrary to the results for the Strassburg limestone, the PTGA test with Arctic dolomite at 1.8 MPa showed reduced reversibility as portrayed in Figure 6.5. SEM images for calcines again revealed little difference. Pressurized carbonation probably altered the sorbent, eliminating pores via enhanced ionic movement for either CaO or MgO. Further tests of Arctic dolomite with total pressure varying from 1.3 to 2.4 MPa, revealed little or no change in reversibility.

6.3.2 Simultaneous SO\textsubscript{2} and CO\textsubscript{2} capture

In fluidized bed combustors, sulphur is invariably present to some degree at least so that simultaneous sorption of SO\textsubscript{2} and CO\textsubscript{2} need to be achieved in order to capture CO\textsubscript{2} in situ. However, previous tests (Sun et al., 2005; Ryu et al., 2006) (also see Chapter 5) have indicated that SO\textsubscript{2} impedes both cyclic CO\textsubscript{2} capture and subsequent calcination under typical FBC operating conditions. The cause of this adverse influence of SO\textsubscript{2} needs to be addressed. During co-capture, it is believed that three reactions occur simultaneously:

\begin{align*}
\text{Carbonation:} & \quad \text{CaO}+\text{CO}_2 & \rightleftharpoons & \text{CaCO}_3 & \Delta H_{298K} = -178 \text{ kJ/mol} \quad (6.1) \\
\text{Sulphation:} & \quad \text{CaO}+\frac{1}{2}\text{O}_2+\text{SO}_2 & = & \text{CaSO}_4 & \Delta H_{298K} = -426.5 \text{ kJ/mol} \quad (6.2) \\
\text{Direct sulphation:} & \quad \text{CaCO}_3+\frac{1}{2}\text{O}_2+\text{SO}_2 & \rightleftharpoons & \text{CaSO}_4+\text{CO}_2 & \Delta H_{298K} = -323.6 \text{ kJ/mol} \quad (6.3)
\end{align*}

Under current ATGR test conditions (e.g. with 80\%v CO\textsubscript{2} at 850\°C and 101 kPa), based on thermodynamic equilibrium, the MgO-CO\textsubscript{2} reaction is thermodynamically inhibited, but the MgO-SO\textsubscript{2} reaction is thermodynamically possible at higher $P_{\text{SO}_2}$ (Hartman and Svobods, 1985). After initial full calcination at 850\°C, Arctic dolomite calcines were subjected to simultaneous carbonation and sulphation for about 30 minutes at both 850 and 750\°C, and then sent directly for XRD analysis without calcination. In another run, the sorbent was directly taken after seven
cycles of co-capture at 850°C and after calcination with gas conditions for baseline test, i.e. 2900 ppm SO\(_2\), 80% CO\(_2\), 3% O\(_2\) and balance N\(_2\) at 850°C and 101 kPa pressure. Neither MgSO\(_4\) nor MgCO\(_3\) was detectable in any sample, indicating that MgO did not react with CO\(_2\), as expected based on thermodynamic grounds, while for SO\(_2\), the MgO was either inert, or reaction proceeded too slowly to be significant. It is also of interest that very little CaO was detected in the non-calcined sorbents, indicating that for Arctic dolomite calcium utilization could be close to unity in the initial cycle. For calcines from multi-cycle co-capture, there was only a tiny CaCO\(_3\) peak, indicating that very little remained uncalcined. As it is thermodynamically possible for MgO to react with SO\(_2\) at the pressures of the PTGA tests, XRD phase analysis for samples from a cyclic SO\(_2\)/CO\(_2\) capture test at 2.4 MPa pressure (triangular points in Figure 6.10), showed no appreciable MgSO\(_4\) phase, probably because of the much lower reactivity of MgO to SO\(_2\) compared to CaO.

Sorbents were calcined after each cycle of co-capture, and mass differences were used to determine the SO\(_2\) and CO\(_2\) capture during each cycle (see Chapter 5), based on the assumption that all of weight loss during calcination is due to CO\(_2\) being driven off. The mass difference method has been used by previous researchers who investigated simultaneous carbonation and sulphation of calcined limestones under PFBC conditions (Tullin and Ljungstrom, 1989; Iisa et al., 1991). Chemical analyses for total carbon and sulfur for ATGR samples confirmed that the difference by the two methods was less than 5%.

Figure 6.6 shows the cyclic performance of all seven sorbents during ATGR co-capture with 8-minute sorption periods. The corresponding baselines for Arctic dolomite and Strassburg limestone for no-SO\(_2\) tests with 80% CO\(_2\) are also shown. The calcium utilizations for all sorbents dropped sharply to about 20% over the first 10 cycles and continued to decrease beyond this. Dolomites did not appear to be any better than limestones when SO\(_2\) was present. In fact,
Chapter 6 Removal of CO₂ by calcium-based sorbents in the presence of SO₂

Arctic dolomite, which had shown the best cyclic reactivity in the “no SO₂ present” test, dropped even more sharply than the other sorbents. The GS dolomite performed in a similar manner. As more sulfur was captured with each successive exposure, the behaviour of all sorbents appeared to be controlled more by the sulfur-altered properties than by the original reactivities.

“Once-through” tests were conducted in the ATGR to investigate the importance of reactions (6.1), (6.2) and (6.3). Strassburg limestone and Arctic dolomite were tested repeatedly, each sample starting from the very beginning and being stopped at a certain point of the sorption from 3 to 90 minutes and then calcined. The results appear in Figure 6.7 for the Strassburg limestone. For comparison, sorbents were also subjected to SO₂ and O₂ in the absence of CO₂, and to CO₂ in the absence of SO₂, with identical gaseous reactant concentrations as for the cyclic co-capture runs.

During the first 14 minutes of co-capture, an almost identical amount of CO₂ was captured as in cases where there was no SO₂ for both sorbents. The CaO was very reactive initially and reacted much more quickly with CO₂ than with SO₂, as in earlier PFBC SO₂-capture studies (Tullin and Ljungstrom, 1989; Iisa et al., 1991). After completing the fast stage of carbonation, sorption became much slower. As indicated by the mass loss after 20 minutes, carbonate was obviously consumed through reaction (6.3) and no further CO₂ could be captured. This indicated that direct sulphation had become dominant in the later stage of sorption, whereas CaO sulphation could only be appreciable at the beginning, and was immediately surpassed due to the formation of a carbonate shell, which was, however, readily available for direct sulphation. Direct sulphation can result in greater calcium utilization than CaO sulphation because of a less compact sulphate layer (Snow et al, 1988; Krishan and Sotirchos, 1993). The overall sulphation was therefore higher than when no CO₂ was present. Similar trends have been reported in Chapter 5 where cyclic co-capture conditions significantly enhance SO₂ capture. Note that the
carbonate content of Arctic dolomite was consumed more quickly than that of Strassburg limestone, indicating that direct sulphation was faster for the dolomite. It is also notable that in Chapter 5, longer sorption times led to faster decreases in calcination rate, due to the sulphate envelopes that impede subsequent calcination.

Figure 6.8 shows the decrease in calcination rates as the calcium utilization for sulphur capture increase for these sorbents – Arctic dolomite, Strassburg limestone and GS dolomite. The calcination rate is defined as

\[ R_{c.o} = \frac{d(\text{Mass of CO}_2 \text{ released})}{d(\text{time})} \bigg|_{\text{at start of } n^{\text{th}} \text{ calcination}} \]  

(6.4)

The rate at which Arctic dolomite calcined dropped off sharply, whereas for other sorbents, the calcination rates also decreased as cycles proceeded, but less strongly. Calcination rates decreased as the sulphate content increased. The faster decay for Arctic dolomite may be attributed to higher reactivity toward SO\textsubscript{2} capture, promoted by higher surface area as well as cracks. The GS dolomite also showed strong ability to capture SO\textsubscript{2}, resulting in a high calcium conversion to CaSO\textsubscript{4}, but its decline in calcination rate was much slower than for the other sorbents. SEM images suggest that GS dolomite particles have a higher tendency to fragment than the other sorbents tested, generating large numbers of fractures, resulting in faster calcination and ensuring that it is more reactive during co-capture.

PTGA co-capture test results for Strassburg limestone and Arctic dolomite appear in Figures 6.9 and 6.10, respectively (with the conversions of CaO to CaSO\textsubscript{4} shown in Figures AVII.5 and AVII.6 in Appendix AVII). As for the ATGR tests, SO\textsubscript{2} clearly impeded CO\textsubscript{2} capture. However, variations in total pressure did not appreciably change the sorbent reversibility, as discussed below.
Chapter 6 Removal of CO$_2$ by calcium-based sorbents in the presence of SO$_2$

Figure 6.11a shows EDX sulfur distributions for the 12$^{th}$ cycle of ATGA co-capture before calcination for Strassburg limestone. Sulphation clearly occurred along the outer rim of particles. Sulfur permeated the particles probably by solid-state ion diffusion, crossing both the sulphate and carbonate layers. Direct sulphation of CaCO$_3$ produces a more porous sulphated layer than CaO sulphation due to the outwards diffusion of CO$_2$ (Snow et al, 1988; Krishan and Sotirchos, 1993). As a result, it is easier for SO$_2$ to continue to diffuse inwards. Cyclic calcination also leads to periodic generation of pores with CaO at the surface, subsequently carbonated to provide more interface at which CaCO$_3$ can react with SO$_2$. Pore size distributions for cyclic co-capture tend to be bimodal, as shown in Figure 6.3. However, pore volumes were much reduced, with the reduction in the $<200$ nm range being due to CaO sintering, as discussed for the case when these was no SO$_2$, whereas the volume reduction for larger pores was due to sulphate filling. Gullett and Bruce (1987), based on N$_2$ adsorption, showed that sulphation generally fills pores of 10-60 nm or larger. Other studies have shown that SO$_2$ tends to block pore entrances by occupying the outer rims of particles featuring mesopores (Simons and Garman, 1986; Sotirchos and Zarkanitis, 1992) due to the expanding product. Once pore mouths are filled, the effective diffusivity is greatly reduced for both CaO carbonation and subsequent calcination.

Figure 6.11b presents the sulfur distribution for Kelly Rock limestone. Although previous SEM photos from the test with no SO$_2$ revealed that Kelly Rock limestone calcines have a grainy structure and should sulfate more uniformly, the sulfur is present in an unreacted-core pattern. The reaction between SO$_2$ and less porous CaCO$_3$, must have taken place at the outside of the particles, blocking inter-grain channels. As a result of the co-capture, the pore size distribution in Figure 6.3b followed a similar trend as for Strassburg limestone, due to the joint effects of CaO sintering and sulphate filling. (The EDX sulfur distribution for Danyang calcines after 2 hours of sulphation and 15 cycles of SO$_2$/CO$_2$ capture/calcination are shown in Figure AVII.2 in
Chapter 6 Removal of CO₂ by calcium-based sorbents in the presence of SO₂

Appendix AVII with the pore size distribution shown in Figure AVII.3; the pore size distribution for Havelock calcines, either fresh, after co-capture and no SO₂ cycling tests are shown in Figure AVII.4).

For Arctic dolomite calcines, more sulfur was found along fractures or cracks as shown in Figure 6.11c. This explains the pore volume generation at pore sizes larger than 200 nm in Figure 6.3c for co-capture. Arctic dolomite must be weak mechanically, perhaps because of discontinuities between the magnesium and calcium parts in fully calcined dolomites, making it possible to generate cracks during cyclic capture, especially for co-capture due to the molar volume of the sulphate product being larger than for the carbonate. But the sulfur cannot permeate uniformly throughout the sorbent, so that sulfate product easily blocks pores and channels, thereby preventing further co-capture.

High-resolution SEM images of co-capture calcines for Strassburg limestone, Kelly Rock limestone, and Arctic dolomite appear in Figure 6.12. Compared with the calcines in the “no-SO₂” studies (Figure 6.2a), the Strassburg sorbent generated similar large pores through sintering, as seen in Figure 6.12a, covered by a layer of sulphate. The sulphate envelope, covering the pores, caused overall loss of pores as indicated in Figure 6.3a. For Kelly Rock limestone, the sorbent appeared to be much less porous after co-capture, compared with its counterpart in the “no SO₂” test due to sulphate product filling inter-grain pore volume. For the Arctic dolomite, the 10-100 nm pores in Figure 6.3c cannot be clearly viewed in SEM pictures. The cracks indicate that this sorbent was easily broken. The better reversibility of Strassburg limestone during co-capture, relative to Arctic dolomite, may be due to larger effective diffusivities because of sintering-generated macrospores. SEM photos (not shown here) from the PTGA Strassburg limestone co-capture tests show patterns very similar to the ATGR ones.
Chapter 6 Removal of CO₂ by calcium-based sorbents in the presence of SO₂

In summary, a CaCO₃ product layer, once formed, greatly decreases the effective diffusivities for further carbonation, but facilitates direct sulphation, which subsequently seals macropores, reducing the effective diffusivities, both for further carbonation and sulphation. Because of the formation of an outer layer of carbonate, direct sulphation becomes dominant in the later stage of co-capture. During calcination of Strassburg limestone, released CO₂ first generates small pores in bulk carbonate, then finds exit paths through partly sulphate-filled macropore channels. The calcination rate is reduced to a variable degree, depending on the extent of filling by the sulphate product. Thus, during co-capture, two patterns of pore evolution are important: sintering occurs as in cyclic no-SO₂ tests while sulphate product irreversibly fills the macropores (Gullet and Bruce, 1987), reducing pore volume and blocking channels to smaller pores important during fast stage carbonation (Bhatia and Perlmutter, 1983; Abanades, 2002).

6.3.3 Change of operating conditions in an effort to improve co-capture

Several measures were next taken to see whether the co-capture performance could be improved. One factor was varied at a time to see whether the decline in calcium utilization with cycling could be arrested.

In ATGA tests, pre-treatment of calcined Strassburg limestone with liquid water to give hydrated lime showed the greatest improvement of all methods tried not only for CO₂ capture, but also for SO₂ retention. The enhanced co-capture of hydrated lime is due to its pore structure, allowing for expansion to accommodate more solid product, as for h-CaO sulphation (Gullet and
Chapter 6 Removal of CO₂ by calcium-based sorbents in the presence of SO₂

Bruce, 1987; Stouffer and Yoon, 1989). However, when both SO₂ and CO₂ capture are enhanced, the ability of sorbents to capture and retain CO₂ decreases.

(A). With other conditions unchanged, calcining at a lower temperature, 750°C, gave a small improvement in co-capture performance probably because the lower temperature retarded sintering, but low-temperature calcination is unlikely to be practical. (B). One test was also performed with 93% CO₂ the balance N₂ balance. The increase of CO₂ concentration helped increase calcium utilization, but only for the first few cycles. As determined in PFBC studies (Snow et al., 1988; Tullin and Ljungstrom, 1989; lisa et al., 1991; Krishnan and Sotirchos, 1993), direct sulphation is inhibited by increasing bulk CO₂ concentrations. The lack of significant reduction in direct sulphation is probably because of limited capacity to increase CO₂ concentrations above 80%v in the ATGR. (C). Both CO₂ and SO₂ capture were enhanced somewhat by steam addition during co-capture. The water vapour might dissociate and interact with ionic surface enhancing mass transfer or kinetic behavior, e.g. via a short-lived surface hydroxyl group as reported for steam enhancement of CaO or MgO sintering (Anderson and Morgan, 1964; Borgwardt, 1989). (D). A run with 800 ml/min flow rate was conducted in an attempt to increase Ca/S molar ratio in the fixed-bed tests, both CO₂ and SO₂ capture improved for the first few cycles compared to the 1600 ml/min run, though with lower utilizations later.

When Arctic dolomite was subjected to similar ATGA tests, no clear improvement was observed as for the limestone.

In PTGA tests, the total pressure and CO₂ partial pressure were varied. As shown in Figures 6.9 and 6.10, changes in total pressure had little influence on CO₂ removal for either sorbent tested. Similarly there was no effect on SO₂ capture. (Figures AVII 7-9 in Appendix AVII also show the lack of dependence of cyclic performance in no SO₂ tests on total pressure,
There is a lack of agreement in the literature on the effect of total pressure on direct sulphation. Iisa and Hupa (1990) believed that an increase of total pressure increased $P_{SO_2}$, resulting in increased sulphation, whereas Qiu and Lindqvist (2000) reported the opposite in the range of 0.6-1.3 MPa. Iisa et al. (1991) tested simultaneous carbonation and sulphation over extended durations and found that sulphation was slower initially, but could reach higher conversions when the total pressure increased from 0.1 to 0.8 MPa. However, there was only a small dependence on pressure between 0.8 and 2 MPa.

The effect of total pressure on co-capture probably depends on multiple factors. When the total pressure is increased, both $P_{CO_2}$ and $P_{SO_2}$ increase proportionally. For bulk diffusion, the diffusion coefficient varies inversely with pressure so that the effect of increased concentrations tends to be neutralized. With increasing total pressure, increasing $P_{CO_2}$ far above its equilibrium value would not appreciably increase the rate of carbonation (Kyaw et al., 1996), but CaO sulphation and direct sulphation might accelerate further because of rate dependence. In addition, direct sulphation is inhibited by increasing $P_{CO_2}$ (Tullin et al., 1993; Liu et al., 2000). If the pore dimensions are small enough for Knudsen diffusion to be rate-controlling, the diffusion coefficient is independent of pressure. However, the mass flux increases with total pressure. Hajaligol et al. (1998) suggest that direct sulphation is Knudsen-diffusion controlled. In the current study, as shown in Figures 6.9 and 6.10, these effects added up to negligible net change in $CO_2$ and $SO_2$ removal.

Variation of $CO_2$ partial pressure while holding other conditions constant affected reversibility. Figure 6.13a shows that a higher $CO_2$ partial pressure greatly improved sorbent reversibility, corresponding to a much-reduced $SO_2$ capture in Figure 6.13b. Increasing of $P_{CO_2}$,
supposedly increased both interparticle and intraparticle diffusion flux and intrinsic carbonation rates, thus speeding up carbonation. Accelerated carbonation, cannot change the final conversion of CaO to carbonate, as revealed in the no-SO$_2$ tests, but it makes direct sulphation dominant at an earlier stage during co-capture. More importantly, direct sulphation is inhibited by increasing CO$_2$ partial pressure (Tullin et al., 1993; Liu et al., 2000), consistent with Le Chatelier’s principle applied to reaction (6.3), resulting in less SO$_2$ being absorbed during cycling as shown in Figure 6.13b. Therefore, increased P$_{CO_2}$ resulted in less direct sulphation, less filling of macropores by the sulphate product and hence higher reactivity for CO$_2$ capture. SEM photos (not shown here) of calcines supported this view by indicating differences in pores for varying P$_{CO_2}$.

The effect of total pressure and CO$_2$ partial pressure were confirmed with Arctic dolomite. All co-capture tests gave a very sharp decay for Arctic dolomite. Changing the total pressure was found to have little effect on the reversibility, as shown in Figure 6.10. However increasing P$_{CO_2}$ greatly improved the reversibility of this sorbent, as indicated by Figure 6.14, mainly due to reduced direct sulphation.

6.4 Conclusions

Five limestones and two dolomites were tested two thermogravimetric reactors, one at atmospheric pressure and the other at pressure up to nearly 2.4 MPa. At atmospheric pressure with no SO$_2$, the various limestones performed similarly in terms of sorbent reversibility, despite appearing to sinter differently. Dolomites performed somewhat better. High-pressure tests showed similar results for Strassburg limestone, but more rapid decay for Arctic dolomite. Sorbent reversibility was generally insensitive to total pressure and to the CO$_2$ partial pressure during carbonation.
Conversions decayed more quickly when SO\textsubscript{2} was present for all sorbents. SEM, EDX and pore size distributions revealed that direct sulphation becomes dominant after completion of an initial fast stage of carbonation, filling larger pores by sulphation from the outside, enveloping the sorbents with an impermeable shell and thus inhibiting further carbonation and impeding subsequent calcination.

For the atmospheric pressure tests, pre-hydration improved co-capture reversibility; steam helped co-capture; increasing the molar Ca/C ratio and increasing the CO\textsubscript{2} molar fraction from 80\% to 93\% had little effect on CO\textsubscript{2} and SO\textsubscript{2} co-capture. Although changing the total pressure did not change sorbent reversibility appreciably, increasing the CO\textsubscript{2} partial pressure was helpful. Reversibility approaching that in tests with no SO\textsubscript{2} present could be achieved by increasing the CO\textsubscript{2} partial pressure, inhibiting direct sulphation. The CO\textsubscript{2}/SO\textsubscript{2} ratio is important in determining the degree of sorbent reversibility.
Figure 6.1. Calcium utilization over 15 cycles for all seven sorbents with 212-250 μm particles and no SO₂ present. ATGR tests. Carbonation: 80% CO₂, 20% N₂, 850°C and 101 kPa, Fast Stage Finished. Calcination: 100% N₂, 850°C and 101 kPa.
Figure 6.2 High-resolution SEM pictures of calcines, with no \( \text{SO}_2 \) present. Same test conditions as in Figure 6.1. (a) Strassburg limestone, after 15 cycles (b) Kelly Rock limestone, after 15 cycles; (c) Arctic dolomite, after 20 cycles.
Chapter 6 Removal of CO\textsubscript{2} by calcium-based sorbents in the presence of SO\textsubscript{2}

Figure 6.3 Evolution of pore size distribution with calcination/carbonation cycling at 850°C.

Test conditions: same as in Figure 6.1 for no SO\textsubscript{2} test and in Figure 6.6 for co-capture.(a) Strassburg limestone; (b) Kelly Rock limestone; (c) Arctic dolomite.
Chapter 6 Removal of CO$_2$ by calcium-based sorbents in the presence of SO$_2$

![Graph 1](image1)

**Figure 6.4** Cyclic performance with no SO$_2$ present: effect of calcination type.

Calcination/carbonation cycling at 850°C with 212-250 μm Strassburg particles.

![Graph 2](image2)

**Figure 6.5** Cyclic performance with no SO$_2$ present: effect of total pressure.

Calcination/carbonation cycling at 850°C PTGA test: 212-250 μm Arctic dolomite.
Chapter 6 Removal of CO\textsubscript{2} by calcium-based sorbents in the presence of SO\textsubscript{2}

Figure 6.6 Performance of all seven sorbents for co-capture. ATGR tests, calcination/carbonation cycling at 850°C and 101 kPa with 212-250μm particles. Sorption: 80% CO\textsubscript{2}, 2900 ppmv SO\textsubscript{2}, 3%v O\textsubscript{2} and balance N\textsubscript{2}, 8 minutes for each cycle. Calcination: 100% N\textsubscript{2}. (Lines show corresponding results with no SO\textsubscript{2} present for two of the sorbents.)
Chapter 6 Removal of CO₂ by calcium-based sorbents in the presence of SO₂

Figure 6.7 ATGR once-through tests, at 850°C and 101 kPa with 212-250 μm Strassburg limestone. Top and bottom curves and for limiting case where there was no SO₂ or CO₂ respectively. Points are for co-capture case showing total (squares) calcium utilization, utilization for CO₂ capture (triangles) and utilization for SO₂ capture (circles).
Chapter 6 Removal of \( \text{CO}_2 \) by calcium-based sorbents in the presence of \( \text{SO}_2 \)

Figure 6.8 Relation between sulfate content and calcination rate for three sorbents. ATGR co-capture tests, same conditions as in Figure 6.

Figure 6.9 Cyclic \( \text{CO}_2 \) retention performances in 850°C PTGA tests: effect of total pressure. Co-capture with 212-250 \( \mu \text{m} \) Strassburg limestone. Sorption: 8 %v \( \text{CO}_2 \), 1125 ppmv \( \text{SO}_2 \), 3% \( \text{O}_2 \), and balance \( \text{N}_2 \), 4 minute for each cycle. Calcination: 101 kPa, 100% \( \text{N}_2 \).
Chapter 6 Removal of CO$_2$ by calcium-based sorbents in the presence of SO$_2$

Figure 6.10 Cyclic CO$_2$ retention performances in 850°C PTGA tests: effect of total pressure.
Co-capture with 212-250 μm Arctic dolomite. Sorption: 8 %v CO$_2$, 1125 ppmv SO$_2$, 3% O$_2$, and balance N$_2$, 4 minute for each cycle. Calcination: 101 kPa, 100% N$_2$, 8%v CO$_2$, 850°C.

Figure 6.11 Sulfur mapping for non-calcined ATGR samples from varied co-capture cycles, same test conditions as in Figure 6.6. (Light points mark sulfur) (a) Strassburg limestone after 12 cycles (b) Kelly Rock limestone after 15 cycles (c) Arctic dolomite, after 7 cycles
Chapter 6 Removal of CO₂ by calcium-based sorbents in the presence of SO₂

Figure 6.12 High-resolution SEM pictures for calcines after ATGR co-capture tests.

(a) Strassburg limestone, after 12th cycle (b) Kelly Rock limestone, after 15th cycle (c) Arctic dolomite, after 7th cycle.
Chapter 6 Removal of CO\textsubscript{2} by calcium-based sorbents in the presence of SO\textsubscript{2}

![Graph showing cyclic performances during PTGA co-capture tests: effect of P\textsubscript{CO\textsubscript{2}}.](image)

Figure 6.13 Cyclic performances during PTGA co-capture tests: effect of P\textsubscript{CO\textsubscript{2}}. 212-250 \textmu m Straussburg limestone. Sorption at 850°C and 1.8 MPa, with 1125 ppmv SO\textsubscript{2}, 3%v O\textsubscript{2} and balance N\textsubscript{2}, 4 minutes for each cycle and calcination at 850°C and 101 kPa, 100% N\textsubscript{2}. (a) For CaO conversion to CaCO\textsubscript{3}; (b) For CaO conversion to CaSO\textsubscript{4}.
Chapter 6 Removal of CO$_2$ by calcium-based sorbents in the presence of SO$_2$

Figure 6.14 Cyclic performance during PTGA co-capture tests: effect of P$_{CO_2}$. 212-250 μm Arctic dolomite particles. Sorption at 850°C, and 1.8 MPa, with 1125 ppmv SO$_2$, 3%v O$_2$ and balance N$_2$, 4 minutes for each cycle and calcination at 850°C and 101 kPa, 100% N$_2$. (a) For CaO conversion to CaCO$_3$; (b) For CaO conversion to CaSO$_4$. 

(a) 

Moles of CO$_2$ retained/moles of total Ca

Number of reaction cycles

(b) 

Moles of SO$_2$ retained/moles of total Ca

Number of reaction cycles

162
CHAPTER 7 AN INVESTIGATION OF ATTEMPTS TO IMPROVE CYCLIC CO₂ CAPTURE BY SORBENT HYDRATION AND MODIFICATION

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7.1 Introduction

Due to the potential of calcium-based sorbents to capture CO₂ at high-temperatures, cyclic performance of sorbents has been investigated in Chapter 6 and in the literature for a variety of applications (Han and Harrison, 1994; Lin et al., 2001; Ortiz and Harrison, 2001; Abanades et al., 2004; Jukkola et al., 2005). The findings generally indicated that different types of limestones show similar trends, involving a loss in sorbent utilization as cycling progresses. In most earlier studies, CO₂ was the only gaseous reactant to react with CaO. Chapter 6, where CaO serves as a CO₂ carrier between a fluidized bed combustor (FBC) and a calciner, demonstrated that the presence of SO₂ greatly impeded sorbent reversibility due to inhibited solid-state diffusion by a sulphate shell, formed mostly by direct sulphation. In this chapter, several other issues with respect to sorbent performance for FBC processes are investigated in detail.

Steam and liquid water could conceivably be utilized in at least four ways to enhance CO₂ capture: 1. Carbonation in the presence of steam. Although under most operating conditions, steam is not directly involved in reactions with sorbents, enhancement due to steam has been reported for CaO recarbonation (Dobner et al., 1977; Han et al., 1994). 2. Steam and liquid water can be utilized to alter CaO pore structure by producing hydroxide-derived CaO (designated here as h-CaO) through one-time hydration. It has long been known that h-CaO can achieve a higher extent of high-temperature sulphation than c-CaO (carbonate-derived CaO) (Gullett and Bruce,
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

1987; Stouffer and Yoon, 1989) because its plate-like pore structure is able to accommodate more SO₂. Somewhat improved cyclic performance for h-CaO has been reported for cyclic CO₂ capture (Hughes et al., 2004) by Kelly Rock and Cadomin limestones. 3. Calcination of sorbents in a pure steam environment could be a convenient way to generate a relatively pure CO₂ stream (after condensation of the steam), as a key component of an overall sequestration scheme. However, the extent to which CaO sintering could be enhanced by steam needs to be investigated because steam has been reported to promote CaO sintering (Borgwardt, 1989b), thus causing decay in sorbent carbonation reactivity. 4. Similar to hydration reactivation technology applied for sulphation enhancement in FBCs (Laursen et al., 2000; 2001), hydration may also be applicable to CO₂ capture.

As the sulphate layer formed during co-capture of SO₂ and CO₂ is mostly responsible for accelerated decay in cyclic CO₂ removal ability (see Chapter 6), regeneration of CaO from sulphate by applying reducing conditions could improve sorbent performance. In practice, a reducing (CO-containing) environment could be realized by feeding a low excess of oxygen in a calciner or in a char-fired furnace in a topping-cycle-based process. Preliminary data need to be collected to investigate the feasibility of this option.

Moreover, a naturally occurring sorbent, e.g., a limestone, could also be artificially modified in order to achieve better reversibility. Work is needed to gain better insight on possible improvements in CO₂ capture using solid sorbents. These issues are investigated in this chapter.

7.2 Experimental details:

Two commercially available sorbents, Strassburg limestone and Arctic dolomite were
Chapter 7 An investigation of attempts to improve cyclic \( \text{CO}_2 \) capture by sorbent hydration

used in the current work. Strassburg limestone was utilized in most of the tests, whereas Arctic dolomite was only used for tests involving steam/water and in some tests involving sorbent modification. ICP chemical analyses are shown in Table 1.2 for both sorbents.

An atmospheric pressure thermogravimetric reactor (TGR) was used in all tests. Details of this system are provided elsewhere (Laursen et al., 2000). All sorbents were characterized based on cyclic calcination/carbonation tests. A total flow of 1600 ml/min was maintained for all calcination and carbonation tests. A typical FBC combustor temperature, 850°C, was chosen for both calcination and carbonation in most runs. In sorption tests with no \( \text{SO}_2 \) present, 100% \( \text{CO}_2 \) was fed for carbonation, whereas in tests with co-capture of \( \text{SO}_2 \) and \( \text{CO}_2 \), or tests with steam vapour, concentrations are given below. Except where otherwise specified, samples were exposed to 100% \( \text{N}_2 \) during each calcination stage.

Two sorption durations were employed in the current work. Sorption was allowed to complete its fast stage (denoted as “fast stage finished” or FSF) in all tests, except for those involving co-capture of \( \text{SO}_2 \) and \( \text{CO}_2 \) in which a fixed time (8 or 12 min) was used for each sorption stage.

Sample size was 850 mg for tests of the effect of steam or liquid water, 500 mg for CO regeneration tests and 400-500 mg for sorbent modification tests. In the CO regeneration tests, a quartz basket was used, whereas a stainless wire mesh was used in all other cases. The variation of sample size in sorbent modification tests is believed to have negligible effect on the reversibility results for the range of conditions studied.

In sorbent modification tests, 212-250 \( \mu \text{m} \) particles of calcined or uncalcined Strassburg limestone were employed as the starting material. Calcium acetate was also tested in some runs because of its good solubility in water. The particles were greatly reduced to fine powders, probably because of CaO hydration, particle breakdown, dissolution of Ca(OH)\(_2\), and subsequent
calcination etc., except when starting with uncalcined limestone. The modifiers, all in highly pure powder or crystalline form, included $\gamma$-$\text{Al}_2\text{O}_3$, $\text{SiO}_2$ gel, $\text{SiO}_2$ sands, $\text{TiO}_2$, $\text{ZrO}_2$, $\text{MgO}$, $\text{CaCl}_2\cdot2\text{H}_2\text{O}$, $\text{NaCl}$, $\text{MgSO}_4\cdot7\text{H}_2\text{O}$, $\text{MgCl}_2\cdot6\text{H}_2\text{O}$ and $\text{Al(NO)}_3\cdot9\text{H}_2\text{O}$, all supplied by Fisher Scientific. High-purity precipitated calcium carbonate (PCC) powder and calcium acetate, as CaO precursors, were obtained from the same source. Kaolinite, as a modifier, was from the Quinsam Company with 45wt% $\text{Al}_2\text{O}_3$, 54wt% $\text{SiO}_2$, and 1% $\text{Fe}_2\text{O}_3$ when fully calcined and negligible CaO content.

The procedure for inert doping was as follows: The CaO and modifier precursors were pre-weighed (usually < 1.5 g in total), then mixed in 70 ml of de-ioned water in a beaker. 5 ml of ethanol were next added to the beaker as a dispersant. The suspension was next stirred over a heating plate at 150°C until dry. The dried samples were then transferred into the TGR for 60 minutes of calcination at 850°C. The prepared samples were mainly characterized by cyclic CO$_2$ capture, with both calcination and carbonation conducted at 850°C by alternating between 100% CO$_2$ and 100% N$_2$ feed gas.

Selected samples were analyzed by EDX element distribution mapping, XRD phase detection and free calcium measurement using the ASTM C25 “fast sugar method” (ASTM C25-90, 1990). EDX element mapping was determined on a HITACHI S-3000 instrument. Before the tests, samples were first embedded in epoxy and then carefully ground and polished to expose cross-sections. A Micromeritics 9300 Poresizer was used to determine the pore size distributions of sorbents. X-Ray diffraction phase detection for the modified samples was conducted on a Siemens Diffraktometer D5000.
7.3 Results and Discussion

7.3.1 Tests involving steam or liquid water

(a) Comparison of performance of h-CaO and c-CaO in no-SO₂ tests.

212-250 μm Strassburg limestone and Arctic dolomite were selected to study the effect of pre-hydration. Room temperature liquid water was used to hydrate the nascent calcines. Figure 7.1 shows different pore structures for c-CaO and h-CaO, which originated from 212-250 Strassburg limestone particles. h-CaO calcines clearly show plate-like pore structures, as reported by Gullett and Bruce (1987). However, as shown in Figure 7.2, h-CaO (derived from Strassburg limestone) performed only a little better than c-CaO when subjected to calcination/carbonation cycles (Figure AVII.1 in Appendix AVII presents similar result for calcines derived from Arctic dolomite). The pore size distribution in Figure 7.3 reveals that the initial h-CaO calcines (derived from Strassburg limestone) contained somewhat more pore volume than c-CaO. After 15 cycles, both lost most pore volume for <220 nm pores while gaining pore volume for >220 nm pores. Given that sintering is responsible for the decay of cyclic performance and change of pore structure during cycling (see Chapters 4 and 6), it appears that both types of CaO sinter similarly during calcination/carbonation cycles. The slight improvement for the h-CaO is probably due to its pore structure allowing better expansion when producing a swelling product, as reported for SO₂ capture (Stouffer and Yoon, 1989; Gullett and Bruce, 1987).

C-CaO and h-CaO derived from Arctic dolomite showed negligible improvement in reversibility and no difference in pore size distribution (Figure AVII.2 in Appendix AVII presents the pore size distribution results for calcines derived from Arctic dolomite) between the
two types of sorbents. The lack of improvement was probably due to the interspersed content of MgO.

**(b) Calcination in steam in no-SO₂ tests**

The affinity between H₂O molecules and CaO sites could affect calcination of limestone (Young, 1966) because steam could easily adsorb on the CaO surface, thereby reducing CO₂ adsorption, and hence lowering the incipient calcination temperature. In this study, steam was used to cyclically calcine Strassburg limestone. In the TGR tests, the steam volumetric fraction was maintained above 95%, with only a small flow of N₂ to protect the top of the reactor. Calcination was conducted at both 850 and 900°C. The cyclic performance in Figure 7.4 shows no appreciable effect of sweep gas (N₂ or steam) or steam temperature. The pore size distributions (Figure 7.5) generally showed similar pore evolution history for N₂ and steam. No enhancement of steam vapour on sintering could be detected. This does not contradict the finding of Borgwardt (1989b) that steam catalyzed CaO sintering to the same degree as CO₂, because, regardless of whether steam or N₂ was used as the sweep gas during CaCO₃ calcination, the sites for CO₂ or steam adsorption on the nascent CaO sites are fixed. This suggests that steam could be used as the sweep gas in a calciner.

**(c) Effect of steam on carbonation with no SO₂ present.**

No appreciable enhancement by steam was observed for either sorbent (Figures AVIII.3 and 4 in Appendix AVIII presents the results for the effect of steam on cyclic carbonation for Strassburg limestone and Arctic dolomite, respectively). This is consistent with the multiple-cycle performance results presented by Han et al. (1994), although they found some enhancement for the first carbonation. Note that the possible adsorptive effect of steam on CaO sites discussed above may not be applicable to carbonation, because the fast carbonation reaction supplants any adsorption of water vapour on CaO sites.
Chapter 7 An investigation of attempts to improve cyclic CO$_2$ capture by sorbent hydration

(d) h-CaO and steam in co-capture of CO$_2$ and SO$_2$

Given the rapid decay of sorbents during co-capture of SO$_2$ and CO$_2$ (see Chapter 6), tests were also conducted starting with h-CaO adding steam during carbonation/sulphation. Results are shown in Figure 7.6 for both sorbents. The baseline test conditions for this co-capture study starting from fresh sorbents were as described in Chapter 6, i.e., sorption at 850°C with 80% CO$_2$, 2900 ppm SO$_2$, 3% O$_2$ and balance N$_2$, with 8 minutes for each cycle, and calcination at 850°C with 100% N$_2$. Strassburg-derived h-CaO showed improvement not only for CO$_2$ capture (Figure 7.6a), but also for SO$_2$. The enhanced co-capture by h-CaO is believed to be due to the better expansion ability of the plate-like pores of h-CaO relative to c-CaO.

Adding steam during the co-capture tests improved the reversibility of Strassburg limestone. It is speculated that this improvement is due to an interaction of H$_2$O with the sorbent surface, possibly through transient surface hydroxyl group formation, commonly invoked to explain water vapour enhancement of CaO or MgO sintering (Anderson, 1964; Borgwardt, 1989b).

Arctic dolomite gave similar results. Its performance is shown in Figure 7.6b for CO$_2$ removal. Hydroxide-derived CaO showed better performance for both CO$_2$ and SO$_2$ capture, probably for the same reason as for the limestone. However, the presence of steam only appreciably helped the co-capture performance over the first few cycles.

Figure AVII.5 presents the results of the effect of steam or hydration treatment on SO$_2$ part capture during the cyclic co-capture tests.
(e) Effect of hydration on CO$_2$ capture with SO$_2$ present

Since steam reactivation can fracture calcium sulphate layers (Laursen et al., 2000; 2001) thereby improving sulphur capture, hydration was also applied in an effort to improve CO$_2$ capture. Strassburg limestone, classified as an unreacted-core type limestone (Laursen et al., 2000) under typical FBC sulphation conditions, was found to have significantly improved SO$_2$ capture when reactivated by hydration.

Steam hydration was first used to fracture the sulphate shell formed during co-capture. In the current studies, steam with a partial pressure of ~95 kPa at 300°C with the balance N$_2$, was employed in all hydration steps for 30 minutes. Three sets of tests were carried out to reveal the effect of hydration on subsequent cyclic CO$_2$ capture. In Test A, 1 h of simultaneous sulphation and carbonation was followed by a series of steps: complete calcination in N$_2$, 8 min of co-capture (one cycle including both sorption and calcination), a complete calcination, a steam hydration step and two cycles of co-capture. Test B differed from test A in that, after the first 8 min of co-capture, the samples were quickly withdrawn from the reactor and not returned until the reactor temperature reached 300°C, so that steam hydration was applied before any appreciable calcination. In test C, the initial one-hour co-sorption in A was replaced by a sulphation step (same SO$_2$/O$_2$ concentration, but with no CO$_2$ present, balanced by N$_2$), followed by 8 min of co-capture, while the other steps were the same as for test A. The conversions of CaO to CaCO$_3$ and CaSO$_4$ after each sorption step are compared in Figure 7.7, where the baselines are also plotted on a cumulative sorption time basis for a typical cyclic SO$_2$/CO$_2$ co-capture test.

Figure 7.7b shows that the initial one-hour and the first 8-minute sorption in all these tests led to a similar extent of sulphation, but Figure 7.7a reveals that the sulphate layer formed in test C served as a greater barrier to carbonation during the following 8-minute co-capture than in the
other two tests. This probably occurred because the calcination step after 1-hour co-capture in tests A and B could expose more CaO surface area as revealed by the lowest carbonation extent achieved during 8 min co-capture. However, after reactivation, test C showed greater improvement for CO₂ capture than test A, although a similar degree of improvement was observed for SO₂ removal. This indicates that the reactivation effect of CaO by hydration is more effective in test C than in test A, probably because of the different porosity of sulphate layers formed in the two tests. For test B, it is not surprising that the hydration effect was very limited because the hydration reaction for the calcine core must be greatly inhibited by the presence of an outer carbonate layer if it is not calcined prior to hydration. However, it is also shown in Figure 7.7a that, after reactivation by hydration, the sorbent performance for CO₂ removal continued to decay with further cycling.

(f) Effect of hydration on CO₂ capture with no SO₂ present

As noted above, the effect of hydration is mainly to break the sulphate shell formed during co-capture. Hydration can also be utilized to break a carbonate shell or to counteract the meso-pore-eliminating sintering process by generating pores for CO₂ capture.

To test the effect of hydration on a carbonate shell, non-cycling carbonation tests were conducted. During continuous carbonation (e.g., after 10 or 60 min), the carbonated sorbents were either subjected to in-situ hydration in the TGR with 95% pure steam (balance N₂) at 300°C or removed from the reactor and subjected to water hydration. Water hydration was performed outside the reactor with room temperature de-ioned water poured continuously over the sorbents held in a stainless wire mesh basket for 10 minutes. The hydrated sorbents from both tests were then heated to 850°C in a pure CO₂ stream. During heating, dehydration should proceed first, producing CaO at a lower temperature. The CaO was then carbonated during further heating for
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

A pre-determined duration. The results are plotted based on cumulative carbonation time in Figure 7.8. Compared with continuous carbonation, CaO conversion after hydration treatment experienced no improvement. This implies that, unlike the hydration of partially sulphated samples, the carbonate layer prevented any hydration reaction on the unreacted CaO core. As noted above, hydration is difficult in the presence of a carbonate shell. This confirms that CaCO₃ product differs from CaSO₄.

As demonstrated in Chapter 6, <220 nm pores are of dominant importance for the fast stage of carbonation. However, these are continuously eliminated by sintering during calcination/carbonation cycling. Hydration can also be used as an alternative way to re-generate pores in this range for further calcination/carbonation cycles. The results are summarized in Figure 7.9. The baseline test shows the cyclic performance of 212-250 µm Strassburg particles resulting from typical calcination/carbonation cycles. After 15 cycles, the calcined sorbents were treated for 10 or 30 minutes with steam at 300°C, steam at 150°C or water at room temperature. It can be seen that, for all methods examined here, 10 minutes of water hydration (filled circles) gave the greatest improvement in cyclic CO₂ capture. As a result of the second water hydration (open circles), the sorbent’s performance increased further. This indicates that hydration, if effective, is able to crack highly sintered sorbents and re-generate the <220 nm pores, which are favourable for subsequent carbonation; it also reveals that repeated hydrations could reduce sintering to some degree and improve sorbent reversibility, probably due to reduced particle size and reduced calcination time, as revealed in Chapter 4. Other tests starting from long-time-sintered (24 hours in an 1100°C oven) 212-250 µm Strassburg particles gave similar results, as indicated in Figure 7.9. The order for the effectiveness of hydration conditions can be ranked as: liquid water >150°C steam >300 °C steam.
Chapter 7 An investigation of attempts to improve cyclic CO$_2$ capture by sorbent hydration

7.3.2 Regeneration of CaO from CaSO$_4$ using CO during calcination

Given that the CaSO$_4$ shell is the major reason for decayed reversibility during co-capture of SO$_2$ and CO$_2$, CO was explored as a possible way to reduce CaSO$_4$ to CaO to improve CO$_2$ capture. In this test, CO was fed during each CaO regeneration step.

When CaSO$_4$ reacts with CO, two routes are possible,

\[
\text{CaSO}_4 + 4\text{CO} = \text{CaS} + 4\text{CO}_2 \quad \text{Undesired reaction} \quad (7.1)
\]

\[
\text{CaSO}_4 + \text{CO} = \text{CaO} + \text{SO}_2 + \text{CO}_2 \quad \text{desired reaction} \quad (7.2)
\]

Chen and Yang (1979), Mattisson and Lyngfelt (1999) and Okumura et al. (2003) found that the fraction of solid products CaS or CaO vary during CaSO$_4$ reduction in CO, with CaO production favoured by higher temperature and lower CO/CO$_2$ ratio.

For the cyclic tests, pure CaSO$_4$ supplied by Fisher Scientific was used as the starting material. The reduction temperature was selected as 950°C. Gas concentrations are shown in Table 7.1. After complete reduction, the feed gas was switched to air. If any CaS was produced, it was then oxidized immediately into CaSO$_4$, thus causing a mass increase. On the other hand, CaO would not undergo any mass change in the presence of air. The results are summarized in Table 7.1, showing that a reducing condition with a CO/CO$_2$ molar ratio of 0.12 produced negligible CaS. This ratio was therefore selected for further testing.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>CO$_2$ (ml/min)</th>
<th>N$_2$ (ml/min)</th>
<th>CO (ml/min)</th>
<th>CO ($%v$)</th>
<th>CO/CO$_2$ molar ratio</th>
<th>CaS product</th>
</tr>
</thead>
<tbody>
<tr>
<td>850°C, too slow</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>950°C</td>
<td>0</td>
<td>2100</td>
<td>180</td>
<td>8$%v$</td>
<td>Infinite</td>
<td>Yes</td>
</tr>
<tr>
<td>950°C</td>
<td>314</td>
<td>1700</td>
<td>90</td>
<td>4$%v$</td>
<td>0.28</td>
<td>Yes</td>
</tr>
<tr>
<td>950°C</td>
<td>314</td>
<td>1700</td>
<td>40</td>
<td>1.9$%v$</td>
<td>0.12</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 7.1 Regeneration conditions and CaS/CaO test
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

This CO regeneration study, unlike the other tests, was performed in a quartz basket with a platinum suspension wire. The change in basket could lead to a change in mass transfer, affecting the kinetics. Therefore new tests conditions were selected, with 500 mg fresh Strassburg limestone at the start of each run and 12 minutes for each sorption stage. Three runs were performed as summarized in Table 7.2: (1) cyclic CO₂ capture with no SO₂ present (denoted no-SO₂ test); (2) CO₂/SO₂ co-capture with all calcinations in pure N₂ (designated normal co-capture); (3) CO₂/SO₂ co-capture with CO, CO₂ and N₂ all present during the regeneration step (Co-capture with CO reduction). Except for the 10th regeneration where complete calcination in N₂ was performed first, followed by reduction using a mixture of CO₂, CO and N₂, all other regeneration steps involved mixed CO₂, CO and N₂ so that CaCO₃ and CaSO₄ decomposed simultaneously.

In the co-capture test with CO reduction, reduction of CaSO₄ was much slower than that of the calcination of CaCO₃, probably because of the low CO concentration (One cycle of co-capture followed by a CaCO₃ calcination in N₂ then by CO reduction is presented in Figure AVIII.6 in Appendix AVIII). Figure 7.10 summarizes all three runs. Because in all CaO regeneration steps (except for the 10th regeneration step), CaCO₃ calcination occurred simultaneously with CaSO₄ decomposition, it is difficult to distinguish the calcium utilization involving CO₂ from that involving SO₂. Therefore, Figure 7.10 plots the ratio of mass increase after each sorption cycle to the initial calcine mass. As the mass increase due to SO₂ capture is much smaller that that due to CO₂ capture, as revealed by the 10th regeneration step, this plot roughly reflects the sorbent performance for cyclic CO₂ removal. It shows that, due to the presence of SO₂, the reversibility decays as a result of cycling. When CO was applied during each cycle to regenerate CaO, there was only a small improvement in reversibility. This is probably because the inhibiting effect of SO₂ on CO₂ capture was not altered, even when CO
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

was present in the regeneration step, although the reduction of CaSO₄ diminished accumulation of the sulphate layer.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Sorption (850°C)</th>
<th>Calcination/regeneration (950°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ (%v)</td>
<td>SO₂ (ppmv)</td>
</tr>
<tr>
<td>1. No SO₂ test</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>2. Normal co-capture</td>
<td>80</td>
<td>2900</td>
</tr>
<tr>
<td>3. Co-capture with CO reduction</td>
<td>80</td>
<td>2900</td>
</tr>
</tbody>
</table>

7.3.3 Modification of sorbents (no SO₂ present)

Sorbent reversibility is the key to successful processes utilizing sorbents for CO₂ removal. Chapter 4 explains that limestones such as Strassburg unavoidably experience similar decay behaviour in calcination/carbonation cycles due to enhanced sintering during calcination. CaO sintering is known to be due to solid-state diffusion of ions (Borgwardt, 1989a, b). For CaO sintering, volume diffusion is usually the most important mechanism, ion mobility among lattices being a decisive factor (Borgwardt, 1989a; German, 1996). Aliovalent ions addition usually enhance sintering in ionic compounds (German, 1996; Borgwardt, 1989a); CO₂ diffusing outwards during the calcination of sorbents can catalyze sintering (Chapter 4).

As discussed in Chapter 6, dolomitic sorbents perform more reversibly than calcitic ones, probably due to the inhibiting effect of well-dispersed inert MgO on reactant ionic diffusion. An attempt was made to artificially modify natural sorbents by doping inter atoms/ions to reduce
Chapter 7 An investigation of attempts to improve cyclic CO$_2$ capture by sorbent hydration

ionic mobility and improve thermal stability. Another possible technical route for sorbent modification is to physically or chemically bond some CaO sites by adding various reactive modifiers.

The tests on modified sorbent reversibility are summarized in Table 7.3. Note that the CaO fraction has been converted to a fully calcined sorbent at 850°C, with all possible gaseous products (CO$_2$, H$_2$O, NO, N$_2$) driven off. (Figure AVIII.7 presents the EDX dopant element mapping, showing good mixing of dopants with calcium sorbents.) Cyclic performance using fresh Strassburg limestone (212 µm) is also shown, and that for fresh Arctic dolomite appears in Figure 7.11e.

Tests using Al(NO$_3$)$_3$·9H$_2$O encountered difficulties during stirring over the heating plate (~150°C) because of the low melting point of the nitrate (73°C). The final modified product showed little carbonation reactivity probably, because of pore-blocking by intermediate melts. However, good reversibility was reported by Li et al (2005) using a similar method. The discrepancy from the current study indicates that the synthetic method is sensitive to conditions at each preparation step. Results for sorbents modified using γ-Al$_2$O$_3$ are displayed in Figure 7.11a. Most of the sorbents showed reduced CO$_2$ capture capacity, but run 4 with 1:1 molar ratio of CaO to Al$_2$O$_3$ showed good reversibility. XRD phase detection (see Figure 7.12) for calcined sorbent from run 4 indicated that the major solid-state reaction product is Mayenite (Ca$_{12}$Al$_{14}$O$_{33}$). A similarly good reversibility was achieved by synthetically mixing pure CaCO$_3$ and Al(NO$_3$)$_3$·9H$_2$O, producing the same solid product Ca$_{12}$Al$_{14}$O$_{33}$ (Li et al, 2005). Results from runs 4 and 5 based on free calcium measured by the fast sugar method (ASTM C25-90, 1990) are also presented in Figure 7.11a. This shows that when the part of CaO consumed by reaction is considered, the residual CaO is a reversible sorbent, although still subject to decay. (The calcium utilization exceeding 100% is due to analytical errors.) Lowering Al$_2$O$_3$ content in the
mixture did not yield satisfactory data. Tests starting with calcium acetate did not generate good reversibility. Thus an optimal mixing ratio may exist.

Some results of tests on two forms of SiO₂ -silica gel and silica sand, are shown in Figure 7.11b. Silica sand is crystalline, and non-porous, whereas silica gel is non-crystalline and highly porous. Thus silica gel develops more reactive OH groups in a water solution. The cyclic capture results showed that those starting with silica gel (e.g. 1:1 ratio of SiO₂ to CaO) had very low carbonation ability, whereas the tests with the same composition, but starting with sand, showed a higher capture capacity. XRD analysis (Figure 7.12) indicated that the solid-state product was predominantly silicate, i.e. Ca₃SiO₄. This implies that different proportions of CaO must be consumed by solid-state reactions between CaO and SiO₂. The different performances of the different forms of SiO₂, could indicate different degrees of basicity in water, and hence different interactions between CaO surfaces and hydroxyl groups. Tests where no carbonation occurred may be due to over-consumption of CaO by solid-state reaction, thus necessitating an optimized mixing ratio. The test starting with calcium acetate and silica sand showed somewhat better reversibility, but decay was not arrested. The run with Kaolinite (run 20) was conducted because Kaolinite is a rich source of Al₂O₃ and SiO₂. However, this modification is not ideal. XRD analysis only shows a large peak of free lime and small peaks for Anorthite CaAl₂(SiO₄)₂ and Mullite 3Al₂O₃ ·2SiO₂. Note that fully calcined Kaolinite could also be amorphous and thus XRD-transparent.

Figure 7.11c shows test results using ZrO₂, which has been reported to be able to improve the thermal stability of CuO as an oxygen carrier in chemical looping combustion (Vázquez et al., 2005). However, no improvement was observed with this modifier in our study. XRD analysis in Figure 7.12 indicates that no solid-state reaction occurred between CaO and ZrO₂.
Chapter 7 An investigation of attempts to improve cyclic CO\textsubscript{2} capture by sorbent hydration

Figure 7.11d presents results for a test with MgO added. XRD analysis in Figure 7.12 does not indicate any solid-state reaction between CaO and MgO. Modified sorbent showed somewhat better reversibility, probably because the mechanical mixing reduced CaO ionic mobility to some degree. However, the reversibility compared to that of calcined dolomite (Figure 7.11e) was still poor. This implies that only good dispersal on an atomic level, such as that found in naturally occurring dolomites, is capable of resisting ionic volume diffusion effectively, thereby leading to improved reversibility.

Figure 7.11e presents test results for calcined Artie dolomite and TiO\textsubscript{2} mixed with Strassburg limestone. The calcined dolomite/limestone mixture not surprisingly shows cyclic sorbent performance between the baseline tests for the dolomite and the limestone alone. With TiO\textsubscript{2} present, however, much of the CaO was consumed (run 28) by solid-state reaction to produce CaTiO\textsubscript{3} as revealed by XRD analysis (Figure 7.12). Decreasing TiO\textsubscript{2} content (run 29) could necessarily release more free CaO for CO\textsubscript{2} capture, but not result in reversible capture. However CaTiO\textsubscript{3} as a modifier was reported to be able to stabilize natural limestones (Aihara, et al., 2001), it was probably the Sol-Gel preparation method employed in the reference work that made the different modification effect.

Precipitated calcium carbonate (PCC) has been proposed as a reversible sorbent for CO\textsubscript{2} capture (Gupta and Fan, 2002). Commercial PCC was therefore tested. It is anticipated that a PCC of high CaCO\textsubscript{3} purity should lack impurities-derived lattice defects, and thus be low in lattice diffusivity and sintering rate. However, the decay trend in this case was similar to that for the other modifications, as shown in Figure 7.11e (run 33). This disappointing result probably arose because high-temperature-induced lattice defects still dominate, again enhancing volume diffusion during sintering. Note that there is likely to be an effect of the PCC preparation method, accounting for the good reversibility reported by Gupta and Fan (2002).
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

Figure 7.11f provides results for a variety of other ionic compounds with the same valence as calcium (except for the NaCl). Our previous test (Sun et al., 2004) with dopants of an aliovalent ionic compound Na₂CO₃ showed that the sorbent became very non-porous, with greatly diminished carbonation ability. NaCl was chosen for the test is because of improvement reported by doping NaCl in natural limestones (Salvador et al., 2003). The results show that, except for the run using MgSO₄, where normal reversibility was observed, all other dopants tested greatly reduced the CO₂ capture capacity. However, a number of runs indicated good reversibility, but at the expense of much reduced early capture capacity (e.g. runs 39 and 40). From the XRD analysis, no solid-state reaction was observed between CaO and the other modifiers in these cases. Measurement for free lime with the fast sugar method indicated that the free calcium content was very close to that of the original mixture, further confirming the lack of reactions. Therefore, the decline in CO₂ capture capacity is likely due to pore-blocking, considering that the temperature of operation (850°C) exceeded the melting points of all the chlorides (675°C for CaCl₂, 800°C for NaCl, 714°C for MgCl₂) (Barin and Knacke 1973; Barin et al., 1977).

7.4 Conclusions

Strassburg limestone and Arctic dolomite were investigated at a typical fluidized-bed combustor temperature of 850°C. Addition of steam during carbonation with no SO₂ present did not arrest the decay caused by cycling, but reduced the rate of decay somewhat for CO₂/SO₂ co-capture. One-time treatment of calcined limestone could produce h-CaO, which showed enhanced CO₂ capture ability with or without SO₂ present, but appeared to be dominated by CaO sintering.
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

Calcination with steam as the fluidizing gas appears to be appealing as it did not augment sintering, and steam calcination can easily produce a relatively pure CO₂ stream in practice after condensing the steam.

Steam and water hydration for partially carbonated sorbents did not show enhanced carbonation, probably because of a compact carbonate layer preventing the diffusion of steam. Addition of steam and water to calcined and highly sintered samples showed improved CO₂ capture ability, attributable to regeneration of <220 nm pores. Among the hydration methods, water achieved better results than steam. Intermittent water hydration during cycling could lead to improved reversibility, probably related to particle size reduction. Steam/water hydration can also be utilized to fracture sulphate layers formed during co-capture of CO₂ and SO₂.

The sulphate layer can also be fractured by using CO to regenerate CaO from CaSO₄. However, CO regeneration is very slow, in part because the CO concentration has to be kept low to obtain CaO rather than CaS as the by-product. CO regeneration can improve sorbent reversibility somewhat, but not significantly.

Various salts, which are inert to CO₂ capture, were added to natural limestone in an effort to find a dopant which could improve sorbent reversibility. Most of the additives did not achieve good results. A ~1:1 molar ratio of CaO to Al₂O₃ showed the most promising results on a free-lime basis.
Table 7.3 Summary of experiments to test possible additives to improve sorbent reversibility.

<table>
<thead>
<tr>
<th>Run number</th>
<th>Precursors</th>
<th>Figure showing the result</th>
<th>Original mixture CaO mass fraction (converted to basis of fully calcined sorbent) (wt%)</th>
<th>Measured CaO mass fraction after being fully calcined by fast sugar method (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Limestone +Al(NO₃)₃·9H₂O</td>
<td>Low reactivity, not shown</td>
<td>36.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Calcined limestone +Al(NO₃)₃·9H₂O</td>
<td>Low reactivity, not shown</td>
<td>36.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Limestone +Al₂O₃</td>
<td>Figure 7.11a</td>
<td>36.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Calcined lime +Al₂O₃</td>
<td>Figure 7.11a</td>
<td>37.0</td>
<td>14.0</td>
</tr>
<tr>
<td>5</td>
<td>Calcined lime +Al₂O₃</td>
<td>Figure 7.11a</td>
<td>53.7</td>
<td>31.0</td>
</tr>
<tr>
<td>6</td>
<td>Calcined lime +Al₂O₃</td>
<td>Figure 7.11a</td>
<td>83.1</td>
<td>37.0</td>
</tr>
<tr>
<td>7</td>
<td>Acetate + Al₂O₃</td>
<td>Low reactivity, not shown</td>
<td>37.3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Acetate + Al₂O₃</td>
<td>Figure 7.11a</td>
<td>81.7</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Limestone +SiO₂ gel</td>
<td>Low reactivity, not shown</td>
<td>49.6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Calcined lime +SiO₂ gel</td>
<td>Low reactivity, not shown</td>
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<td></td>
</tr>
<tr>
<td>11</td>
<td>Calcined lime +SiO₂ gel</td>
<td>Figure 7.11b</td>
<td>96.1</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Acetate + SiO₂ sand</td>
<td>Low reactivity, not shown</td>
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<td></td>
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<tr>
<td>13</td>
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<td>Low reactivity, not shown</td>
<td>81.8</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Calcined lime +SiO₂ sand</td>
<td>Figure 7.11b</td>
<td>49.1</td>
<td></td>
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<td>15</td>
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<td>Figure 7.11b</td>
<td>81.8</td>
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<tr>
<td>16</td>
<td>Acetate + SiO₂ sand</td>
<td>Figure 7.11b</td>
<td>48.2</td>
<td>40.0</td>
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<td>17</td>
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<td>Figure 7.11b</td>
<td>65.1</td>
<td></td>
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<td>Figure 7.11b</td>
<td>31.8</td>
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<td>Figure 7.11b</td>
<td>81.7</td>
<td></td>
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<tr>
<td>20</td>
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<td>CaO + ZrO₂</td>
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<td>77.6</td>
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<td>23</td>
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<td>Figure 7.11c</td>
<td>31.2</td>
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<td>Figure 7.11c</td>
<td>82.0</td>
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</tr>
<tr>
<td>25</td>
<td>CaO + MgO</td>
<td>Figure 7.11d</td>
<td>54.6</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>CaO + MgO</td>
<td>Figure 7.11d</td>
<td>28.2</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>Acetate + MgO</td>
<td>Figure 7.11d</td>
<td>58.3</td>
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</tr>
<tr>
<td>28</td>
<td>CaO + TiO₂</td>
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<td>42.0</td>
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<td>29</td>
<td>CaO + TiO₂</td>
<td>Figure 7.11e</td>
<td>77.3</td>
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</tr>
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<td>Acetate + TiO₂</td>
<td>Low reactivity, not shown</td>
<td>45.0</td>
<td></td>
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<tr>
<td>31</td>
<td>Limestone +calcined dolomite</td>
<td>Figure 7.11e</td>
<td>54.5</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Calcined limestone +calcined dolomite</td>
<td>Figure 7.11e</td>
<td>69.2</td>
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<tr>
<td>33</td>
<td>Pure PCC</td>
<td>Low reactivity, not shown</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Limestone +MgSO₄·7H₂O</td>
<td>Figure 7.11f</td>
<td>73.6</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>Calcined limestone +NaCl</td>
<td>Figure 7.11f</td>
<td>91.8</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Calcined limestone +NaCl</td>
<td>Figure 7.11f</td>
<td>95.7</td>
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<td>38</td>
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<td>72.3</td>
<td>68.5</td>
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<tr>
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<td>Limestone +CaCl₂</td>
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<td>85.1</td>
<td>81.0</td>
</tr>
<tr>
<td>41</td>
<td>Limestone +CaCl₂</td>
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<td>94.3</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

Figure 7.1 High-resolution SEM photos of calcines derived from initial calcination of 212-250 μm Strassburg limestone particles; (a) h-CaO (b) c-CaO.

Figure 7.2 Cyclic performance: comparison of c-CaO and h-CaO (no SO₂ present, sorbent derived from 212-250 μm Strassburg limestone). Test conditions: 850°C calcination and carbonation, carbonation in 100% CO₂, calcination in 100% N₂. Fast stage of carbonation finished.
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

Figure 7.3 Pore size distribution: comparison of c-CaO and h-CaO (no SO₂ present, sorbent derived from Strassburg limestone). Samples are the same as in Figure 7.2.

Figure 7.4 Effect of steam calcination on cyclic capture (No SO₂ present, 212-250 µm Strassburg limestone). Test conditions: 850°C calcination and carbonation, Carbonation in 100% CO₂. Calcination in 95% steam, balance N₂. Fast stage of carbonation finished.
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

Figure 7.5 Pore size distribution: effect of steam calcination (No SO₂ present, Strassburg limestone). Same samples as in Figure 7.4.
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

Figure 7.6 Calcium utilization for CO₂ capture: effect of varying operating conditions, 212-250 μm particles. Test conditions: 850 °C calcination and sorption. Sorption in 80% CO₂, 3% O₂, 2900 ppm SO₂ and balance N₂ or with steam. Calcination in 100% N₂. 8 minutes for each sorption.
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

Figure 7.7 Effect of hydration on co-capture (CO₂+SO₂). 212-250 μm Strassburg limestone.

Procedure: 1-h co-capture or SO₂ sorption followed by 30 min hydration and 8 min cycles of re-capture: (a) Conversion of CaO to CaCO₃; (b) Conversion of CaO to CaSO₄.
Chapter 7 An investigation of attempts to improve cyclic CO$_2$ capture by sorbent hydration

Figure 7.8 Effect of intermediate hydration of carbonates on further carbonation (no SO$_2$ present)

A: 10 min carbonation plus 30 min steam hydration at 300°C plus 30 min carbonation; B: 60 min carbonation plus 30 min steam hydration at 300°C plus 30 min carbonation; C: 60 min carbonation plus 10 min liquid water steam hydration at room temperature plus 30 min carbonation. 850°C for both calcination (100% N$_2$) and carbonation (100% CO$_2$).
Chapter 7 An investigation of attempts to improve cyclic CO$_2$ capture by sorbent hydration

Figure 7.9 Effect of intermediate steam (95% v) or water (100%) hydration at various temperatures of sintered calcines on cycling (no SO$_2$ present). 850°C for both calcination (100% N$_2$) and carbonation (100% CO$_2$).
Figure 7.10 Variation of mass increase due to sorption divided by total initial mass of CaO with cycling. Test conditions are provided in Table 7.3.
Chapter 7 An investigation of attempts to improve cyclic CO₂ capture by sorbent hydration

Figure 7.11 Effect of various dopants on CaO reversibility in cyclic calcination/carbonation. Cycling conditions: 850°C for calcination (in 100% N₂) and carbonation (in 100% CO₂): (a) γ-Al₂O₃; (b) SiO₂ and Kaolinite; (c) ZrO₂; (d) MgO; (e) dolomite, TiO₂, precipitated calcium carbonate; (f) other dopants as identified in Table 7.3.
Figure 7.12 XRD analyses results for typical runs

For all the runs
- CaO
- CaO
- CaO

Run 20 CaO+ Kaolinite (SiO₂-Al₂O₃ peak cannot be clearly viewed)
Run 35 CaO+NaCl (NaCl peak cannot be clearly viewed)
Run 22 CaO+ZrO₂
Run 15 CaO+ SiO₂ sand (Ca₃SiO₄ peak cannot be clearly viewed)
Run 28 CaO+TiO₂
Run 11 CaO+SiO₂ Gel (Ca₃SiO₄ peak cannot be clearly viewed)
Run 25 CaO+MgO
Run 4 CaO+Al₂O₃

CaTiO₃
ZrO₂
MgO
Ca₃Al₂O₆
CHAPTER 8 SEQUENTIAL CAPTURE OF CO$_2$ AND SO$_2$ UNDER FBC CONDITIONS

A shortened version of this chapter has been accepted by Environmental Science and Technology, in press. Authors: P. Sun, J. R. Grace, C. J. Lim and E. J. Anthony.

8.1 Introduction

Initiated by climate change concerns and the need to reduce CO$_2$ (greenhouse gas) emissions by the power industry, several novel CO$_2$ capture concepts have been proposed based on calcium-based sorbents as CO$_2$ carriers between a combustor (also acting as a carbonator) and a calciner (acting as a sorbent regenerator) (Shimizu et al., 1999; Abanades et al., 2003). Given the thermodynamics of the CaO-CO$_2$ carbonation reaction, higher CO$_2$-removal could be achieved in pressurized fluidized bed combustors (PFBC) than at atmospheric pressure.

The cyclic CO$_2$ capture ability during calcination/carbonation cycles, referred to as sorbent reversibility in this study, is a key factor affecting process economics for calcium-based CO$_2$ sorbents (Lin et al., 2001). Most studies have focused on the reversibility of natural sorbents in the presence of a single gaseous reactant, CO$_2$ (Abanades, 2002; Abanades and Alvarez, 2003; Abanades et al., 2004; Alvarez and Abanades, 2005). However, the work in Chapters 5 and 6 using an atmospheric TGR, and previous work in a bubbling fluidized bed (Ryu et al., 2006) under FBC conditions have demonstrated that SO$_2$ greatly decreases the reversibility of calcium-based sorbents compared to a CO$_2$-only environment. An important factor for minimizing the loss of sorbent reversibility is to use as large a molar ratio of CO$_2$/SO$_2$ as possible in combustors. However, the total SO$_2$ is pre-determined for a combustor of a fixed fuel type and demand. Therefore, methods of separately removing SO$_2$ and CO$_2$ in sequential reactors need to be
Chapter 8 Sequential capture of CO₂ and SO₂ under FBC conditions

considered. In the current study, the technical feasibility of alternative configurations is investigated.

In addition to favourable economics, several criteria have to be met to achieve excellent capture of both SO₂ and CO₂ in fluidized bed combustion. Firstly, when capturing CO₂, sorbents should retain a high level of reversibility to minimize sorbent consumption. Secondly, the kinetics of carbonation and calcination should be fast to prevent the equipment from being too large. Furthermore, there should be no obvious impact of the sulphate layer or carbonate layer on downstream capture. Other requirements, such as flexible operation, may also be important.

Calcium sites needed for SO₂ removal account for only a small portion of those required for CO₂ removal given the relative number of moles of the two species. For instance, a boiler firing coal containing 60%wt C and 2%wt S has a molar C/S ratio of 79. However, sulphur capture is irreversible, whereas carbonation is, at least in principle, reversible. To realize sequential capture, there are at least four candidate processes, each based on existing technology, as shown in Figure 8.1:

Option A: Fresh sorbent is sent to an atmospheric fluidized bed combustor (FBC) first for SO₂ capture before being cycled to a carbonator/calciner system. The carbonator could be operated at atmospheric pressure and a relatively low temperature (e.g. 600°C) to achieve higher CO₂ removal efficiency.

Option B: Fresh sorbent is cycled in the carbonator/calciner system for CO₂ capture until its reactivity is lost. The residues are then sent for SO₂ capture to an atmospheric FBC, where the sorbents are maintained as long as needed to maximize overall or calcium utilization for S-capture, before being discharged.

Option C: Sorbents are first sent to a pressurized fluidized-bed combustor (PFBC) for SO₂ capture before being cycled within a carbonator/calciner system. A recent economic study
(MacKenzie et al., 2006) shows that a PFBC for CO$_2$ capture compares favourably with amine-based capture. Choosing practical operating temperature and pressure levels for the carbonator and calciner requires system integration, as well as removal efficiency, thermodynamics and transportation of CO$_2$-rich off-gas. The separation of the CO$_2$ removal system from the combustor allows a lower carbonator operating temperature.

**Option D:** Sorbents are cycled first in a carbonator/calciner system for CO$_2$ capture, and then sent to a PFBC for SO$_2$ capture. In the PFBC, the sulphation could be realized either through CaO sulphation or CaCO$_3$ direct sulphation. The often-cycled sorbents could be sent to the PFBC, with or without a final calcination. Sending calcined CaO to a PFBC may not be attractive, but in this chapter this condition provides comparisons with direct sulphation using CaCO$_3$.

The operating temperatures and pressures in Figure 8.1 are for illustrative purpose. Actual test conditions for these options are specified where they are discussed:

Several reactions are important in this chapter,

Carbonation and calcination: \[ \text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 \] \[ \Delta H_{298_K} = -178 \text{ kJ/mol} \] \(8.1\)

Lime sulphation: \[ \text{CaO} + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4 \] \[ \Delta H_{298_K} = -502 \text{ kJ/mol} \] \(8.2\)

Direct sulphation: \[ \text{CaCO}_3 + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2 \] \[ \Delta H_{298_K} = -324 \text{ kJ/mol} \] \(8.3\)

Note that the carbonator and calciner in each of the above options have considerable flexibility in their operation, in particular in temperature and pressure, because of their separation from the combustor. In the experimental work presented below, however, in order to facilitate comparison of the options, carbonation and calcination conditions were all conducted at the same temperature for the cyclic CO$_2$ capture.
Chapter 8 Sequential capture of CO₂ and SO₂ under FBC conditions

Practical heat supply issues for the calcination are not stressed in this study. For example, the calciners in the various options of Figure 8.1 are not necessarily oxy-fired, but could utilize multiple heat sources, such as steam or a solid heat carrier, depending on the available technology and cost. The pressure level of the carbonator/calciner could be varied to take advantage of thermodynamic limits and system requirements.

8.2 Experimental Details

The pressurized TGA (PTGA) system, consisted of a Cahn 100 balance of 1 μg sensitivity, a reactor and a control system. The reactor is made of Inconel 600 alloy, allowing high temperatures and high pressures. Dwyer mass flow controllers connected to a computer adjusted the gas flow rates to obtain desired gas concentrations of mixed gases directed into the bottom of the reactor. The PTGA pressure level was set by a pressure regulator, with a bypass to allow atmospheric pressure operation. Operating temperatures were 850°C for both calcination and sorption.

Table 8.1 Gas compositions for the four options examined. All reactions were conducted at 850°C.

<table>
<thead>
<tr>
<th>Option</th>
<th>Pressure (MPa)</th>
<th>SO₂ (ppmv)</th>
<th>Other components</th>
<th>Cyclic CO₂ sorption stage</th>
<th>Carbonation</th>
<th>Calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Composition</td>
<td>Pressure (MPa)</td>
</tr>
<tr>
<td>A</td>
<td>0.1</td>
<td>5000</td>
<td>3% O₂, balance N₂</td>
<td>14% CO₂, balance N₂</td>
<td>1.82</td>
<td>100% N₂</td>
</tr>
<tr>
<td>B</td>
<td>0.1</td>
<td>5000</td>
<td>3% O₂, balance N₂</td>
<td>14% CO₂, balance N₂</td>
<td>1.82</td>
<td>100% N₂</td>
</tr>
<tr>
<td>C</td>
<td>1.82</td>
<td>1500 or 5000</td>
<td>15% CO₂, 3% O₂, balance N₂</td>
<td>14% CO₂, balance N₂</td>
<td>1.82</td>
<td>100% N₂</td>
</tr>
<tr>
<td>D</td>
<td>1.82</td>
<td>5000</td>
<td>15% CO₂, 3% O₂, balance N₂</td>
<td>14% CO₂, balance N₂</td>
<td>1.82</td>
<td>100% N₂</td>
</tr>
</tbody>
</table>
Chapter 8 Sequential capture of CO$_2$ and SO$_2$ under FBC conditions

Gas concentrations for the various tests are summarized in Table 8.1. As described above, all options involved: a SO$_2$ sorption stage and a CO$_2$ sorption stage. The SO$_2$ sorption stage was realized through sulphation alone, direct sulphation, or simultaneous sulphation and carbonation. The CO$_2$ sorption was simulated by cycling sorbents between a carbonator and a calciner. During these tests, except where indicated, the carbonation operated at 1.82 MPa and 850°C with 14% CO$_2$ balanced by N$_2$, whereas the calcination was at 0.1 MPa and 850°C in a pure N$_2$ atmosphere. Note this cycling condition is different from that proposed in Figure 8.1. The selection of the current cycling condition is only for convenience to compare tests with different histories before or after cycling. A 4-minute sorption time was adopted for each cycle, enough for fresh sorbents to reach the slow stage of carbonation, whereas the calcination portion of each cycle was prolonged until further mass loss was negligible.

The chemical analyses of the 212-250 μm Strassburg limestone and Arctic dolomite tested are shown in Table 1.2. All runs started with 50±2 mg of fresh sorbent.

8.3 Results and discussion

To simulate option A, calcined Strassburg limestone was sulphated for 10 minutes and then sent for cyclic carbonation and calcination. Cyclic carbonation/calcination of this fresh limestone without sulphation was also performed at 850°C and 0.1 MPa, with pure N$_2$ for calcination, 14% CO$_2$ and the balance N$_2$ for carbonation, to provide a baseline, shown as the upper line in Figure 8.2. The pre-sulphated PTGA tests show the following features during carbonation/calcination cycles. Carbonation still consisted of fast and slow stages. The conversions corresponding to the onset of the slow stage decreased sharply with cycling. The first calcination following the first carbonation lasted much longer before leveling off than the initial calcination and following
cycles. After 10 minutes of sulphation, ~12% calcium utilization was achieved. The partially sulphated sorbents still showed high reactivity to CO₂.

The above findings suggest interaction between the pore structure and the relevant gas-solid reactions. Strassburg limestone has been found to sulphate in a shrinking core manner (Laursen et al., 2000) and can only achieve ~35% calcium utilization during long-term (usually >24 h) sulphation due to pore-mouth plugging. After long-term sulphation, the sulphate layer was compact, as evidenced by low effective diffusivity in sulphation (Krishan and Sotirchos, 1994) and surface texture (Duo et al., 2000). A separate run indicated that the Strassburg limestone, calcined after prolonged sulphation, did not carbonate significantly further. It is believed that the residual carbonation in Figure 8.2 is due to an intermediate degree of sulphation. The remaining pore passages could still provide some surface area for carbonation, while the blocked or the partially blocked pore mouths were responsible for the much lower CaO conversion to carbonate.

It is important to note that CaO carbonation and sulphation have different dependence on pore passages. Previous studies, mostly with liquid N₂ adsorption (Gullelt and Bruce, 1987; Stouffer and Yoon, 1989; Sotirchos and Zarkanitis, 1992; Mahuli et al., 1997; Wu et al., 2002), indicate that CaO sulphation tends to fill pores of diameter 10-60 nm or larger, easily blocking pore mouths of this size range. Higher effective diffusivity in the sulphate layer is usually the key to improve sulphation. On the other hand, the work in Chapter 4 and in the literature (Bhatia and Perlmutter, 1983; Alvarez and Abanades, 2005) show that the fast stage of CaO carbonation depends on surface area residing in smaller pores and is less likely to experience pore blockage.

The slow calcination after the first carbonation must be due to constricted passages, with sulphate causing blockage, resulting in lower effective diffusivity. With further cycling, during which sintering eliminates smaller pores while creating larger ones (see Chapters 4 and 6), the larger pores increase the effective diffusivity, helping to speed up calcination in later cycles.
Chapter 8 Sequential capture of CO\textsubscript{2} and SO\textsubscript{2} under FBC conditions

Figure 8.3a shows a Scanning Electron Microscope (SEM) image for the sulphated, then cycled calcine. A porous texture is seen, indicating the start of macropore growth due to sintering that also provides passages for CO\textsubscript{2}. Smooth coverage by a sulphate layer can be clearly identified.

This study found that a potential problem of this option is poor control of the extent of sulphation, which may severely reduce carbonation ability and retard calcination. In addition, reversibility was far from ideal. Hence option A is not considered further.

In option B, the sorbents are first sent to a carbonator/calciner to concentrate CO\textsubscript{2}. After the initial, 2\textsuperscript{nd}, 7\textsuperscript{th} and 15\textsuperscript{th} calcination, sorbents were sulphated for 2400 s under atmospheric conditions. The subsequent sulphation results for the cycled sorbents appear in Figure 8.4. Compared with the initial calcines, the cycled sorbents showed a decreased extent of sulphation. However, after 15 carbonation/calcination cycles, calcines demonstrated better sulphation ability than after 2 and 7 cycles. This must be due to the dependence of sulphation on surface area and pore volume. Sulphation suffers from pore-mouth blocking because of the much higher molar volume of CaSO\textsubscript{4} product relative to the original limestone. This is especially true for Strassburg limestone, which sulfates as an unreacted core type (Laursen et al., 2000). Improved performance after the 15\textsuperscript{th} calcination is believed to be due to enlarged macropores generated during cycling. Chapter 4 and previous studies (Alvarez and Abanades, 2005) have generally shown that, as a result of the intermediate stage of CaO sintering, carbonation/calcination cycling eliminates pores in the <220 nm mesopore range and generates macropores of diameter >220 nm. Growth in macropore volume could increase effective diffusivity for subsequent sulphation, resulting in higher calcium utilization than for fewer cycles.

Therefore, when using cycled limestones as SO\textsubscript{2} sorbents, after the first few cycles of carbonation/calcination, reduction in surface area or pore volume may result in less sulphation,
but with further cycling, the change of pore structure or improved effective diffusivity due to macropore growth benefited sulphation, again demonstrating different pore dependence of the carbonation and sulphation processes. Whereas the fast stage of carbonation relies primarily on pores in the ~220 nm size range (see Chapter 4) and slows down greatly as these pores are filled, sulphation utilizes macropores larger than ~220 nm to achieve higher conversion, presumably with increased internal diffusivity.

EDX (Energy-Dispersive X-ray) analyses in Figure 8.5 reveal that both the initial calcines and those after 15 cycles sulphated either in an unreacted-core manner or with the pore-plugging mechanism. Although macropores were generated during cyclic sintering, the unreacted-core behaviour did not change, either because the larger pores may still reside at the outer layer of particles, or SO₂ molecules could still not enter the smaller pores.

Arctic dolomite was also tested based on option B. The results appear in Figure 8.6. Unlike the Strassburg limestone, the calcium utilization after 40 minutes of sulphation decreased monotonically with cycling. Calcines from the 15th cycle did not perform significantly differently from those after the 7th. Different sintering degrees for the Arctic dolomite and Strassburg limestone appear to have affected re-sulphation behaviour. As revealed in Chapter 6, sintering of calcined Arctic dolomite eliminates <100 nm pores, while not generating larger pores because of the presence of MgO. Therefore, unlike Strassburg limestone, cycling did not improve sulphation of Arctic dolomite.

Overall option B is more attractive than option A in that it makes better use of the sorbents for both carbonation and sulphation. The highly cycled sorbents, considered as spent for further CO₂ removal, still capture SO₂ due to a more favourable pore structure.

A PFBC-based system can also be applied in a similar manner to the AFBC-based systems discussed above. This was tested in Options C and D. A key difference is that in PFBC-based
systems, sulphation may either be through direct sulphation of carbonate, or by sulphation of CaO, possibly accompanied by parallel carbonation. During the tests, a batch of fresh sorbent was first sulphated directly for 600 or 2400 s at high CO₂ partial pressure to prevent calcination. The sorbents were then sent to carbonation/calcination cycles. The total pressure was preset to 1.82 MPa. Except where specified, gas concentrations for the PFBC sorption step were maintained as 15%v CO₂, 5000 ppmv SO₂ and 3%v O₂, with N₂ as the balance. The sharp peaks in Figure 8.7 are related to gas switching, picked up by the sensitive load cells and should be disregarded. Figure 8.7a shows the test history with 600 s direct sulphation. In another set of tests, fresh sorbents were calcined first, and then exposed to the same test conditions, so that simultaneous carbonation and sulphation could occur. Figure 8.7b shows the results.

The conditions and durations tested are listed in Table 8.2. The extents of sulphation are based on recorded mass changes. The mass change in direct sulphation only involves reaction (8.3). The mass change in simultaneous sulphation and carbonation is due not only to carbonation reaction (8.1), but also to reactions (8.2) and (8.3). CaO conversions were calculated with the aid of a full calcination following sorption, as shown in Chapter 5. Note all sulphations were performed here before carbonation/calcination cycling.

Several findings require discussion. First, Figure 8.7a indicates that the first calcination after direct sulphation was slower than the initial calcination of fresh limestone. This is due to the sulphate layer along the outer rim of the particles because direct sulphation occurs (Hajaligol et al., 1988; Tullin et al., 1993; Qiu and Lindqvist, 2000) in a typical unreacted core manner. This implies that overly sulphated sorbents may not show favorable cyclic performance compared to fresh sorbents.
Chapter 8 Sequential capture of CO₂ and SO₂ under FBC conditions

Table 8.2 Sulphation extents after direct sulphation

<table>
<thead>
<tr>
<th>Sulphation type</th>
<th>Conditions (850°C, 1.82 MPa)</th>
<th>Duration for sorption step (s)</th>
<th>Sulphation extent (based on total Ca)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct¹</td>
<td>Strassburg limestone, 1500 ppm SO₂</td>
<td>600</td>
<td>2.1%</td>
</tr>
<tr>
<td>Direct</td>
<td>Strassburg limestone, 1500 ppm SO₂</td>
<td>2400</td>
<td>6.1%</td>
</tr>
<tr>
<td>Direct</td>
<td>Strassburg limestone, 5000 ppm SO₂</td>
<td>600</td>
<td>4.8% (Figure 8.3c)²</td>
</tr>
<tr>
<td>Direct</td>
<td>Strassburg limestone, 5000 ppm SO₂</td>
<td>2400</td>
<td>13.3% (Figure 8.3d)²</td>
</tr>
<tr>
<td>With carbonation²</td>
<td>Strassburg limestone, 1500 ppm SO₂</td>
<td>600</td>
<td>4.7%</td>
</tr>
<tr>
<td>With carbonation</td>
<td>Strassburg limestone, 5000 ppm SO₂</td>
<td>600</td>
<td>7.6% (Figure 8.3b)²</td>
</tr>
<tr>
<td>Direct</td>
<td>Arctic dolomite, 5000 ppm SO₂</td>
<td>600</td>
<td>9.5%</td>
</tr>
<tr>
<td>With carbonation</td>
<td>Arctic dolomite, 5000 ppm SO₂</td>
<td>600</td>
<td>15.3%</td>
</tr>
</tbody>
</table>

¹ Direct: means direct sulphation is occurring

² With carbonation: means sulphation occurring simultaneously with carbonation.

*Corresponding to the same samples as shown in Figure 8.3b-d.

Secondly, Table 8.2 shows that 600 s of simultaneous carbonation and sulphation of CaO gave higher CaO conversion to CaSO₄ than 600 s of direct sulphation. The porous nature of the calcines applied in simultaneous capture was responsible for the higher sulphation extent and the subsequent faster calcination seen in Figure 8.7. However, the effect of the mode of sulphation on the calcination rate became less significant with further cycles.

In Figure 8.8, after the sulphation stage Strassburg limestone is seen to have exhibited similar calcination/carbonation reversibility as in the baseline cycling tests with fresh limestone. They all appeared to have no memory of the direct sulphation histories. Note that the results plotted here are on a free calcium basis, where free calcium refers to the part of calcium existing in any form other than sulphate. Similar trends are observed in Figure 8.9 for simultaneous sulphation and carbonation, except that the run with 5000 ppm SO₂ experienced somewhat lower reactivity for the first cycle, presumably because of incomplete recovery of effective diffusivity. The results imply that in a PFBC system, SO₂ removal could be achieved by either direct
Chapter 8 Sequential capture of CO₂ and SO₂ under FBC conditions

sulphation or simultaneous sulphation and carbonation. If the extent of sulphation does not exceed those in Table 8.2, subsequent carbonation/calcination cycles give similar cyclic performance as for fresh limestone.

High-resolution SEM images of calcines from the above runs appear in Figure 8.3. Figure 8.3b shows a grainy structure compared with that after CaO sulphation in Figure 8.3a or after direct sulphation in Figures 8.3c and 8.3d. The grain structure is probably inherited from the initial calcination, with sintering commencing after a few cycles. As the sulphation extent is not high (7.6%), the sulphate layer probably did not completely cover the outer surface, resulting in faster calcination as discussed above. For direct sulphation, however, complete coverage occurred as seen in Figures 8.3c and 8.3d for different durations, indicating that direct sulphation proceeds more like the unreacted core case. The original grain boundaries are still visible after 600 s of direct sulphation (Figure 8.3c), whereas blocks of sulphate layers appear in the 2400 s runs (Figure 8.3d). Both calcines show pores acting as passages through which CO₂ can permeate. These pores were generated originally by calcination after direct sulphation, and then by sintering-related large-pore growth, probably related to more reactive CaO pores coated with a sulphate layer.

Dolomites are commonly used as sorbents in PFBCs. Here Arctic dolomite was tested in the same manner as the Strassburg limestone, based on the most promising option, option C. As seen in Chapter 6, Arctic dolomite was more reactive than Strassburg limestone for sulphation, probably because of its high surface area, with 600 s of direct sulphation resulting in 9.5% calcium utilization, whereas 600 s of simultaneous reaction with SO₂ and CO₂ gave 15.3% calcium utilization, as seen in Table 8.3. The enhanced sulphation via simultaneous exposure to SO₂ and CO₂ greatly affected subsequent cyclic CO₂ capture. As seen in Figure 8.10, reversibility deteriorated greatly, whereas the 9.5% calcium conversion to sulphate through
Chapter 8 Sequential capture of CO\textsubscript{2} and SO\textsubscript{2} under FBC conditions

direct sulphation had relatively little effect on subsequent carbonation/calcination cycles as shown in Figure 8.11. As the volume of pores <100 nm is especially important to carbonation, it can be concluded that simultaneous carbonation and sulphation exposure greatly reduced the pore volume in this size range. (All calcium utilizations are again based on free calcium oxide).

SEM photos for calcines from both of these runs are compared in Figure 8.12. The one which experienced direct sulphation appeared to have more porous grains than the one subjected to co-capture. As indicated by the much slower calcination in the co-capture case, the sulphate layer greatly reduced the effective diffusivity, probably due to the uniform distribution of sulphate in the co-capture product, whereas in the case of direct sulphation, the entire sulphate layer was an outer envelope so that further sulphation proceeded to a much lesser extent. After calcination, the pore channels could be emptied more easily by the CO\textsubscript{2}, generating sorbents with higher effective diffusivity and higher CaO availability for subsequent CO\textsubscript{2} capture.

As for option B, sorbents after being cycled in the carbonator and calciner could also be used as SO\textsubscript{2} sorbents in a PFBC. To test this option D, Strassburg calcines after initial calcination and after 7\textsuperscript{th} and 15\textsuperscript{th} cycles of calcination/carbonation cycles were subjected to simultaneous carbonation and sulphation for 2400 s in an atmosphere containing 5000 ppm SO\textsubscript{2}, 15\% CO\textsubscript{2} at 850\degree C and 1.82 MPa. After that, the conversion was determined by calcining until there was no further mass change. A typical run with 7 calcination/carbonation cycles is shown in Figure 8.13. After cycling, 2400 s of co-capture generated a compact sulphate layer that extended the final calcination period (more than 2000 s required to level off). As plotted in Figure 8.14, the conversion of CaO to CaCO\textsubscript{3} decayed with cycling, presumably because of CaO sintering. However, the conversion of CaO to CaSO\textsubscript{4}, after 15 calcination/carbonation cycles was higher than after 7 cycles. Recall that for AFBC-based option B, the sintered pore structure or growth of macropores enabled a higher degree of sulphation due to increased effective
Chapter 8 Sequential capture of CO\textsubscript{2} and SO\textsubscript{2} under FBC conditions

diffusivity. Similar factors are believed to be responsible for the somewhat enhanced extent of sulphation in this co-capture case. In Figure 8.14, the sulphation extents for 2400 s sulphation based on option B, labeled as AFBC, are plotted for comparison. The conversion of CaO to CaSO\textsubscript{4} is similar for PFBC and AFBC conditions, whereas that for PFBC co-capture exceeds that for AFBC sulphation, consistent with findings in Chapters 5 and 6 that under comparable conditions, co-capture gives a greater extent of sulphation.

As shown in Figure 8.15, tests with Arctic dolomite did not show any enhancement of sulphation by using highly cycled sorbents. This confirms the trend found for option B, and is believed to reflect the monotonic elimination of pores for Arctic dolomite during cycling as discussed above.

The cycled sorbent can also be directly sent to a combustor for sulphation before being calcined. In one run, Strassburg limestone after 15 calcination/carbonation cycles, after the carbonation stage, was immediately exposed to PFBC conditions for 2400 s of sorption followed by complete calcination. It was found that 2400 s of further sorption in CO\textsubscript{2}/SO\textsubscript{2} gave a 10.3% calcium utilization for sulphation, less than the 19% achieved by calcined sorbents after 15 cycles. Given that actual sulphation requirements are low when CaO is in large excess to meet the carbonation demand, the highly cycled sorbents without calcination are likely to be able to achieve the desired SO\textsubscript{2} removal efficiencies.

In all the options discussed above, the flue gases after being scrubbed of SO\textsubscript{2} in an AFBC or PFBC, are then sent for downstream CO\textsubscript{2} removal. There is still concern that the lack of efficient SO\textsubscript{2} capture upstream would cause further decay, reducing CO\textsubscript{2} capture as observed in Chapters 5 and 6. To test the tolerance of sorbents to residual sulfur, results of a test with 14v% CO\textsubscript{2} and only 100 ppmv SO\textsubscript{2} are shown in Figure 8.16. This again shows some decay due to the presence
Chapter 8 Sequential capture of CO$_2$ and SO$_2$ under FBC conditions

of SO$_2$ for the Strassburg limestone, indicating that high-efficiency SO$_2$ removal is essential to protect the sorbents downstream.

8.4 Conclusions

In fluidized bed combustion operations, calcium-based sorbents (limestones and dolomites) are commonly used for sulphur capture. There is also interest in using these sorbents for cyclic calcination/carbonation in order to provide a concentrated CO$_2$ steam suitable for regeneration. This chapter addresses the question of whether the sorbents should be subjected to sulphation before, after or simultaneously with calcination/carbonation cycling.

Options B and D, where the sorbents are exposed to calcination/carbonation cycle, before being sent to fluidized-bed combustion to capture SO$_2$, are clearly better than other two options where sulphation occurs before calcination/carbonation, or where sulphation and carbonation occur simultaneously. (The basic features of a process based on Option B are presented in Appendix AIX through Aspen simulation.) The dolomite tested showed similar trends to the limestone in most cases. Even a small amount of SO$_2$ present can cause rapid deterioration in the ability of calcium-based sorbents to undergo cyclic calcination/carbonation cycles, due to pore blockage and formation of a relatively impermeable outer shell.
Chapter 8 Sequential capture of CO₂ and SO₂ under FBC conditions

(a) Option A

(b) Option B
Figure 8.1 Candidate processes for CO₂ and SO₂ removal with calcium-based sorbents; Options A and C: sulphation before calcination/carbonation; Options B and D: calcination/carbonation before sulphation; Options C and D involve pressurized fluidized-bed combustion (PFBC).
Figure 8.2 Sorbent performance: conversion history based on option A. 212-250 μm Strassburg limestone. Sulphated first for 10 minutes at 850°C and 0.1 MPa, 850°C calcination/carbonation cycles. Baseline conditions for fresh limestone: see Table 8.1 for CO₂ sorption stage.
Figure 8.3. SEM photos for calcines from different runs; for (b), (c) and (d), see Table 8.2, for test conditions. (a) CaO sulphation, followed by 4 calcination/carbonation (c/c) cycles, 12% calcium utilization for sulphation (on molar base). Test conditions: as for solid points in Figure 8.2. Option A. (b) Co-capture for 600 s followed by 4 c/c cycles, Option C. (c) Direct sulphation, 5000 ppm SO$_2$, for 600 s followed by 4 c/c cycles, Option C. (d) Direct sulphation, 5000 ppm SO$_2$, for 2400 s followed by 4 c/c cycles, Option C.
Chapter 8 Sequential capture of CO$_2$ and SO$_2$ under FBC conditions

Figure 8.4 Sulphation of cycled sorbents after different number of calcination/carbonation cycles. 212-250 μm Strassburg limestone. (Option B)

Figure 8.5 EDX sulfur-mapping of calcines for 212-250 μm Strassburg limestone. Test conditions as in Figure 8.4. (a) Sulphation of Strassburg limestone for 2400 s (Fresh sorbent) (b) Sulphation of Strassburg sorbent after 15 calcination/carbonation cycles.
Figure 8.6 Sulphation of cycled sorbents after different number of calcination/carbonation cycles. 212-250 μm Arctic dolomite (Option B). For conditions, see Table 8.1.
Chapter 8 Sequential capture of CO₂ and SO₂ under FBC conditions

Figure 8.7 Mass change profiles during typical runs for Option C with 212-250 µm Strassburg limestone. (a) Direct sulphation for 600 s. (b) Simultaneous sulphation and carbonation for 10 minutes. Test conditions: Both direct sulphation and simultaneous sulphation and carbonation: 5000 ppm SO₂, 15% CO₂, 3% O₂, N₂ balance before calcination/carbonation cycling, 1.82 MPa, 850°C.
Figure 8.8 Cyclic calcination/carbonation performance of 212-250 μm Strassburg limestone after direct sulphation (Option C). See Table 8.1 for calcination/carbonation cycling conditions.

Figure 8.9 Cyclic performance of 212-250 μm Strassburg limestone after simultaneous sulphation and carbonation, and a complete calcination. Option C with 212-250 μm Strassburg limestone. See Table 8.1 for calcination/carbonation cycling conditions.
Chapter 8 Sequential capture of CO₂ and SO₂ under FBC conditions

Figure 8.10 Cyclic performance of 212-250 μm Arctic dolomite after simultaneous sulphation and carbonation, and calcination. Option C. Baseline conditions for fresh sorbent: See Table 8.1 for calcination/carbonation cycling conditions.

Figure 8.11 Cyclic performance of 212-250 μm Arctic dolomite after direct sulphation and calcination. Option C. Baseline test conditions for fresh sorbent: See Table 8.1 for calcination/carbonation cycling conditions.
Chapter 8 Sequential capture of CO\textsubscript{2} and SO\textsubscript{2} under FBC conditions

Figure 8.12 Surface texture of cycled 212-250 μm Arctic particles different sulphation history (a)

Same test conditions as in Figure 8.10  (b) Same test conditions as in Figure 8.11.
Chapter 8 Sequential capture of CO$_2$ and SO$_2$ under FBC conditions

Figure 8.13 Mass change profiles with simultaneous carbonation and sulphation after 7 cycles of carbonation and calcination. Option D with 212-250 μm Strassburg particles.

Figure 8.14 Sulphation and carbonation extents during co-capture with cycled 212-250 μm Strassburg limestone particles. Option D vs. Option B. See Table 8.1 for conditions.
Figure 8.15 Sulphation and carbonation extents during co-capture with cycled 212-250 μm Arctic dolomite particles. Option D vs. Option B. See Table 8.1 for conditions.
Chapter 8 Sequential capture of CO$_2$ and SO$_2$ under FBC conditions

Figure 8.16 Effect of small residual SO$_2$ on calcination/ carbonation cycling. 212-250 μm Strassburg limestone particles. Points: Sorption with 14% CO$_2$, 100 ppmv SO$_2$, 3% O$_2$ and balance N$_2$ at 850°C and 1.82 MPa. Calcination in 100% N$_2$ at 850°C and atmospheric pressure. Cycling conditions for fresh sorbent with no SO$_2$ present: see Table 8.1 for carbonation conditions.
CHAPTER 9 CO-CAPTURE OF H₂S AND CO₂ IN A PRESSURIZED-GASIFIER-BASED PROCESS

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9.1 Introduction

Calcium-based sorbents have been receiving widespread attention as candidates to remove the greenhouse gas CO₂ in-situ from reactors in combustors (Shimizu et al., 1999; Abanades et al., 2003), gas shift reactors (Han and Harrison, 1994) and steam reformers (Balasubramanian et al., 1999; Ortiz and Harrison, 2001; Ziock et al., 2004a; 2004b; Johnsen et al., 2006), while improving higher hydrogen yields in the latter two cases. They may also be attractive to integrate CO₂ capture and enhanced H₂ production in fossil fuel gasifiers in an attempt to produce H₂ in a more economical and environmentally advantageous manner. The overall Pressurized Gasifier/calciner process utilizes calcined limestone as a CO₂ carrier, circulating between a pressurized gasifier and a calciner. As an example of this process, Lin and coworkers (Lin et al., 2002a; b) proposed and tested a HyPr-RING process where CO₂ is cyclically absorbed in high-pressure gasifiers by hydrated lime.

Another advantage of using calcium-based sorbents in gasifiers is that H₂S can be removed simultaneously due to the parallel reactions:

Carbonation \( \text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 \) \( \Delta H_{298K} = -178 \text{ kJ/mol} \) (9.1)

Sulfidation \( \text{CaO} + \text{H}_2\text{S} \rightleftharpoons \text{CaS} + \text{H}_2\text{O} \) \( \Delta H_{298K} = -59.4 \text{ kJ/mol} \) (9.2)

Direct Sulfidation \( \text{CaCO}_3 + \text{H}_2\text{S} \rightleftharpoons \text{CaS} + \text{H}_2\text{O} + \text{CO}_2 \) \( \Delta H_{298K} = 118.7 \text{ kJ/mol} \) (9.3)
Chapter 9 Co-capture of H\textsubscript{2}S and CO\textsubscript{2} in a pressurized-gasifier-based process

Many tests have focused on sulfidation mechanisms and sorbent performance (Efthimiadis and Stotirchos, 1992; Fenouil et al., 1994; Krishnan and Sotirchos, 1994; Fenouil and Lynn, 1995a, b, c; Yrjas et al., 1996; Zevenhoven et al., 1996; 1998; Chauk et al., 2000; García-Labiano et al., 2004). The CaO-H\textsubscript{2}S reaction was found to be fast and to achieve high, or even complete, conversions (Borgwardt et al., 1984; Efthimiadis and Stotirchos, 1992; Fenouil and Lynn, 1995a, c; Chauk et al., 2000), whereas the CaCO\textsubscript{3}-H\textsubscript{2}S reaction is much slower and achieves much lower conversions (Krishnan and Sotirchos, 1994; Fenouil and Lynn, 1995b; Zevenhoven et al., 1998). Although particle-size-dependent, both sulfidation and direct sulfidation have usually been reported to be controlled by product layer diffusion (Fenouil and Lynn, 1995a, b, c; Zevenhoven et al., 1998; Chauk et al., 2000; García-Labiano et al., 2004).

To the best of our knowledge, simultaneous removal of H\textsubscript{2}S and CO\textsubscript{2} has never been explicitly studied before. Recent studies (Sun et al., 2005, 2006; Ryu et al., 2006) on simultaneous SO\textsubscript{2} and CO\textsubscript{2} removal based on a PFBC/calciner process (Shimizu et al., 1999; Abanades et al., 2003) have shown that SO\textsubscript{2} inhibits the reversibility for CO\textsubscript{2} capture. The objective of the current study was to investigate whether H\textsubscript{2}S has a similar deleterious effect on sorbent reversibility in a pressurized gasifier (PG)/calciner process.

9.2. Experimental Details

The pressurized TGA (PTGA) system consists of a Cahn 100 balance of 1 μg precision, a reactor column and a control system. The reactor is made of Inconel 600 alloy, allowing high temperatures and high pressures to be used. The desired gas concentrations were achieved by means of computer controlled of the mass flow controllers. Mixed gases were directed into the reactor from the bottom. The total gas flow rate was normally ~500 ml/min for both calcination and sorption. The PTGA pressure was set by a pressure regulator. A bypass gas line allows
Chapter 9 Co-capture of $H_2S$ and $CO_2$ in a pressurized-gasifier-based process

atmospheric operation. Typical operating temperatures were 850°C for both calcination and sorption.

Strassburg limestone, Arctic dolomite and Kelly Rock limestone were studied. Particles were screened to 212-250 μm except where specified. Table 1.2 shows the chemical analyses for all these sorbents. All runs started with 50±2 mg of fresh sorbent in a platinum sample basket. Strassburg limestone was intensively tested in parametric tests.

The cyclic co-capture test procedure is illustrated in Figure 9.1 for a typical run. After calcination at atmospheric pressure, the reactor was pressurized to the desired level with $N_2$. The $N_2$ stream was quickly replaced by a pre-determined syngas stream containing $CO_2$, $H_2S$, CO, $H_2$ and $N_2$. About 20 s later, sorption started when the syngas front reached the sorbent. A time lag of 20 s was therefore excluded from the timing of all runs. Switching to $N_2$ immediately finished the sorption stage and started the calcination and depressurization. When no further mass change was observed, the next cycle was started.

For each cycle, as shown in Figure 9.1, the mass increase due to $H_2S$ capture was obtained by comparing the mass at the completion of calcination for that cycle with that for the previous cycle. The mass increase due to both $H_2S$ and $CO_2$ capture was derived from the total mass increase during the pressurized sorption stage. Thus calcium utilizations due to $H_2S$ and $CO_2$ could be estimated separately. This method of separating the mass increase due to carbonation and to sulfidation was also used in the “once-through” tests below.

Gasifiers can be operated under various conditions, for example air-, oxygen- or steam-fired; pressurized or atmospheric; and at widely varying temperatures. Thermodynamic calculations by the HSC4 package (Ronie, 1997) show that higher temperatures and lower pressures favour higher equilibrium hydrogen yields. Higher temperatures and higher pressures
are advantageous for tar cracking and solid conversions. For carbonation, lower temperatures and higher pressures are preferable from an equilibrium viewpoint.

In this work, baseline co-capture operating conditions were selected as 850°C and 0.76 MPa. The inlet gas flow rate was controlled by mass flow controllers to obtain a mixture of 1%\(v\) \(\text{H}_2\text{S}\), 20%\(v\) \(\text{CO}_2\), 12.6%\(v\) \(\text{H}_2\), 1.5%\(v\) \(\text{CO}\), with the balance \(\text{N}_2\). \(\text{H}_2\text{S}\) and \(\text{CO}_2\) concentrations were also varied for parametric studies. Over 10%\(v\) \(\text{H}_2\) was added to prevent decomposition of \(\text{H}_2\text{S}\). CO addition was used to prevent the reaction of \(\text{CaS}\) solid product with \(\text{CO}_2\). Oxidation of \(\text{CaS}\) by \(\text{CO}_2\) has been observed at both atmospheric and pressurized conditions, with the final product being \(\text{CaCO}_3\) (Qiu et al., 2001; Anthony et al., 2003). Fenouil and Lynn (Fenouil and Lynn, 1995a) suggested that the \(\text{CO} : \text{CO}_2\) molar ratio should exceed 1% to prevent the \(\text{CaS} - \text{CO}_2\) reaction in the temperature range of 600-900°C. In addition, thermodynamics predict that under the current test conditions, the reverse water-gas shift reaction generates \(\text{H}_2\text{O}\) and \(\text{CO}\).

Chemical equilibrium calculations were also performed for various temperatures at a total pressure of 0.76 MPa for the above initial concentrations, i.e. 1%\(v\) \(\text{H}_2\text{S}\), 12.6%\(v\) \(\text{H}_2\), 20%\(v\) \(\text{CO}_2\), 1.5%\(v\) \(\text{CO}\) and the balance \(\text{N}_2\). The calculated equilibrium \(\text{CO}_2\) partial pressure is about 14%\(v\) for 700°C, and 12%\(v\) for 850°C. Equilibrium predictions show that a maximum of 0.05%\(v\) \(\text{COS}\) is expected, with the majority of sulfur existing as \(\text{H}_2\text{S}\). Neither decomposition of \(\text{H}_2\text{S}\) nor oxidation of \(\text{CaS}\) was appreciable for the current tests.

During cyclic co-capture tests, the sorption time was 3 minutes, except for one test where it was 8 minutes.
Chapter 9 Co-capture of H\textsubscript{2}S and CO\textsubscript{2} in a pressurized-gasifier-based process

9.3 Results and Discussion

9.3.1 "Once-through" tests.

Before the cyclic co-capture tests, a set of tests, denoted "Once-through tests", was conducted with 50±2 mg Strassburg limestone to evaluate the relative importance of different reactions. These tests included sulfidation with no CO\textsubscript{2} present, carbonation with no H\textsubscript{2}S present, and a set of duplicate co-capture tests stopped at varying times. All tests were performed at 850°C and 0.76 MPa. Gas concentrations were maintained as similar as possible to those in the baseline co-capture run. For example in the "no CO\textsubscript{2} present" test, a mixture of 1%v H\textsubscript{2}S, 12.6%v H\textsubscript{2}, 1%v CO, with the balance N\textsubscript{2}, was introduced so that all reactive components remained the same as in the co-capture tests, except for the absence of CO\textsubscript{2}. Similarly for the "no H\textsubscript{2}S present" test, the H\textsubscript{2}S portion was replaced by pure N\textsubscript{2}.

The calculated conversions based on mass changes are plotted in Figure 9.2. Co-capture slowed down CO\textsubscript{2} capture to some degree, especially before the carbonation reached a near-plateau (slower stage). The carbonation portion of the co-capture, stopped at 3, 9, 30 and 60 minutes, gave lower conversions of CaO to CaCO\textsubscript{3} than for continuous CO\textsubscript{2} capture with no H\textsubscript{2}S present. For the sulfidation portion, prolonged co-capture resulted in a similar extent of sulfidation as for continuous sulfidation with no CO\textsubscript{2}. In our high-pressure measurements, the sulfidation reaction does not appear to have been as fast as for atmospheric studies described in previous work (Borgwardt et al., 1984; Efthimiadis and Stotirchos, 1992; Agnihotri et al, 1999; Chauk et al., 2000). García-Labiano et al.(2004), Agnihotri et al. (1999) and Hu et al. (2006) found that increasing total pressure, with the volume fraction of H\textsubscript{2}S held constant, decreased the sulfidation rate, likely because of the decrease in effective diffusivity in the product layers (García-Labiano et al., 2004).
Chapter 9 Co-capture of $H_2S$ and $CO_2$ in a pressurized-gasifier-based process

A significant observation is that, unlike results for SO$_2$/CO$_2$ co-capture (Sun et al., 2006), direct sulfidation, i.e. reaction (9.3), played little role, even with the sorption time extended well beyond the slow stage of carbonation. The evidence for this is that no appreciable consumption of carbonate was found after 60 minutes duration. This probably occurred because direct sulfidation of limestone (CaCO$_3$) is much slower than sulfidation of calcined limestone (Fenouil and Lynn, 1995a; b; Yrjas et al., 1996) (i.e. CaO), so that an increase in total pressure would further decrease the direct sulfidation rate by decreasing the effective diffusivity in the product layer (García-Labiano et al., 2004; Hu et al., 2006). In contrast, direct sulphation, in previous co-capture studies of SO$_2$ and CO$_2$ under excess oxygen conditions (Sun et al., 2006), became dominant during the slow stage of carbonation, consuming carbonate and causing rapid decay in carbonation during cycling.

Figure 9.2 shows no sign of a decrease in the extent of sulfidation after the slow stage of carbonation. Sulfidation is known to be solid-state diffusion-controlled reaction (Borgwardt et al., 1984; Fenouil and Lynn, 1995a; Zevenhoven et al., 1996; Chauk et al., 2000). Borgwardt et al. (1984) and Chauk et al. (2000) proposed that the diffusing ions are O$^2-$ and S$^{2+}$. In this case, the ions have to permeate through two product layers (CaCO$_3$ and CaS) to reach either reactive CaO sites or the bulk sorbent. Comparing the co-capture with continuous sulfidation where no CO$_2$ was present suggests that the effective diffusivity for the sulfidation portion of the co-capture was similar to that for continuous sulfidation with no CO$_2$ present. Given that CaCO$_3$ only serves as a porous network to diffusing ions and that CaO sulfidation is product-layer-controlled (Borgwardt et al., 1984; Fenouil and Lynn, 1995a; Zevenhoven et al., 1996; Chauk et al., 2000), the diffusion resistance in the CaS layer is larger than that in carbonate layer so that the mobility of ions diffusing through CaCO$_3$ plus CaS is similar to that where they diffuse through CaS alone. This is probably related to the sintering of CaS at high temperatures.
Chapter 9 Co-capture of H₂S and CO₂ in a pressurized-gasifier-based process

Zevenhoven (1998) and Fenouil and coworkers (1994, 1995a) showed that CaS sintering could be the major factor accounting for the slower sulfidation at high temperatures, e.g. at 850°C.

9.3.2 Parametric tests

A series of parametric studies was carried out on Strassburg limestone. The first parameter varied was the H₂S/CO₂ molar ratio. Figure 9.3 shows the cyclic performance for the baseline run and the effect of changing both P_{CO₂} and P_{H₂S}, with a cycle time of 3 minutes for the sorption stage.

General features of the co-capture were first studied by comparing the baseline co-capture run (20% CO₂, 1% H₂S, 12.6% H₂, 1.5% CO, balance N₂) and its counterpart without any H₂S present (i.e. 20% CO₂, 12.6% H₂, 1.5% CO, balance N₂). In the test with no H₂S present, a time of 3 minutes was sufficient to reach the slow stage of carbonation. Changing the partial pressure of CO₂ from 8% to 20% had little influence on the final carbonation conversion for each cycle, and hence on the reversibility of sorbents during cycling without H₂S, provided that the fast stage of carbonation was complete and that P_{CO₂} was well in excess of the equilibrium P_{CO₂}, which is around 50 kPa at 850°C. Thus the test with no H₂S present also provided a baseline for comparison of runs with different inlet H₂S and/or CO₂ concentrations.

Figure 9.3a shows that the reversibility based on total Ca further decreased during co-capture compared to the test with no H₂S present. However, the additional decay was limited compared with sulphation for co-capture of CO₂/SO₂ (Chapter 5 or Sun et al., 2005). Shown in Figure 9.3a for the run with 20% CO₂ and 1% H₂S, a deliberately prolonged 16th cycle demonstrated that the sorbent still had good ability to react further with CO₂.

Under current test conditions, high conversions of CaO to CaS could be achieved, as revealed by Figure 9.3c. CaO conversions were also re-plotted based on free CaO, i.e. excluding the portion utilized for sulfidation. Figure 9.3b shows that on this basis, CaO retained
Co-capture of $H_2S$ and $CO_2$ in a pressurized-gasifier-based process

reversibility at a level only slightly less than that in the No $H_2S$ tests during cycling, when also capturing $H_2S$. This reversibility is regarded as favourable because the capture-ability of natural sorbents is almost retained. In the following discussions, all cyclic performance is assessed based on free lime content. The close-to-$H_2S$-free performance also suggests that the cumulative CaS layer did not appreciably reduce cyclic $CO_2$ capture. Below it is shown that a CaS layer slowed carbonation, but the reduction in the achievable extent of carbonation for each cycle was not appreciable after the first few cycles.

An important finding is that the $CO_2$ removal performance observed in this study was much better than in our previous sulphation study where, under oxidizing conditions, $SO_2$ was found to seriously impede $CO_2$ co-capture (see Sun et al., 2005; 2006 or Chapters 5 and 6). The most probable reason is that CaS (molar volume 29 cm$^3$/mol) has a much lower molar volume than CaSO$_4$ (46 cm$^3$/mol), whereas carbonate product (CaCO$_3$) has a molar volume of 36.9 cm$^3$/mol. All are larger than the molar volume of CaO (17 cm$^3$/mol), suggesting that some swelling does occur for all three reactions involving CaO, i.e.: sulphation, carbonation and sulfidation. However the sulphate product is significantly less porous, resulting in much lower effective diffusivity. As a result, sulphation produces premature blocking for sorbents, especially for pore mouth diameters in the range of 10-100 nm (Gullett and Bruce, 1987; Stouffer and Yoon, 1989). Given the smaller molar product volume, sulfidation is less likely to suffer from plugging of pores than sulphation. SEM images in Figure 9.4 show major differences in surface texture for a $H_2S/CO_2$ run (Figure 9.4a) compared with a $SO_2/CO_2$ run (Figure 9.4b) for the same temperature and similar gas concentrations, but a different total pressure. The calcine from the $H_2S/CO_2$ test shows a much more porous surface than its $SO_2/CO_2$ counterpart, due to the difference in molar volumes of the solid products. Therefore, during co-capture, the difference
in product layer compactness for sulphate and sulfide, produced very different degrees of inhibition for parallel carbonation and subsequent calcination.

Conversion of CaO to CaS over 15 cycles is plotted on a cumulative time basis in Figure 9.3c and compared with a test with similar conditions, but with no CO₂ present (the baseline). The sulfidation performance for cyclic co-capture was much higher than for continuous sulfidation with no CO₂ present. EDX sulphur-mapping in Figure 9.5 proves that continuous sulfidation results in unreacted cores, whereas for cyclic co-capture, the sulphur penetrated more deeply into the interior of the particles.

9.3.3 Effect of CO₂ and H₂S Partial Pressures

To further elucidate the effect of varying P_{CO₂} and P_{H₂S}, it is helpful to study the kinetic dependence on these partial pressures. Although the sorption stage involved multiple reactions and mass transfer limitations, apparent rates can be compared, because all runs started with the same sample size. The first and the fifth cycles for relevant co-capture runs are compared in Figure 9.6 with the corresponding test where there was no H₂S present.

In Figure 9.6a, it is seen that addition of H₂S slowed down the sorption process markedly. Whereas 3 minutes were sufficient to finish the fast stage of carbonation without H₂S present, the mass climbed much more slowly and did not level off after 3 minutes when sulfidation was occurring in parallel. Sulfidation apparently either reduced the availability of CaO for the subsequent carbonation or added more diffusion resistance, retarding the carbonation. Increasing the CO₂ mole fraction from 20 to 40% speeds up carbonation. Kyaw et al. (1996) showed that increasing P_{CO₂} well beyond its equilibrium level (~ 50 kPa at 850°C) did not increase the intrinsic carbonation rate, so that this accelerated carbonation is probably mainly due to enhanced intraparticle and interparticle mass transfer. It is notable that the apparent sorption rates shown here mostly reflect carbonation kinetics because carbonation is much faster than
sulfidation as indicated in Figure 9.2. Figure 9.6b shows that the relative difference between runs with varying operating conditions in the first cycle persist at the fifth cycle, but the mass increases due to carbonation over the 3-minute sorption period are similar, i.e. the presence of H$_2$S did not affect the achievable extent of carbonation as much as in the first cycle. This is because the capture capacity is limited by the changes of sorbent properties during cycling, e.g. sintering reduced the ability to capture CO$_2$, and because some CaO has been consumed by sulfidation during previous cycles.

Figure 9.3 portrays the effect of increasing partial pressure of CO$_2$ on cyclic co-capture performance. Figures 9.3a and 9.3b show that increasing P$_{CO2}$ from 20 to 40%v improved carbonation for the first few cycles, but the improvement disappeared upon further cycling. Sulfidation, however, was seen to decrease markedly in Figure 9.3c. As discussed above, based on the evidence in Figure 9.6, it is believed that increased CO$_2$ can accelerate carbonate formation for all cycles. As a result, the CaO-H$_2$S reaction was slowed either because of increased mass transfer resistance due to the CaS layer or because of the reduced availability of CaO. From the observation that, relative to the baseline continuous sulfidation with no CO$_2$ present, 20%v P$_{CO2}$ enhanced sulfidation, but the enhancement decreased when P$_{CO2}$ was increased to 40%v, it can be deduced that there should be an optimum P$_{CO2}$ for maximum sulfidation. The optimum occurs probably because calcination/carbonation enhances sulfidation by periodically exposing highly-reactive CaO sites to H$_2$S, but the enhancement is counteracted by a faster-growing carbonate layer with increasing P$_{CO2}$.

Increasing P$_{H2S}$ from 0 to 0.5% greatly slowed carbonation rates, as seen in Figure 9.6. This retarding effect only lasted for the first few cycles and had little influence on the extent of cyclic CO$_2$ capture after further cycling, as seen in Figure 9.3c. A further increase in P$_{H2S}$ from 0.5 to 1% had a much smaller effect. These results indicate that sulfidation reduced rates of carbonation
mainly by competitively occupying CaO sites. The CaS layer did not appear to be a major barrier retarding carbonation since the test for free lime (excluding the sulphide part) gave results very similar to that without H₂S in Figure 9.3c. Also shown in Figure 9.3c, the cyclic extent of sulfidation increased slightly with an increase of P_{H₂S} from 0.5 to 1%, with 20% CO₂ present, due to the increased driving force for sulfidation.

The total calcium utilization in Figure 9.3d, obtained by summation of the free-CaO conversion to CaCO₃ and that to CaS, showed little decrease with cycling for the tests with various CO₂ and H₂S partial pressures. This is unlike the sulphation for SO₂/CO₂ (Chapter 5), where there was a sharp decline in the total calcium utilization.

9.3.4 Effect of temperature

Gasifiers can be operated at lower temperatures than combustors. Lower temperatures are advantageous for in-situ carbonation, provided that the desired gas compositions can be obtained. Since the water-gas-shift reaction is exothermic, CO₂ concentrations also tend to be high at lower temperature. With a high molar ratio of CO₂ to H₂S in a gasifier, it may be desirable to achieve a higher extent of carbonation while deliberately limiting the extent of sulfidation. Control of temperature provides a means of optimizing the fractional sorbent utilization for CO₂ and H₂S.

Figure 9.7 shows cyclic performance results for 700°C sorption conducted to compare with the base run at 850°C, with all calcinations performed at 850°C. The mass breakthrough histories during sorption for the selected cycles (first and fifth) at 700 and 850°C are also compared in Figure 9.6. Much faster sorption (mainly due to enhanced carbonation) can be observed for the lower temperature, with the rates and the achievable mass increases between the two temperatures narrowing markedly by the fifth cycle. As discussed above, the narrowing is due to the limitation of capture capacity. For further cycling, more narrowing must occur, so that the
cyclic performance shown in Figure 9.7a gave similar results for the two temperatures except for the first two cycles. Figure 9.7b, however, confirms that the lower temperature led to much lower conversions of CaO to CaS, presumably either because of a change in sulfidation kinetics, or because of a faster-growing carbonate layer favoured by lower temperatures. The wider difference for sulfidation extents and close approach of the carbonation extents for the two temperatures, suggest that the variation of thickness of the CaS product layer did not appreciably affect cyclic carbonation performance, as long as the slower portion of carbonation process (see Figure 9.2) could be attained during each sorption cycle.

9.3.5 Effect of particle size

The effect of particle size is shown in Figure 9.8. For most runs, 50±2 mg of sample was used for the 212-250 μm particles, but for the 38-45 μm particles, this was found to exceed the capacity of the basket due to the different bulk density for a closed packing, so only 23 mg were used in this test. Compared to the baseline run for the 212-250 μm particles, a slightly faster decay in CO$_2$ capture was found in Figure 9.8a for the finer material. On the other hand, there was a marked enhancement of CaO conversion to CaS, as shown in Figure 9.8b. This indicates that intraparticle diffusion played an important role during sulfidation, consistent with the conclusion from a previous high-pressure sulfidation study (Garcia-Labiano et al., 2004). Our findings are also consistent with a previous report that sulfidation is very sensitive to particle size (Efthimiadis and Stotirchos, 1992). For carbonation, on the other hand, the influence of particle size is minor as the cyclic calcium utilization is likely limited by sintering-related pore structural changes at the surface. Despite the much-enhanced H$_2$S removal, the increasing CaS layer did not hinder carbonation appreciably, as discussed above. Compared to the findings for SO$_2$/CO$_2$ co-capture (Chapters 5 and 6), the CaS layer is much more permeable than a CaSO$_4$
Chapter 9 Co-capture of H₂S and CO₂ in a pressurized-gasifier-based process

layer for carbonation. Due to the enhanced H₂S capture, the total calcium utilization achieved a relatively high level after 15 cycles as shown in Figure 9.8c. Note, however, that due to the irreversible nature of the sulfidation, over-sulphided sorbent would have limited ability to capture CO₂.

9.3.6 Effect of residence time

To simulate the effect of residence time on the reversibility, a run with an 8-minute sorption time was carried out, with the sorption time being the only quantity varied compared to the baseline co-capture run. Extension of the sorption time would necessarily result in higher conversions, as can be readily seen in the once-through test. During co-capture, as found in Figure 9.9a, the higher conversion for CaO to CaCO₃ only occurred for the first few cycles. The extended sorption time offered negligible enhancement of CO₂ removal after further cycling, probably because carbonations extended beyond 3 minutes are predominantly in the slower stages. A 9th cycle deliberately extended to 20 minutes still showed unrealized carbonation and sulfidation capacity, as shown in Figures 9.9a and 9.9b. In Figure 9.9b, it is found that cumulative sulfidation with 8 minutes of exposure for each cycle and 20 minutes for the 9th cycle gave a conversion similar to that for a large number of 3-minute runs having the same cumulative time. It appears that when after calcination, when fresh CaO is cyclically exposed to gaseous reactants, sulfidation and carbonation occur simultaneously, but carbonation reaches a much slower stage after ~ 3 minutes, whereas sulfidation maintains a nearly unchanged rate until the next calcination reactivation step, in spite of the increase in sorption time from 3 to 8 minutes.

9.3.7 Effect of total pressure

Changing the total pressure of the reactor from 0.76 to 1.7 MPa accelerated the mass uptake, mostly due to enhanced carbonation during each cycle, as shown in Figure 9.6 for both the first and the fifth cycles. The change presumably resulted from both enhanced external CO₂
mass transfer and more favourable intraparticle mass transfer. However, the higher conversions to carbonate only applied to the first few cycles. The achievable conversions of calcium to carbonate remain similar to those for a total pressure of 0.76 MPa as seen in Figure 9.10a. As discussed above, with further cycling, the carbonation conversion would ultimately be limited by the achievable carbonation when it reaches the slower stage of carbonation, regardless of how much the rate of carbonation was enhanced. Figure 9.10b shows, however, that less H$_2$S was captured at the higher pressure, especially after 5 cycles. As noted above, increasing the total pressure decreases the sulfidation rate (Agnihotri et al., 1999; García-Labiano et al., 2004; Hu et al., 2006). Enhanced carbonation could be another factor slowing down the sulfidation. The net effect of the two reactions is that the total calcium utilization was only a little lower at 1.7 MPa than at 0.76 MPa.

9.3.8 Effect of sorbent type

The cyclic performances for Arctic dolomite and Kelly Rock limestone are compared with that of Strassburg limestone in Figure 9.11. All sorbents showed much-reduced CO$_2$ capture ability, especially for the first few cycles, compared to corresponding tests where there was no H$_2$S. The H$_2$S in the mixed gas decreased the rate of carbonation, with the greatest decay being experienced by the most reactive sorbents, namely Arctic dolomite, which has been found to be more reactive in the initial cycles for both sulphation and carbonation, due to its well-preserved surface pore structure and surface area (see Chapters 5 and 6). Cyclic performance for all sorbents could approach the baseline for tests with no H$_2$S. The Arctic dolomite gave more conversion than the other two sorbents, both in terms of CO$_2$ capture and sulphur retention.

Figure 9.12 compares the textures of calcines for the Arctic dolomite and Kelly Rock limestone. Figure 9.4a for Strassburg calcines indicates that all sorbents showed porous surfaces, differing greatly from the surfaces observed previously for SO$_2$/CO$_2$ capture tests (see Chapter 6).
Chapter 9 Co-capture of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) in a pressurized-gasifier-based process

The macropores for the Strassburg limestone suggest more sintering than for the Arctic dolomite. The Kelly Rock limestone appears to be grainier, containing more pore volume between grains; it probably sinters in a similar matter to the Strassburg limestone.

Sulphur-mapping in Figure 9.13 for Arctic dolomite and Kelly Rock limestone, in combination with Figure 9.5b for Strassburg limestone at the same test conditions, shows dispersed sulphur distributions for all three sorbents, despite the evidence that more sulphur is distributed on the outer area of grains or particles. As discussed above, cyclic operation could enhance \( \text{H}_2\text{S} \) capture by cyclically exposing fresh \( \text{CaO} \) to \( \text{H}_2\text{S} \).

9.3.9 Cycled sorbents in sulfidation

A gasifier could be integrated with a steam reformer operating with sorption-enhancement by a calcium-based sorbent. The highly cycled sorbent discharged from a downstream separate reformer could then be used as a sorbent for \( \text{H}_2\text{S} \) capture in the gasifier. Removal of \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) would then be performed in two separate reactors. In the final test, Strassburg limestone particles after 15 cycles of carbonation and calcination at 850°C and 0.76 MPa were sent to be sulphidized under the same condition as in the sulfidation test with no \( \text{CO}_2 \). The results (not plotted here) showed almost no difference between fresh Strassburg limestone and its cycled calcines. As cycling between calcination and carbonation is known to decrease the surface area and total pore volumes of the sorbents and to shift pores to larger sizes (see Chapter 4), this test indicates that sulfidation is not very sensitive to change of either of these properties. This may arise because the \( \text{H}_2\text{S}-\text{CaO} \) reaction is product-layer controlled, but with a high enough effective diffusivity that it is less sensitive to change in pore structure.

In a practical process, sorbent may experience hundreds or thousands of cycles. Therefore the results shown in this work, mostly based on 15 cycles, are not enough to represent a practical situation. However, as shown above in this chapter, in Chapter 6 and in some previous work and
Chapter 9 Co-capture of \( H_2S \) and \( CO_2 \) in a pressurized-gasifier-based process

(Shimizu et al., 1999; Alvarez and Abanades, 2005), the most severe decay in reversibility occurs during early cycles. Extended continuous fluid reactor studies are needed before practical long-term processes can be designed and executed with confidence.

9.4 Conclusions

Simultaneous capture of \( CO_2 \) and \( H_2S \) was studied under simulated gasification conditions for three calcium-based sorbents. The reversibility of sorbents was nearly as good as for cases where no \( H_2S \) was present, especially for limestone sorbents. Cyclic sulfidation led to higher extents of sulphur retention than continuous sulfidation with no \( CO_2 \) present. In a practical system, the sulfidation will not increase the sorbent required for the \( CO_2 \) capture very much, given the high stoichiometric ratio of carbon to sulphur in most fuels.

Varying the reactant gas concentrations not only affected the physical limitations, but also caused complex interactions between solid product layers and solid-state diffusion. Parametric studies indicated that the effect of sulfidation on cyclic carbonation was usually weak. However, \( H_2S \) competes with \( CO_2 \) for fresh CaO, so that a higher extent of sulfidation is not helpful in achieving good \( CO_2 \) capture. Faster carbonation usually reduced the extent of sulfidation by tying up free Ca. Because of the weak effect of \( H_2S \), co-capture of \( CO_2 \) and \( H_2S \) in a gasifier appears to be much less problematic than co-capture of \( CO_2 \) and \( SO_2 \), examined in our previous work.
Chapter 9 Co-capture of $H_2S$ and $CO_2$ in a pressurized-gasifier-based process

Figure 9.1 Illustration of operating procedure and masses used to calculate of calcium utilization for $CO_2$ and $H_2S$ capture. Co-capture at 850°C and 0.76 MPa. Calcination: in 100% $N_2$. Sorption: 1%v $H_2S$, 20%v $CO_2$, 12.6%v $H_2$ and 1.5%v CO with the balance $N_2$. 

235
Chapter 9 Co-capture of $H_2S$ and $CO_2$ in a pressurized-gasifier-based process

Figure 9.2 Once-through tests with 212-250 μm Strassburg limestone. Initial calcination at 850°C and 101 kPa with 100% $N_2$. Co-capture at 850°C and 0.76 MPa with 1%v $H_2S$, 20%v $CO_2$, 12.6%v $H_2$ and 1.5%v $CO$, balance $N_2$. Carbonation with no $H_2S$: same as for co-capture tests except with no $H_2S$. Sulfidation with no $CO_2$: same as co-capture tests except with no $CO_2$. 
Chapter 9 Co-capture of H₂S and CO₂ in a pressurized-gasifier-based process
Chapter 9 Co-capture of $H_2S$ and $CO_2$ in a pressurized-gasifier-based process

(a) After 15 cycles of $H_2S$ and $CO_2$ capture
(b) After 15 cycles of $SO_2$ and $CO_2$ capture

Figure 9.4 High-resolution SEM photos of co-capture 212-250 μm Strassburg limestone calcines: (a) $H_2S$ and $CO_2$ capture in 1%v $H_2S$, 20%v $CO_2$, 12.6%v $H_2$, 1%v $CO$, balance $N_2$ at 0.76 MPa, 3 min sorption for each cycle. (b) $SO_2$ and $CO_2$ capture in 1125 ppmv $SO_2$, 8%v $CO_2$, 3%v $O_2$ and balance $N_2$ at 1.8 MPa, 4 min of sorption for each cycle. Sorption and calcination temperatures for both cases were 850°C. All calcinations in 100% $N_2$.

(a) Calcine from 1 h continuous sulfidation at 850°C, 0.76 MPa with 1%v $H_2S$, 12.6%v $H_2$, 1.5%v $CO$, balance $N_2$ (no $CO_2$). (b) Calcine from cyclic $H_2S$/CO$_2$ sorption for 15 cycles at 850°C, 0.76 MPa with 1%v $H_2S$, 20%v $CO_2$, 12.6%v $H_2$, 1.5%v $CO$, balance $N_2$; Calcination at 850°C and 101 kPa with 100% $N_2$; 3 min for each sorption stage.

Figure 9.5 EDX sulfur mapping for 212-250 μm reacted Strassburg limestone. (a) Calcine from 1 h continuous sulfidation at 850°C, 0.76 MPa with 1%v $H_2S$, 12.6%v $H_2$, 1.5%v $CO$, balance $N_2$ (no $CO_2$). (b) Calcine from cyclic $H_2S$/CO$_2$ sorption for 15 cycles at 850°C, 0.76 MPa with 1%v $H_2S$, 20%v $CO_2$, 12.6%v $H_2$, 1.5%v $CO$, balance $N_2$; Calcination at 850°C and 101 kPa with 100% $N_2$; 3 min for each sorption stage.
Chapter 9 Co-capture of $H_2S$ and $CO_2$ in a pressurized-gasifier-based process

![Figure 9.6 Mass changes during first and fifth cycles of $H_2S/CO_2$ capture tests. 212-250 μm Strassburg limestone. Tests conditions except where specified: sorption at 850°C and 0.76 MPa with 20% $CO_2$, 1%$H_2S$, 12.6%v $H_2$, 1%v $CO$, balance $N_2$. 850°C; Calcination at 850°C and 101 kPa with 100% $N_2$. 3 minutes for each sorption stage.](image-url)
for each sorption cycle

Figure 9. Effect of changing temperature on cyclic capture of H,S and CO, and CaO. 212-250 pm Strassburg lime stone. Sorption at 0.76 MPa, all with 20\% CO, 12.6\% H2, 1.9\% CO, balance N2. Calcination at 850°C and 101 kPa with 100\% N2, 3 min.

(e) Total calcium utilization

Number of reaction cycles

0
10
20

0
10
20

Moles of H2S retained/moles of total Ca

Moles of CO2 retained/moles of free Ca

Number of reaction cycles

0
10
20

0
10
20

Calcination to CaO

Calcination to CaSO4

Calcination to CaSO4
Chapter 9 Co-capture of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) in a pressurized-gasifier-based process

![Graph 1: Total calcium utilization vs. Number of reaction cycles for different particle sizes.](image1)

![Graph 2: Moles of \( \text{H}_2\text{S} \) retained/moles of total Ca vs. Number of reaction cycles for different particle sizes.](image2)

![Graph 3: Moles of \( \text{CO}_2 \) retained/moles of free Ca vs. Number of reaction cycles for different particle sizes.](image3)
Figure 9.9 Effect of cyclic sorption on cyclic capture of H₂S and CO₂. 212-220 mm stainless-steel limestone sorption at 850°C and 0.76 MPa with 20% CO₂, 12% H₂S, 6% H₂, 1% CO, balance N₂. Calculation at 850°C and 101 kPa, with 100% N₂. 3 min for each.

(q) CaO conversion to CaS

(a) CaO conversion to CaCO₃

Cumulative sorption time (min)

Moles of H₂S retained/moles of total Ca

Number of reaction cycles

Moles of CO₂ retained/moles of free Ca
Chapter 9 Co-capture of H\(_2\)S and CO\(_2\) in a pressurized-gasifier-based process

1% H\(_2\)S, 12.6% H\(_2\), 19% CO, balance N\(_2\). Calcination at 850°C and 101 kPa with 100% N\(_2\). 3 min for each sorption stage.

Figure 9.10: Effect of total pressure on cyclic capture of H\(_2\)S and CO\(_2\). 212-250 Jm Strasserburg limestone. Sorption at 850°C, with 20% CO\(_2\).

(b) CaO conversion to CaS

(a) CaO conversion to CaCO\(_3\)

Number of reaction cycles

Moles of H\(_2\)S retained/moles of total Ca

Moles of CO\(_2\) retained/moles of free Ca
Figure 9.11 Effect of sorbent type on cyclic capture of H$_2$S and CO$_2$. 212-250 μm. Sorption at 850°C and 0.76 MPa, with 20% CO$_2$, 1% H$_2$S, 12.6%v H$_2$, 1%v CO, balance N$_2$. Calcination at 850°C and 101 kPa with 100% N$_2$. 3 min for each sorption stage.
Chapter 9 Co-capture of H₂S and CO₂ in a pressurized-gasifier-based process

Figure 9.12 SEM photos for different sorbents after 15 co-capture cycles. Same test conditions as for Figure 9.10. (a) Arctic dolomite (b) Kelly Rock limestone

Figure 9.13 Sulfur mapping for calcines of different sorbents after co-capture. Same test conditions as for Figure 9.10. (a) Arctic dolomite after 15 cycles. (b) Kelly Rock after 15 cycles.
CHAPTER 10 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

10.1 Conclusions

Calcium-based sorbents for the capture of CO₂ capture were investigated in this thesis, covering topics ranging from reaction kinetics to application in combustors or gasifiers, the mechanism of simultaneous CO₂ and SO₂ removal, attempts to improve sorbent reversibility and alternative techniques for cyclic removal of CO₂.

The major conclusions drawn in this thesis work are:

(1) Kinetic study of the CaO-CO₂ reaction found that the reaction rate is first-order with respect to \((P_{CO₂}-P_{CO₂,eq})\), for \((P_{CO₂}-P_{CO₂,eq}) \leq 10 \text{ kPa}\). The order abruptly changes to zero when \((P_{CO₂}-P_{CO₂,eq}) > 10 \text{ kPa}\). Atmospheric pressure TGA results were supported by pressurized PTGA results. A possible explanation is that the intermediate complex CaO•CO₂ becomes immediately saturated on CaO sites when the CO₂ driving force exceeds 10 kPa, and the reaction rate then becomes determined by the rate of formation of CaCO₃ through surface reaction from the complex. Based on the data obtained from the zero-order region, the activation energies were found to be 29 ± 4 kJ/mol and 24 ± 6 kJ/mol for Strassburg limestone and Arctic dolomite, respectively.

(2) Experimental data obtained in both atmospheric and pressurized thermogravimetric reactors indicate that carbonation is insensitive to the CO₂ partial pressure in terms of final conversion and apparent carbonation rate. There is a need to predict the carbonation history using a structural model. However, normal structural gas-solid models, such as the grain model and random pore model cannot predict the entire carbonation history. Previous experimental observations for this reaction (Abanades and Alvarez, 2003;
Chapter 10 Conclusions and recommendations for future work

Alvarez and Abanades, 2005a) showed that the reaction is highly dependent on pore size distribution. A new reaction model was formulated based on discrete-pore-size-distribution. This model utilizes measured rate constant and measured pore size distribution data as input. The effective diffusivity in the product layer is the only fitting parameter, dependent on the evolution of the pores. The model is able to predict atmospheric and pressurized thermogravimetric reactor carbonation data with fitted activation energies of 215 and 187 kJ/mol for the limestone and dolomite tested.

3) Sorbent reversibility, or sorbent cyclic CO₂ removal ability during calcination/carbonation cycling, is of critical importance for practical application of calcium-based sorbents. The decay in the reversibility of limestones has been found (Salvador et al., 2003; Alvarez and Abanades, 2005a) to be almost independent of reactor type and operating conditions. Similar results were found in our experiments in both an atmospheric pressure TGA unit and an atmospheric pressure thermogravimetric reactor (Chapters 4 and 6). In Chapter 4, a detailed study was conducted showing the evolution of limestone pore size distribution during calcination/carbonation cycling. It was found that when the fast stage of carbonation is completed during each cycle, sintering occurs mostly during the calcination stage. Periodic calcination causes a much higher degree of sintering than holding samples under calcination condition for the same cumulative time because the cyclic release of CO₂ during calcination enhances sintering. The evolution of pore size distribution during calcination/carbonation cycling shows that <~220 nm pores shrink, limiting the achievable conversion for the next fast stage of carbonation. A simultaneous calcination and sintering model was formulated based on a simple description of pore evolution, consistent with experimental evidence. The model can satisfactorily explain the experimental data. It correctly predicts that cyclic CO₂ capture
is not very sensitive to the particle size, sample size and operating conditions. Extrapolation of long-term cycling results predict residual CO$_2$ capture ability of ~2-3% after 1000 cycles.

(4) Because the molar ratio of carbon to sulfur in conventional fuels, e.g. coal, is usually high, e.g. >50, it has commonly been assumed that the calcium oxide needed for SO$_2$ capture accounts for an insignificant fraction of the sorbent for CO$_2$ removal. Strassburg limestone and Arctic dolomite were investigated in an atmospheric pressure thermogravimetric reactor for co-capture of SO$_2$ and CO$_2$ at fluidized bed combustion temperatures, e.g. 850°C. A high partial pressure of CO$_2$ (80%v) had to be maintained to make carbonation favourable. It was found that the sorbent cyclic performance for CO$_2$ removal was appreciably impeded by the presence of SO$_2$, even though the CO$_2$ concentration was much higher than the SO$_2$ concentration. Parametric studies indicated that the impeding effect is sensitive to such factors as temperature, CO$_2$ and SO$_2$ concentrations, particle size and reaction time. Whereas SO$_2$ inhibits the capture of CO$_2$, carbonation was found to enhance the capture of SO$_2$. The calcination rate was also observed to decrease as a result of the presence of the sulphate layer which forms during cyclic co-capture.

(5) To further investigate the co-capture of SO$_2$ and CO$_2$, five limestones and two dolomites were tested at both atmospheric and elevated pressure, with a maximum total pressure up to nearly 2.4 MPa. When no SO$_2$ was present, the limestones performed similarly in terms of sorbent reversibility, and dolomites performed better. Conversions decayed more rapidly when SO$_2$ was present for all sorbents. Direct sulphation became dominant after completion of an initial fast stage of carbonation, filling larger pores by sulphation from the outside, enveloping the sorbents with an impermeable shell, inhibiting further
carbonation and retarding subsequent calcination. Of the various attempts to improve sorbent reversibility, increasing the CO₂ partial pressure was most helpful.

(6) In Chapter 7, tests with steam, CO and modified sorbents led to the following conclusions: (i) Steam addition during carbonation did not improve sorbent reversibility when no SO₂ was present, but helped somewhat for CO₂/SO₂ co-capture tests. One-time hydration of calcined limestone improved CO₂ removal to some degree with or without SO₂ present. (ii) Calcination in a steam environment did not appreciably enhance sorbent sintering. Steam and water hydration were unable to reactivate partially carbonated sorbents to give higher extents of carbonation. (iii) Use of low-temperature steam or liquid water to reactivate highly cycled sorbent can improve CO₂ removal. Periodic hydration of highly cycled sorbents can lead to some improvement in reversibility. Steam/water hydration was also found to be effective during cyclic CO₂ and SO₂ co-capture by breaking sulphate layer. (iv) Use of CO to cyclically regenerate CaO from CaSO₄ did not give good results because the regeneration of CaSO₄ is very slow since the CO concentration has to be maintained at a low level to obtain CaO, rather than CaS, as the by-product. (v) Using inerts to modify natural limestone was unsuccessful, except that a 1:1 molar CaO:Al₂O₃ mixture showed good reversibility, but low CO₂ capture capacity.

(7) Given that co-capture of SO₂ and CO₂ was found to be difficult because SO₂ severely impeded CO₂ removal, four FBC-based processes were investigated as possible means of sequentially capturing SO₂ and CO₂. Test results at low and high pressure indicate that the best option involved highly cycled limestones as SO₂-sorbents in atmospheric FBC combustors after many cycle of CO₂ capture. Highly sintered limestone remains a good
Chapter 10 Conclusions and recommendations for future work

sorbent for SO2 because of the generation of macropores during calcination/carbonation cycling.

(8) An alternative route for CO2 capture based on calcium sorbent was investigated in which the sorbent is applied to fossil fuel gasification, with CO2 removed in situ in the gasifier. Appropriate operating conditions can be chosen to produce a hydrogen-rich syngas stream in a single step. The sorbent performance was investigated with H2S present in a pressurized TGA system. The results contrasted sharply with those under oxidizing condition with SO2 and CO2 present. No obvious inhibition was found on sorbent performance due to the presence of H2S. Parametric studies, on the effect of particle size, sorption time, total pressure, temperature and partial pressure of CO2 and H2S and sorbent type showed complex interactions between the solid product layers and diffusing ions. The results generally indicate that co-capture of H2S and CO2 is feasible. Combining the results for sorbent performance with thermodynamic considerations (covered in Chapter 1) shows that one-step hydrogen production from gasification should be achievable.

10.2 Recommendations for future work

(1) In Chapter 7, preliminary sorbent modification work demonstrated that improving sorbent reversibility using additives is possible, but at the penalty that sorbent removal capacity decreased. Sorbent modification is a complex topic, more research effort is still needed to develop more stable sorbents. Due the sensitivity of sorbent performance to the preparation procedure, a standardized preparation approach needs to be developed and cross-checked; Investigation is needed on whether there is an optimum mixing ratio that can give best sorbent performance. More work is also needed on sorbent modification.
Chapter 10  Conclusions and recommendations for future work

Other preparation methods employed in catalyst preparation should be tested, for example, Sol-Gel or co-precipitation; More additives shall be tested; Pelletization technology should be tested together with modifiers. At least one previous study (Gupta, et al. 2004) has shown that pelletization can enhance sorbent reversibility.

(2) New sorbents other than calcium-based sorbents should be tested for the combustor and gasifier processes, such as lithium-based sorbents. Since preliminary data (Kato, 2001; Kato et al., 2002a,b) suggest that these are highly reversible sorbents. Brief test results on the carbonation and sulphation ability of \( \text{Li}_4\text{SiO}_4 \) are included in Appendix X.

(3) Advanced analytical techniques should be used in the study of sorbent performance. For example, in-situ infrared spectroscopy technology could be used to evaluate the stabilizing mechanism by the formation of \( \text{Ca}_12\text{Al}_{14}\text{O}_{33} \) in CaO composite.

(4) Chapter 7 showed that periodic hydration can improve sorbent reversibility. Chapter 4 also suggested that shorter residence times for each cycle of sorption could reduce sorbent sintering. These methods focusing on affordable natural sorbents deserve more testing.

(5) Calcination is a key step, but little work has been done to investigate practical and affordable calcination methods.

(6) Most work to date has been at the bench scale using batch reactors. More tests are needed on continuous reactors. If continuous reactors could be operated on interconnected columns, questions on long-term sorbent performance, the effects on recycling ratio of sorbents, and optimal operating methods for the calciner, could be more easily answered.

(7) This work showed that calcium-based sorbents have difficulties when co-capture of \( \text{SO}_2 \) and \( \text{CO}_2 \) is required. Applying the sorbents to capture \( \text{CO}_2 \) under steam reforming conditions may be more practical. Fixed bed tests (Ortiz and Harrison, 2001) and
Chapter 10 Conclusions and recommendations for future work

Fluidized bed tests (Johnsen et al., 2006) have all been carried out in batch-wise mode. A challenge is to demonstrate sorption-enhanced hydrogen production in a more practical system, e.g. with interconnected fluidized beds.

(8) The proposed process Option B in Chapter 8 deserves tests on a larger scale reactor and detailed economic study.

(9) The feasibility of co-capture of H$_2$S and CO$_2$ needs more research. Calcium-based sorbent could potentially serve as a catalyst for gasification and tar cracking (Jia et al., 2004; Xu et al., 2005). However, H$_2$S capture is limited by chemical equilibrium, so a downstream second-stage desulfurizer may be needed to meet emission standards. This concept needs to be further demonstrated with interconnected fluidized bed reactors.
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Literature cited


The objective of this appendix is to compare the fitting result by the use of nonlinear fitting and linear fitting for the kinetic data in Chapters 2 and 3.

A1.1 Dataset and equation used

1. Four datasets

Dataset 1: rate constant, $k_s$ measurement for Strassburg limestone in Chapter 2.

Dataset 2: rate constant, $k_s$ measurement for Arctic dolomite in Chapter 2.

Dataset 3: diffusivity, $D_p$, data for Strassburg limestone in Chapter 3.

Dataset 4: diffusivity, $D_p$, data for Arctic dolomite in Chapter 3.

2. Two equations

Equation 1: $r_0 = \frac{56 \times S_0}{3} k_s = \frac{56 \times S_0}{3} k_0 \exp\left(-\frac{E_1}{RT}\right)$ (see equation 2.10, in zeroth reaction order range), $S_0 = 29 \text{ m}^2/\text{g}$ for Strassburg limestone; $31 \text{ m}^2/\text{g}$ Arctic dolomite, $R=0.008314 \text{ kJ/mol/K}$. $r_0$, $k_s$, and $E_1$ are the kinetic rate, rate constant, and activation energy in Chapter 2. $k_0$ is a pre-exponential factor.

Equation 2: $D_p = D_{p0} \exp\left(-\frac{E_2}{RT}\right)$. $D_p$ and $E_2$ are the effective diffusivity and activation energy in Chapter 3 with $D_{p0}$ being the pre-exponential factor.

3. Four fittings (all fittings were performed using MATLAB 6.5 fitting tools)

Fit 1: nonlinear equation: $y = A \exp(-B/T)$; data format: $k_s$ vs T; then obtain $k_0$ from A, and $E_1$ from B.
Appendix I About kinetic data fitting

Fit 2: linear equation: $y = A + Bx$; data format: ln($k_s$) vs 1/T; then obtain $k_0$ from A, and $E_1$ from B.

Fit 3: nonlinear equation: $y = A \exp(-B/x)$; data format: $D_p$ vs T; then obtain $Dp_0$ from A, and $E_2$ from B.

Fit 4: linear equation: $y = A + Bx$; data format: ln($D_p$) vs 1/T; then obtain $Dp_0$ from A, and $E_2$ from B.

4. Goodness of fit parameters:

a. Adjusted R-square $= 1 - \frac{SSE(n - 1)}{SST(v - 1)}$

SSE: sum of squares of the regression: $SSE = \sum_i (\hat{y}_i - \bar{y}_i)^2$

SST: total sum of squares about the mean: $SST = \sum_i (y_i - \bar{y}_i)^2$

$m$: number of fitted coefficients

$n$: number of data points

$v = n - m$ = number of degree of freedom

b. RMSE: Root Mean Square Error, also known as the fit standard error and the standard error of the regression, $\sqrt{\frac{SSE}{v}}$
Appendix I About kinetic data fitting

AI.2 Fitting results

The fitting results are shown in Tables AI.1 and AI.2. For dataset 1 and dataset 2, nonlinear fitting provided a somewhat better result in term of the goodness of fit. The nonlinear results have therefore been adopted in Chapter 2. For dataset 3 and dataset 4, nonlinear fittings failed to give physically correct values, either because of the data quality or the fitting tool used (MATLAB 6.5). The fitting results using linear fitting methods were therefore adopted in Chapter 3.

Table AI.1 Fitting results with nonlinear equations. Values in [] are values with 95% confidence level. Values in bold are utilized in Chapter 2.

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<td>( E_t=0.005 ) [-132, 132]</td>
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Appendix I About kinetic data fitting

Table A1.2 Fitting results with linear fit to logarithmic equations. Values in [] are values with 95% confidence level; Values in bold are adopted in Chapter 3.

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</tr>
<tr>
<td>Dataset 2</td>
<td>$k_0 = 0.0011 \ [0.0005, 0.0025]$</td>
<td>$E_r = 24.05 \ [17.75, 29.25]$</td>
<td>0.937</td>
</tr>
<tr>
<td>Dataset 3</td>
<td>$D_{p0} = 0.27 \ [1.8E-2, 4.13]$</td>
<td>$E_p = 215 \ [249, 183]$</td>
<td>0.94</td>
</tr>
<tr>
<td>Dataset 4</td>
<td>$D_{p0} = 0.0008 \ [1.67E-5, 0.038]$</td>
<td>$E_p = 187 \ [248, 126]$</td>
<td>0.877</td>
</tr>
</tbody>
</table>

Al. 3 Comparisons with experimental data and equations with fitted parameters

The fitted kinetic data are then used to compare the experimental data. The comparisons appear in Figures AVI.1-6. Note that for dataset 3 and 4, the prediction using nonlinear fitting results were not able to present physically correct values and therefore are not plotted in Figures AVI. 5-6.
Appendix I About kinetic data fitting

Figure AI.1 Comparison of experimental and fitting results (Dataset 1)

Figure AI.2 Comparison of experimental and fitting results (Dataset 1). Same as above but in Arrhenius plot
Appendix I About kinetic data fitting

Figure AI.3 Comparison of experimental and fitting results (Dataset 2)

Figure AI.4 Comparison of experimental and fitting equation (Dataset 2) Same as above but in Arrhenius plot
Appendix I About kinetic data fitting

Figure AI.5 Comparison of experimental and fitting equation (Dataset 3) in Arrhenius plot (Data predicted by the nonlinear fitted equation is off this chart)

![Figure AI.5](image1)

Figure AI.6 Comparison of experimental and fitting equation (Dataset 4) in Arrhenius plot (Data predicted by the nonlinear fitted equation is off this chart)

![Figure AI.6](image2)
Appendix I About kinetic data fitting

AI. 4 Conclusions

Based on the 95% confidence level data range, nonlinear fitting gives better results for the experimental rate constants for datasets 1 and 2 where the activation energy is relatively small. In these cases, the fitted results and goodness of fitting are similar between the linear fitting and the nonlinear fitting. For the diffusivities (where the activation energy is much larger), nonlinear fitting failed to yield physically meaningful results, either because of the failure of the fitting tools or because of the quality of data. Hence a linear fit was applied after taking logarithms.

Based on the results in this Appendix, the best fitting methods may be related to the range of activation energy itself. As the temperature step size in studies is usually uniformly distributed by experimenters, when activation energy is large, the reaction rate increases quickly with temperature, tending to make the measured data points too dispersed to give an accurate nonlinear fit when there are not enough data points in the high temperature.
Appendix II Molar volume ratio for a dolomite employed in the model of Chapter 3

APPENDIX II MOLAR VOLUME RATIO FOR A DOLOMITE EMPLOYED IN THE MODEL OF CHAPTER 3

(The symbols employed in this appendix are summarized in the nomenclature section of Chapter 2)

An XRD study by Engler et al. (1988) has shown that no solid solution is present for fully calcined dolomite. Thus a fully calcined dolomite can be considered as a physical mixture of MgO and CaO, with other impurities as minor constituents. CaO and MgO crystals are both cubic, with the cube edge length 4.8\times10^{-9} \text{ m} for CaO and 4.2\times10^{-9} \text{ m} for MgO (Boynton, 1979). Considering a dolomite with molar ratio of CaO to MgO of \eta, the molar volume ratio of CaO to MgO is

\[ \delta = \frac{4.8^3}{4.2^3} \eta \]  
(AII 1)

For the Arctic dolomite investigated in the current work, \eta = 1.1 so that \delta = 1.64.

Note that the surface area is also composed of both CaO and MgO. With the assumption that these are randomly interspersed, the surface area ratio of CaO to MgO is also \delta.

At time t, the reactant radius surface has reached \( R_{i,r} \) and the product radius is \( R_{i,p} \), as illustrated by Figure 2.2. The solid matrix inside the annular region \( V_{i,r} - V_{i,p} \), contains not only product CaCO₃, but also inert MgO. In this region, the volumes of the different compartments, i.e. CaO consumed, CaCO₃ produced and MgO remaining are

\[ V_{\text{CaO}} = (V_{i,r} - V_{i,0}) \frac{\delta}{1 + \delta} \]  
(AII 2)

\[ V_{\text{CaCO}_3} = (V_{i,r} - V_{i,0}) \frac{\delta}{1 + \delta} Z \]  
(AII 3)

\[ V_{\text{MgO}} = (V_{i,r} - V_{i,0}) \frac{1}{1 + \delta} \]  
(AII 4)
Appendix II Molar volume ratio for a dolomite employed in the model of Chapter 3

If the annular layer $V_{i,r} - V_{i,p}$ is assumed to be non-porous, a mass balance on the carbonation reaction leads to,

$$V_{i,r} - V_{i,p} = V_{CaCO3} + V_{MgO} = (V_{i,r} - V_{i,0}) \frac{\delta}{1 + \delta} Z + (V_{i,r} - V_{i,0}) \frac{1}{1 + \delta}$$  \hspace{1cm} (A II.5)

Rearrangement leads to

$$V_{i,p} = Z' V_{i,0} - (Z' - 1) V_{i,r}$$  \hspace{1cm} (A II.6)

where $Z' = \frac{\delta}{1 + \delta} Z + \frac{1}{1 + \delta}$ is the molar product-to-reactant volume ratio for the dolomite.

Equation (A II.6) for a dolomite is identical with equation (2.32) for a limestone, only with $Z'$, a lower molar ratio of product to reactant, replacing $Z$. 

274
APPENDIX III INITIAL PORE SIZE DISTRIBUTION EMPLOYED IN THE MODEL OF CHAPTER 3

(The symbols employed in this appendix are summarized in the nomenclature section of Chapter 3)

Mercury intrusion is known to be able to measure the sizes of larger pores than gas adsorption, so the former was used to obtain the initial pore size distribution in the current study.

It is not clear from the literature whether or not the initially measured pore volume involves overlapping. Here this issue is addressed and the initial condition from mercury intrusion data is obtained.

Bhatia and Perlmutter (1980) used measured total pore volume $V_m$ as the non-overlapping pore volume $V_{0,E}$. With the aid of equation (2.2), this leads to,

$$ V_0 = 1 - \exp(-V_{0,E}) = 1 - \exp(-V_m) \neq V_m $$  \hspace{1cm} (AIII.1)

where $V_0$ is the initial pore volume considering overlap.

Gavalas (1980) derived the probability density $\lambda(R_{i,m})$ by initial mercury intrusion or gas adsorption data, $V_{i,m}(R_{i,m})$,

$$ \lambda(R_{i,m}) = \frac{V_{i,m}(R_{i,m})}{2\pi R_{i,m}^2} \frac{1}{1 - \int_{R_{i,m}}^{\infty} V_{i,m}(R^*) dR^*} $$  \hspace{1cm} (AIII.2)

where $R_{i,m}$ (i=1 to N), is obtained from the mercury intrusion data, calculated from Washburn equation (Lowell and Shields, 1991). The value of $\lambda(R_{i,m})$ is close to $I(R_{i,m})/2$. Gavalas (1980) also showed that the initial total pore volume can be expressed as,

$$ V_0 = \varepsilon = 1 - \exp\left(-\sum_{i=1}^{N} 2\pi \lambda_{R_{i,m}} \right) $$  \hspace{1cm} (AIII.3)
Appendix III Initial pore size distribution employed in the model of Chapter 3

Equation (AIII.3) indicates that the measured pore volume does not account for overlap. This is a reasonable approximation when the initial volume is small, as $\frac{1}{1 - \int V_{i,m}(R^*)dR^*}$ goes to unity, $V_0$ by (AIII.3) is the total measured volume $V_0 \approx \left( \sum_{i=1}^{N} 2\pi \lambda_i R_{i,m}^2 \right) = V_m$, $V_m = \sum V_{i,m}(R_{i,m})$ and $V_{i,m}(R_{i,m})$ is the measured pore volume of each pore radius $R_{i,m}$. However usually the initial volume is not small enough for this approximation to be valid, so at time zero, $V_0$ determined from equation (AIII.3), is usually smaller than the measured pore volume $V_m$. This contradicts the assumption that the measured pore volume $V_m$ should equal the true volume $V_0$ at time zero.

To deal with this difficulty, a simplified treatment is introduced below.

It is believed that the primary difficulty arises from the definition of pore radius. In mercury intrusion data, if pores are assumed to be cylindrical, pore radius is related to intrusion pressure by the Washburn equation. The measured nominal pore size is $R_{i,m}$, $i=1$ to N. Pore volume is $V_{i,m}(R_{i,m})$, so that total pore volume is

$$V_m = \sum V_{i,m}(R_{i,m}) = \sum_{i=1}^{N} \pi R_{i,m}^2 l_i.$$  \hspace{1cm} (AIII.4)

In the current model, a different set of cylindrical pores is needed with initial pore radius $R_{i,0}$ $(i=1$ to $N)$. When considering overlap, the overall pore volume $V_0$ is set equal to the measured $V_m$. 

276
Appendix III  Initial pore size distribution employed in the model of Chapter 3

Initial radii of pores with overlap as input of the model $\Rightarrow$

Measured equivalent radii represent intruded Hg volumes $\Rightarrow$

Figure AIII.1 Illustration of the relation between initial pore radii based on measured pore volume data

The relationship between the two sets of pores is illustrated in Figure AIII.1. Each incremental pore volume corresponds to a certain pore radius, so that there should be no overlap. $R_{i,m}$ can be regarded as an equivalent radius of voids filled at a certain intrusion pressure, whereas the pore system with radius $R_{i,0}$ $(i=1, N)$ introduced here involves overlap. The two sets of radii share the same total pore length, i.e.

$$l(R_{i,m}) = l(R_{i,0}) = l_i \quad i=1 \text{ to } N$$  \hspace{1cm} (AIII 5)

Total pore length per unit volume (m/m$^3$), is obtained given from the measured data,

$$l(R_{i,m}) = \frac{V_{i,m}(R_{i,m})}{\pi R_{i,m}^2} = l_i \quad i=1 \text{ to } N$$  \hspace{1cm} (AIII 6)

In the pore system with overlap,

$$V_0 = 1 - \exp(-V_{0,e}) = 1 - \exp(-\sum_{i=1}^{N} \pi l_i R_{i,0}^2)$$  \hspace{1cm} (AIII 7)
Appendix III Initial pore size distribution employed in the model of Chapter 3

where \( V_{0,E} \) represents the pore volume without overlap.

The two sets of pore system \( (R_{1,0} \text{ vs } R_{1,m}, \text{ or } V_0 \text{ vs } V_m) \) are related by the initial total pore volume, i.e. \( V_0 \) equal \( V_m \), so that

\[
V_0 = 1 - \exp(-V_{0,E}) = V_m \quad \text{(AIII.8)}
\]

Equation (AIII.8) further leads to

\[
V_{0,E} = -\ln(1-V_m) \quad \text{(AIII.9)}
\]

As \( V_{0,E} = \sum_{i=1}^{N} V_{i,0,E} = \sum_{i=1}^{N} \pi R_{i,0}^2 \) and \( V_m = \sum_{i=1}^{N} V_{i,m} = \sum_{i=1}^{N} \pi R_{i,m}^2 \), the two sets of pores can be related by,

\[
V_{i,0,E} = \frac{V_{0,E}}{V_m} V_{i,m} = \frac{-\ln(1-V_m)}{V_m} V_{i,m} = \frac{-\ln(1-V_m)}{V_m} \pi R_{i,m}^2 \quad \text{(AIII.10)}
\]

Since \( V_{i,0,E} = \pi R_{i,0}^2 \), equation (AIII.10) finally gives

\[
R_{i,0} = \sqrt{\frac{-\ln(1-V_m)}{V_m}} R_{i,m} \quad \text{(AIII.11)}
\]

Pore radius \( R_{i,0} \) and \( V_{i,0,E} = \pi R_{i,0}^2 \) are used as initial model input.

Finally the directly measured pore volume \( A_m \) (m\(^3\) pore/kg particle) needs to be converted to the fractional pore volume \( V_m \) (m\(^3\)/m\(^3\)) in equation (AIII.11). For a differential pore size distribution

\[
A_m = \sum_{i=1}^{N} A_{i,m} \quad \text{(AIII.12)}
\]

where \( A_{i,m} \) (in m\(^3\) pore/kg particle) is the differential pore volume enclosed by pores of radius \( R_{i,m} \).

278
Appendix III  Initial pore size distribution employed in the model of Chapter 3

For measured pore size $R_m$, the fractional volume $V_{i,m}$ (m³ pore/m³ space) can be related to the measured volume fraction by:

$$V_{i,m} = \frac{A_{i,m} \rho_s}{1 + A_{i,m} \rho_s}$$  \hspace{1cm} (AIII.13)

which gives the value of $V_m$ in (AIII.11) with $V_m = \sum_{i=1}^{N} V_{i,m}$. 

279
APPENDIX IV A FORTRAN PROGRAM EMPLOYED IN CHAPTER 3

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CC-A COMPUTER PROGRAMM FOR CARBONATION CALCULATION-
CC-A NEW STRUCTRUAL MODEL
CC-NOTE: ALL THE OTHER RELATED CALCULATIONS CAN BE MADE BY
CC-ADJUSTING SOME STATEMENTS
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
PROGRAM PORES
PARAMETER(MR=29, MT=518000)
DIMENSION R0(MR),V0BAR(MR),V0(MR),RR(MR),RP(MR),C(MR),VRE(MR),
+ VPE(MR),V1(MR),T(MT),X(MT),THICK(MT),CCC(MR,MT)
REAL MCAO,K0,KS,KSB
REAL L0(MR), LA(MR)
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCC--VARJBLES-DEFENTTIONS—
CCCC--MR: PORE GROUP NUMBERS; MT: TIME STEPS--
CCCC--R0, V0BAR,V0 RELATED MEASURED PORE PROPERTIES~
CCCC--C IS CO2 CONCENTRATION--
CCCC--VRE,VPE ARE VARIABLES WITH NO CONSIDERATION OF OVERLAP--
CCCC--T INCLUDE TIME; X IS CONVERSION; THICK IS PORE WALL
CCCC--THINKNESS--
CCCC--MCAO, KO, KS, KSB ARE ALL CONSTANT RELATING RATE LAW--
CCCC--L0 PORE LENGTH--
CCCC--V0BAR(I) the increamental volume in cc/g--
CCCC--ALL UNITS SHOULD BE CONVERTED INTO SI UNITS; --
CCCC--DCA IS DENSITY IN KG/M3; INPUT PORE RADII IN ANSTRANM, THEN
CCCC--CHANGED to M
CCCC--INPUT PORE VOLUME V0BAR AND VT CONVERTED FROM CC/G TO
CCCC--M3/KG
CCCC--MOLAR WEIGHT MCAO IN KG/MOL--
CCCC--INPUT CONCENTRATION ARE INITIALL IN BAR THEN CONVERTED TO C-
CCCC--M3/M3--
CCCC--THERMOAL CONSTANT R IN CM3/K/MOL--
CCCC--KS AND KSB ARE RATE CONSTANT IN DIFFERENT RXN ORDER ZONE--
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
WRITE(*,*)'RUNNING............'
CCCC--INPUT MEASURED PORE PARAMETERS--
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
OPEN(1,FILE='inputlimestone.txt',STATUS='OLD')
DO I=1,MR
READ (1, *) R0(I), V0BAR(I)
END DO
CLOSE (1)

DR=10000*1.E-10/MR  
DCA=3.34*1.E3

VT=0.0  
DO I=1,MR  
LA(I)=V0BAR(I)/(R0(I)**2.)  
R0(I)=(1.E-10)*R0(I)  
V0BAR(I)=V0BAR(I)*1.E-3  
VT=VT+V0BAR(I)  
END DO

VOLUME=0.0  
DO I=1,MR  
V0(I)=V0BAR(I)*DCA/(1+VT*DCA)  
RR(I)=R0(I)  
RP(I)=R0(I)  
VRE(I)=V0(I)  
VPE(I)=V0(I)  
L0(I)=V0(I)/3.1415/(R0(I)**2.)  
VOLUME=VOLUME+V0(I)  
END DO

VPRIME=-Log(1.-VOLUME)  
VVV=VPRIME/VOLUME  
DO I=1,MR  
R0(I)=(V0(I)*VVV/3.1415/L0(I))**0.5  
RR(I)=R0(I)  
RP(I)=R0(I)  
VRE(I)=V0(I)*VVV  
VPE(I)=V0(I)*VVV  
END DO

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC  
CCCCC-INPUT DENSITY, STEP LENGTH, Z VALUE, TEMPERATURE, RATE  
CCCCC-CONSTANT  
CCCCC-INITIAL VALUES, FITTED DIFFUSIVITY, EQUILIBRIUM CONCENTRATION

MCAO=56.*1.e-3  
DTIME=0.006  
Z=2.17  
PC=20.  
TT=600  
PE=10**(-8308/(TT+273)+7.079)  
TSTOP=MT  
C0=(PC-PE)/(82.05e-6*(TT+273.15))  
CSTAR=0.1/(82.05e-6*(TT+273.15))
Appendix IV A Fortran program employed in Chapter 3

DP=1.22e-13
KS=3.1e-5
KSB=KS/CSTAR
N=2
NT=1
T(1)=0.0
X(1)=0.0
DO NN=2,MT
  CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
  CCCCCCCCCCCC-CALCULATED NEW REACTION FRONT-
  CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
  VRET=0.0
  DO MM=1,MR
    IF((1.E10*RP(MM)).LE.1.) THEN
      C(MM)=0.0
      RK=DTIME*MCAO/DCA*KS*C(MM)
      GOTO 100
    END IF
    IF(NN.EQ.2) THEN
      C(MM)=C0
      RK=DTIME*MCAO/DCA*KS
    ELSE
      C(MM)=C0-KS/DP*RR(MM)*LOG(RR(MM)/RP(MM))
      IF (C(MM).LE.CSTAR) THEN
        N=0
        RK=DTIME*MCAO/DCA*KS
      ELSE
        C(MM)=C0-(KS/DP*RR(MM)*LOG(RR(MM)/RP(MM))
      END IF
    END IF
    RK1=DTIME*MCAO/DCA*KSB*C(MM)
    RK2=DTIME*MCAO/DCA*KSB*C0/(1.+KSB/DP*RR(MM)+1./2.*RK1)
    + *LOG((RR(MM)+1./2.*RK1)/RP(MM))
    RK3=DTIME*MCAO/DCA*KSB*C0/(1.+KSB/DP*RR(MM)+1./2.*RK2)
    + *LOG((RR(MM)+1./2.*RK2)/RP(MM))
    RK4=DTIME*MCAO/DCA*KSB*C0/(1.+KSB/DP*RR(MM)+RK3)
    + *LOG((RR(MM)+RK3)/RP(MM))
    RK=1./6.*(RK1+2.*RK2+2.*RK3+RK4)
    ELSE
      C(MM)=C0-(KS/DP*RR(MM)*LOG(RR(MM)/RP(MM))
      N=0
      RK=DTIME*MCAO/DCA*KS
    END IF
  ENDIF
  100 CONTINUE
  RR(MM)=RR(MM)+RK
  VRE(MM)=3.14159*L0(MM)*RR(MM)**2.
  VRET=VRET+VRE(MM)
Appendix IV A Fortran program employed in Chapter 3

END DO
VR=1.-EXP(-1.*VRET)
VP=(1.-Z)*(VR-VOLUME)+VOLUME

CCC
CCC-CALCULATED NEW PRODUCT FRONT-
CCC

VPET=0.0
DO K=1,MR
IF((1.E10*RP(K)).LE.1.) THEN
RK=0.0
GOTO 200
END IF
IF(RP(K).LE.0.) THEN
RP(K)=0.0
RK=0.0
GOTO 200
ENDIF
IF (N.NE.0) THEN
C(K)=C0/(1.+KSB/DP*RR(K)*LOG(RR(K)/RP(K)))
RK1=DTIME*MCAO/DCA*KSB*C(K)*(1.-Z)*(1-VR)/(1-VP)*RR(K)/RP(K)
IF((RP(K)+1./2.*RK1).LE.0.) THEN
RP(K)=0.0
RK=0.0
GOTO 200
ENDIF
C(K)=C0/(1.+KSB/DP*RR(K)*LOG(RR(K)/(RP(K)+1./2.*RK1)))
RK2=DTIME*MCAO/DCA*KSB*C(K)*(1.-Z)*(1-VR)/(1-VP)
+ *RR(K)/(RP(K)+1./2.*RK1)
IF((RP(K)+1./2.*RK2).LE.0.) THEN
RP(K)=0.0
RK=0.0
GOTO 200
ENDIF
C(K)=C0/(1.+KSB/DP*RR(K)*LOG(RR(K)/(RP(K)+1./2.*RK2)))
RK3=DTIME*MCAO/DCA*KSB*C(K)*(1.-Z)*(1-VR)/(1-VP)
+ *RR(K)/(RP(K)+1./2.*RK2)
IF((RP(K)+RK3).LE.0.) THEN
RP(K)=0.0
RK=0.0
GOTO 200
ENDIF
C(K)=C0/(1.+KSB/DP*RR(K)*LOG(RR(K)/(RP(K)+RK3)))
RK4=DTIME*MCAO/DCA*KSB*C(K)*(1.-Z)*(1-VR)/(1-VP)
+ *RR(K)/(RP(K)+RK3)
RK=1./6.*(RK1+2.*RK2+2.*RK3+RK4)
ELSE
C(K)=C0-KS/DP*RR(K)*LOG(RR(K)/(RP(K)))
ENDIF

283
Appendix IV A Fortran program employed in Chapter 3

RK=DTIME*MCA0/DCA*KS*(1-Z)*(1-VR)/(1-VP)*RR(K)/RP(K)
END IF
200 CONTINUE
RP(K)=RP(K)+RK
VPE(K)=3.14159*L0(K)*RP(K)**2.
VPET=VPET+VPE(K)
THICK(k)=RR(k)-RP(k)
END DO
VP=1.-EXP(-1.*VPET)

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCC-UPDATE OVERALL CONVERSION AND SAVE DATA--
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
X(NN)=1 .-(1 .-VR)/(1 .-VOLUME)
NT=NT+1
T(NN)=DTIME*(NN-1)
IF (T(NN).GT.TSTOP) GOTO 400
END DO
400 CONTINUE
OPEN(2,FILE=DATAX.DAT•,STATUS='OLD')
DO J=1,10000,10
WRITE(2,*)T(J),X(J),CCC(14,J)
END DO
CLOSE(2)

END
APPENDIX V LINEARIZATION OF EQUATION (4.5)

(The symbols employed in this appendix are summarized in the nomenclature section of Chapter 4)

The objective of this appendix is to linearize the following equation,

\[ u_{\text{bed}} \frac{\partial C(t, z)}{\partial z} - D_z \frac{\partial^2 C(t, z)}{\partial z^2} = \rho_{\text{CaCO}_3}(n)(1 - \varepsilon_b) \frac{\partial X(t, z)}{\partial t} \]  \hspace{1cm} (AV.1)

The boundary conditions are,

At \( z = 0 \), \( C(t, z) = 0 \) \hspace{1cm} (AV.2)

At \( z = L \), \( \frac{\partial C(t, z)}{\partial z} = 0 \) \hspace{1cm} (AV.3)

\[ \frac{dX}{dt} = \frac{1 - \frac{C(z)}{K_e}}{\rho_{\text{CaCO}_3}(n) R \left\{ \frac{1}{3k_m K_e} + \frac{(1 - X)^{-2/3}}{k_e} + \frac{R}{3D_e K_e} [(1 - X)^{-1/3} - 1] \right\}} \]  \hspace{1cm} (AV.4)

(AV.4) is rewritten as

\[ \frac{dX}{dt} = \frac{1 - \frac{C(z)}{K_e}}{f(X)} \]  \hspace{1cm} (AV.5)

with

\[ f(X) = \rho_{\text{CaCO}_3}(n) R \left\{ \frac{1}{3k_m K_e} + \frac{(1 - X)^{-2/3}}{k_e} + \frac{R}{3D_e K_e} [(1 - X)^{-1/3} - 1] \right\} \]  \hspace{1cm} (AV.6)

so that equation (AV.1) can be written as

\[ u_{\text{bed}} \frac{\partial C(t, z)}{\partial z} - D_z \frac{\partial^2 C(t, z)}{\partial z^2} = \rho_{\text{CaCO}_3}(n)(1 - \varepsilon_b) \frac{1 - \frac{C(z)}{K_e}}{f(X)} \]  \hspace{1cm} (AV.7)

At any time step, from \( t \) to \( t + dt \), use one-order upwind schemes to linearize equation (AV.7)
Appendix V Linearization of Equation (4.5)

$$u_{\text{bed}} \frac{C_{i+1} - C_i}{\Delta z} - D_z \frac{\Delta z}{\Delta z} = \rho_{CaCO3} (n)(1 - \varepsilon_b) \frac{1 - C_i}{f(X)}$$

(AV.8)

After rearrangement,

$$C_i \left[ \frac{u_{\text{bed}}}{\Delta z} + \frac{2D_z}{\Delta z^2} + \frac{\rho_{CaCO3} (n)(1 - \varepsilon_b)}{f(X)K_e} \right] = C_{i+1} \left[ \frac{D_z}{\Delta z^2} \right] + C_{i-1} \left[ \frac{u_{\text{bed}}}{\Delta z} + \frac{D_z}{\Delta z^2} \right] + \frac{\rho_{CaCO3} (n)(1 - \varepsilon_b)}{f(X)K_e}$$

(AV.9)

At boundary points:

$$C_1 = 0$$

(AV.10)

$$C_M = C_{M-1}$$

(AV.11)

M is the maximum number of the cells

The discrete equation (AV.9) complies with the four principles proposed by Partankar (1980) in order to achieve convergence during iterative solving.
%%Simultaneous calcination and sintering modeling
%% input fitted parameters, temperature, cycle numbers, experimental data,
%% initialization, reactor dimensions, gas property etc.
%% xcarb: carbonation conversion at each cycle; scycle, ss: surface area;
%% ecycle, ee, ee2: porosity
%% units: mass in gram; rous is true density of CaCO3, 2.71g/cc, converted to
%% mol/m3; rounn2 is density for N2; visa is viscosity; variables are usually in SI units, if%
%% not specified
maxcycle=1000;
T=850;
AA=1.2591;
BB=0.5922;
Z = 2.71/100/(3.34/56);
xcarb=zeros(1,maxcycle+1);
scycle=zeros(1,maxcycle);
est=zeros(1,maxcycle);
tcycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
tcycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
tcycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
tcycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
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ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=zeros(1,maxcycle);
ecycle=z
Appendix VI A Matlab program employed in Chapter 4

diapass=2.*(areapass/pi)^0.5;
u0=hotflow/area;
hbed=mass/areapan/(1-fbed)/(2.71*1.e6);

roun2=1.229*(20+273.5)/(T+273.5); %in kg/m3
visa=3.93*1.e-5; %in Pa.s or kg/m/s at 850 deg C; 4.17 AT 800, 3.93 at 700 deg,
% 4.4 at 900 deg C
visb=visa/roun2; %in m2/s

ubed=0.012;
upass=(u0*area-ubed*areapan)/areapass;
ergun=(150*(l-fbed)^2/fbed^3*visa*ubed/r^2+1.75*(1-...
fbed)/fbed^3*roun2*ubed^2/r)*hbed;
red=upass*diapass/visb;
coeff=0.96;
beida=diapass/diabed;
qm=coeff*areapass*(2.*roun2*ergun)^0.5/(1-beida^4.)^0.5;
qv=upass*areapass;

%----about steps
stept=1;
tfinal=floor(lastt/stept);
lfinal=20;
stepl=hbed/(lfinal-l);

rep=ubed*2.*r/visb;
d0=0.163*1.e-4*((T+273.5)/(20.+273.))^(1.75);
sc=visb/d0;
sh0=0.6*(rep*sc)^(1./2); %for creeping flow
km=sh0^2/d0/r;
ez=2.4*10^(-5) % Obtained from charts of Chemical Reaction Engineering, 2rd ed.
%Levespiel P310
ez=2*r*ubed/Peclet*0.2;
Peclet=2*r*ubed/ez;

sa=1.5;
sg=70;
eg=1-Z;
radius1=25*1.e-9;
radius2=300*1.e-9;
rouscaco3=2.71/100.*1.e6;
Appendix VI A Matlab program employed in Chapter 4

rouscao=3.34*1.e6; % g/m3
vg=eg/rouscao/(1-eg);
coeffa=(sg-sa)/(vg);

%---kinetics data------
Ke=10^(-8308/(T+273)+7.079)/(82.05*1.e-6*(T+273.15));%Ke in mol/m3
ks=3.013*1.e7*exp(-200/0.008314/(T+273.5)); %in mol/m2/s

%% Calculation of the outer loop %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
for ncycle=1:maxcycle
x=zeros(tfinal,lfinal);
c=zeros(tfinal,lfinal);
creal=zeros(tfinal,lfinal);
cr=zeros(tfinal,lfinal);
ss=zeros(tfinal,lfinal);
ee=zeros(tfinal,lfinal);
ffl=zeros(1,lfinal);
crbed=zeros(l,tfinal);
xbed=zeros(l,tfinal);
drive=zeros(l,tfinal);
sbed=zeros(l,tfinal);
ebed=zeros(l,tfinal);
xint=zeros(l,lfinal);
deint=zeros(1,lfinal);
rous=2.71/l00.*1.e6*xcarb(ncycle);
if (ncycle > 1)
  for mm=1:lfinal
    ss(1,mm)=si;
  end
else
  for mm=1:lfinal
    ss(1,mm)=si;
  end
end

for i=1:lfinal
  %de(i)=0.163*1.e-4*((T+273.5)/(20.+273.))^1.75*e(i)^2;
  de(i)=0.163*1.e-4*((T+273.5)/(20.+273.5))^1.75*0.54*e(i)^2;
end
%% Call subroutine to solve concentration c---
for i=1:tfinal
    xint=x(i,:);
    c(i,:)=solvec(xint,de);
    for j=1:lfinal
        rk1=stept*(1.-c(i,j)/Ke)/fx(min(x(i,j),0.999999),de(j));
        rk2=stept*(1.-c(i,j)/Ke)/fx(min(x(i,j)+rk1/2.,0.999999),de(j));
        rk3=stept*(1.-c(i,j)/Ke)/fx(min(x(i,j)+rk2/2.,0.999999),de(j));
        rk4=stept*(1.-c(i,j)/Ke)/fx(min(x(i,j)+rk3,0.999999),de(j));
        rk=1/6.*(rk1+2.*rk2+2.*rk3+rk4);
        if(rk+x(i,j)>l)
            rk=0.99999999-x(i,j);
        end
        x(i+1,j)=x(i,j)+rk;
        creal(i+1,j)=creal(i,j)+rous*rk;
        pre=rous*r/ks;
        cr(i+1,j)=pre*(1.-min(c(i,j)/Ke,0.999999))/fx(min(x(i,j),0.999999),de(j));
        mps=2.45*(1+AA*(cr(i+1,j)*BB)*exp(-29600/(T+273.5))*(ss(i,j)*1000-sa*1000)^2;
        ps=(sg-sa)*rk*xcarb(ncycle);
        ss(i+1,j)=ss(i,j)+ps-stept*mps;
    end
end

%% Update properties for this moment---
xbed(i)=0.0;
drive(i)=0.0;
ebed(i)=0.0;
sbed(i)=0.0;
crbed(i)=0.0;
for j=1:lfinal;
    crbed(i)=crbed(i)+cr(i,j)*stepl;
    xbed(i)=xbed(i)+x(i,j)*stepl;
    drive(i)=drive(i)+c(i,j)*stepl;
    ebed(i)=ebed(i)+ee(i,j)*stepl;
    sbed(i)=sbed(i)+ss(i,j)*stepl;
end
    crbed(i)=crbed(i)/hbed;
    xbed(i)=xbed(i)/hbed;
    drive(i)=1-drive(i)/hbed/Ke;
    sbed(i)=sbed(i)/hbed;
    ebed(i)=ebed(i)/hbed;

if x(i,lfinal)>0.99995
%%%%%%% Appendix VI A Matlab program employed in Chapter 4

% The Matlab program code is as follows:

```matlab
crcycle(ncycle)=crbed(i-10);  
scycle(ncycle)=sbed(i);  
ecycle(ncycle)=ebed(i);  
tcycle(ncycle)=i*stept;  
break  
end
end

%% Update properties for this cycle, calculate V1 and V2, surface area and  
%% porosity will be used as initial consitions for next cycle

vbed(ncycle)=ecycle(ncycle)/rouscao/(1-ecycle(ncycle));  
pore1(ncycle)=vg+(scycle(ncycle)-sg)/coeffa;  
pore2(ncycle)=vbed(ncycle)-pore1(ncycle);  
xcarb(ncycle+1)=pore1(ncycle)*rouscao*56/(1-Z);  
ee2(ncycle+1)=(ecycle(ncycle)*Z+(1-Z)*xcarb(ncycle+1))*(ecycle(ncycle)-1))/((1-

% Subroutine for gas-solid rate model

function f=fx(conve,diffu)
global r rous km Ke ks fbed ubed ez stepl lfinal
aa=1/3./km/Ke;  
bb=r/3./diffu/Ke*((1-conve)^(-1/3.)-1);  
cc=1/3.*ks*(1-conve)^(-2./3);  
f=r*rous*(aa+bb+cc);

% Subroutine for discrete fixed bed mass balance equation

function conl=solvec (xxx,dede)
global r rous km Ke ks fbed ubed ez stepl lfinal
f=zeros(l ,lfinal);  
aip=zeros(l,lfinal);  
aie=zeros(l,lfinal);  
aiw=zeros( 1, lfinal);  
con=zeros(l,lfinal);  
sp=zeros(l,lfinal);  
pt=zeros(l, lfinal);  
qt=zeros(l, lfinal);
```

291
Appendix VI A Matlab program employed in Chapter 4

```matlab
%aie(1)=ez/step1^2;
%aiw(1)=0.0;
%con(1)=0.0;
%sp(1)=-1.*ubed/step1;
%aip(1)=aie(1)+aiw(1)-sp(1);

aie(1)=0.0;
aiw(1)=0.0;
con(1)=1.e30*0.0;
sp(1)=-1.e30;
aip(1)=aie(1)+aiw(1)-sp(1);

aie(lfinal)=0.0;
aiw(lfinal)=1.e30;
con(lfinal)=0.0;
sp(lfinal)=0.0;
aip(lfinal)=aie(lfinal)+aiw(lfinal)-sp(lfinal);

for i=2:lfinal-1
aie(i)=ez/step1^2;
aiw(i)=ubed/step1+ez/step1^2;
con(i)=rous*(1-fbed)/fx(xxx(i),dede(i));
sp(i)=-1.*rous*(1-fbed)/Ke/fx(xxx(i),dede(i));
aip(i)=aie(i)+aiw(i)-sp(i);
end

pt(l)=aie(l)/aip(l);
qt(l)=con(l)/aip(l);
for i=2:lfinal
    denom=aip(i)-pt(i-1)*aiw(i);    
    if(abs(denom) <= 1.e-18)
        denom=1.e-18;
    end
    denom=1./denom;
    pt(i)=aie(i)*denom;
    qt(i)=(con(i)+aiw(i)*qt(i-1))*denom;
end

if(qt(lfinal) < 0.0)
    qt(lfinal)=0.0;
end

f(lfinal)=qt(lfinal);
for ii=2:lfinal
    iii=lfinal+1-ii;
    f(iii)=f(iii+1)*pt(iii)+qt(iii);
end
```

292
Appendix VI A Matlab program employed in Chapter 4

conl=f,
Figure AVII.1  (Comparing with other runs in Figure 6.2) High-resolution SEM pictures of calcines, with no SO$_2$ present. Same test conditions as in Figure 6.1. Danyang limestone.

(a) SO$_2$ only  
(b) co-capture of SO$_2$ and CO$_2$

Figure AVII.2  (Comparing with other runs in Figure 6.11) Sulfur mapping for non-calcined ATGR samples. 850°C for both tests. SO$_2$ only test: 2900 ppm SO$_2$, 3% O$_2$ and balance N$_2$ for 2 hours; Co-capture test conditions as in Figure 6.6, 15 cycles. (Light points mark sulfur). Danyang limestone.
Appendix VII Supplementary results within the scope of Chapter 6

Figure AVII.3  (Comparing with other runs in Figure 6.3) Evolution of pore size distribution with calcination/carbonation cycling at 850°C. Test conditions: same as in Figure 6.1 for SO₂ test and in Figure 6.6 for co-captures. Danyang limestone.

Figure AVII.4  (Comparing with other runs in Figure 6.3) Evolution of pore size distribution with calcination/carbonation cycling at 850°C. Test conditions: same as in Figure 6.1 for no SO₂ test and in Figure 6.6 for co-captures. Havelock limestone.
Appendix VII Supplementary results within the scope of Chapter 6

Figure AVII.5 (This is for conversion of CaO to CaSO₄, comparing that for CaO to CaCO₃ shown in Figure 6.9) Cyclic CO₂ retention performances in 850°C PTGA tests: effect of total pressure. Co-capture with 212-250 μm Strassburg limestone. Sorption: 8 %v CO₂, 1125 ppmv SO₂, 3% O₂, and balance N₂, 4 minute for each cycle. Calcination: 101 kPa, 100% N₂.

Figure AVII.6 (This is for conversion of CaO to CaSO₄, comparing that for CaO to CaCO₃ shown in Figure 6.10) Cyclic CO₂ retention performances in 850°C PTGA tests: effect of total pressure. Co-capture with 212-250 μm Arctic dolomite. Sorption: 8 %v CO₂, 1125 ppmv SO₂, 3% O₂, and balance N₂, 4 minute for each cycle. Calcination: 101 kPa, 100% 8%v CO₂, 850°C.
Appendix VII Supplementary results within the scope of Chapter 6

Figure AVII.7 Cyclic performances in no SO₂ only tests: effect of total pressure. Atmospheric calcination. 850°C, 8% CO₂ balanced by N₂, 212-250 μm Straussburg limestone.

Figure AVII.8 Cyclic performances in no SO₂ only tests: effect of temperature. 8%v CO₂ balanced by N₂, 212-250 μm, and Straussburg limestone
Appendix VII Supplementary results within the scope of Chapter 6

Figure AVII.9 Cyclic performances in no SO$_2$ only tests: effect of P$_{CO_2}$. Pt=18.2 bars CO$_2$ only, Straussburg, 212-250 μm
Figure AVIII.1 Performance of c-CaO and h-CaO (no SO$_2$ present, sorbent derived from 212-250 μm Arctic dolomite). Same test conditions as specified in Figure 7.2.

Figure AVIII.2 Pore size distribution: comparison of c-CaO and h-CaO. (no SO$_2$ present, sorbent derived from Arctic dolomite)
Appendix VIII Supplementary results within the scope of Chapter 7

Figure AVIII.3 Effect of steam on cyclic capture (No SO₂ present, 212-250 μm Strassburg limestone). Test conditions: 850°C calcination and carbonation;Carbonation in 86% CO₂ and 14% steam; Calcination in 100% N₂.

Figure AVIII.4 Effect of steam on cyclic capture (No SO₂ present, 212-250 μm Arctic dolomite). Test conditions: 850°C calcination and carbonation; Carbonation in 86% CO₂ and 14% steam; Calcination in 100% N₂.
Appendix VIII Supplementary results within the scope of Chapter 7

Figure AVIII.5 Calcium utilization for SO$_2$ capture: effect of varying operating conditions
Comparing with Figure 7.6 Calcium utilization for SO$_2$ capture: effect of varying operating conditions, 212-250 µm particles Test conditions: 850 °C calcination and sorption, Sorption in 80% CO$_2$, 3% O$_2$, 2900 ppm SO$_2$ and balance N$_2$ or with steam. Calcination in 100% N$_2$ 8 minutes for each sorption.
Appendix VIII Supplementary results within the scope of Chapter 7

Figure AVII.6 Close-up view of one cycle of $\text{SO}_2/\text{CO}_2$ sorption followed by a $\text{CaCO}_3$ calcination in $\text{N}_2$ and then a slow reduction of $\text{CaSO}_4$ at cycle 9. Test conditions are described in Table 7.3.
Appendix VIII Supplementary results within the scope of Chapter 7

(a) CaO with Al₂O₃, light color: Al
(b) Calcium acetate with Al₂O₃, light color: Al
(c) CaO with SiO₂, light color: Si
(d) CaO + ZrO₂, light color: Zr
(e) CaO with MgO, light color: Mg
(f) CaO with TiO₂, light color: Ti

Figure AVIII.7 EDX element mapping for modified sorbents with the light color points marking the element of the dopants
Appendix IX A case study based on Option B proposed in Chapter 8

APPENDIX IX A CASE STUDY BASED ON OPTION B PROPOSED IN CHAPTER 8

AIX.1 Case study

A case study was conducted to provide practical information on the application of calcium-based sorbents. The process simulated is shown schematically in Figure AIX.1, based on Option B in Chapter 8.

AIX.2 Major features of the process simulation:

- Steady-state operation.
- Pressure drop and power needed for pure oxygen production are not considered.
- The FBC is simulated as a Gibbs reactor. The reactor labeled DESUL is simulated as a conversion reactor for SO$_2$ removal. CaO utilization for SO$_2$ capture is assumed to be 50%, with the Ca/S molar ratio maintained at 2:1. This determines the split at the CAOSLT block.
- The O$_2$/Fuel stoichiometric ratio in the FBC is taken as 1.3, whereas it is assumed to be 1.1 in the Calciner.
- The FBC and DESUL reactors operate at 1 atm and 850°C, whereas the CARBNER (carbonator) is at 650°C and 1 atm, and the CALCINER at 950°C and 1 atm. (Note in this Appendix, the unit of pressure takes “atm” as requested by the software.)
- All cyclones are assumed to provide perfect gas/solid separation.
- Solid drainage are specified as follows: After the first cyclone (CYC1), 5% of solids from the LOOPSPT block are drained, while the other 95% is recycled to the FBC; after CYC3, 10% of the solids from the CACO3SPT block are drained, the other 90% being recycled to the CARBNER.

304
Appendix IX A case study based on Option B proposed in Chapter 8

- The CaCO₃ feed stream is determined as the minimum feed needed to achieve a zero carbon emission in the STACKFLG stream.

- FUEL2 for the calciner is adjusted so that the net heat duty of the CALCINER and DECOM2 reactors is zero. In other words, the fuel fed to CALCINER is set to provide the heat needed to carry out the calcination reaction at 950°C.

- Intended to exploration of issues relating to fuel and sorbent consumption, this simulation ignores detailed calculation of heat losses and heat transfer in all reactors. The heat duty analysis is instead based on empirism, e.g. overall heat transfer efficiency etc.
Figure AIX.1 Case study flowsheet for FBC-based SO₂/CO₂ sequential capture process (based on Option B in Chapter 8)
Appendix IX A case study based on Option B proposed in Chapter 8

AIX.3 Fuel and sorbent properties

- Because of the assumption of perfect separation in all cyclones, the particle size distributions for both the fuel and sorbent did not need to be specified.

- The sorbents were assumed to be pure, i.e. 100% CaCO₃, treated as a conventional solid in the Aspen simulation.

- In the Aspen simulation, fuel was treated as non-conventional solid. The fuel analysis (except for varying sulfur content in the sensitivity analysis) is shown in Table VIII.1. Note the fuel selected is an idealized fuel. It is only chosen for illustration purpose.

- This simulation assumes fuel types. The fuel applied in the CALCINER is assumed to be similar to that in the FBC, except that it has a lower ash content and contains no sulfur. The latter is to prevent the deactivation of sorbents because of the presence of SO₂ in the calciner. In practice, the fuel could be natural gas, biomass or some and other fuels.

Table AIX. 1 Proximate and ultimate analysis for the fuels simulated.

<table>
<thead>
<tr>
<th></th>
<th>Fuel in FBC</th>
<th>Fuel in calciner low ash, low S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat value (LHV) (kJ/kg)</td>
<td>36,370</td>
<td>36,370</td>
</tr>
<tr>
<td>Proximate analysis (%wt)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>FC</td>
<td>45.1</td>
<td>47</td>
</tr>
<tr>
<td>VM</td>
<td>45.1</td>
<td>47</td>
</tr>
<tr>
<td>ASH</td>
<td>9.2</td>
<td>6</td>
</tr>
<tr>
<td>Ultimate analysis (%wt)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASH</td>
<td>9.2</td>
<td>6</td>
</tr>
<tr>
<td>C</td>
<td>67.1</td>
<td>68</td>
</tr>
<tr>
<td>H</td>
<td>4.8</td>
<td>5</td>
</tr>
<tr>
<td>N</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>S</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>16.4</td>
<td>20</td>
</tr>
</tbody>
</table>

AIX.4 Typical run summary
Appendix IXA case study based on Option B proposed in Chapter 8

The results for the mass flow rates of major streams with CaO conversion to CaCO₃ are shown in Table AIX.2, with 40% the CaO conversion to CaCO₃ assumed in the carbonator. The predicted gas emissions are shown in Table AIX.3. The favourable mass balance implies that good convergence has been achieved. Overall, 1 mole of CaCO₃ can be responsible for cumulatively removing 7.2 moles of CO₂ from the FBC over successive cycles. This is largely due to the recycle of sorbents in this system. A relatively pure CO₂ stream can be obtained as long as just enough excess oxygen can be generated to meet the combustion requirement in the calciner. The overall stream result is shown in Table AIX.4

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>FUEL1</th>
<th>AIR</th>
<th>FUEL2</th>
<th>O₂</th>
<th>CACO3F</th>
<th>DRAIN1</th>
<th>DRAIN2</th>
<th>CO₂</th>
<th>STACKFLG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position in Fig. 10.1</td>
<td>Fuel in FBC</td>
<td>Air in FBC</td>
<td>Fuel in Calciner</td>
<td>O₂ in Calciner</td>
<td>CaCO₃ Feed</td>
<td>Solid drain in FBC</td>
<td>Gas product from calciner</td>
<td>Gas product from calciner</td>
<td></td>
</tr>
<tr>
<td>Flow rate (kg/hr)</td>
<td>40000</td>
<td>286065</td>
<td>29277</td>
<td>46266</td>
<td>44405</td>
<td>5166</td>
<td>31932</td>
<td>160404</td>
<td>248515</td>
</tr>
<tr>
<td>Balance</td>
<td>SOLIDIN=446,013 kg/hr</td>
<td>SOLIDOUT=446,017 kg/hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ sorbent consumption</td>
<td>Moles of CO₂ removed/ Moles of CaCO₃ fed= 7.2 (mole CO₂/mole CaCO₃)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table AIX.3 Summary of gas emissions

<table>
<thead>
<tr>
<th>CO₂ (%) (wet basis)</th>
<th>Flue gas to stack</th>
<th>CO₂ stream</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (%) (wet basis)</td>
<td>0</td>
<td>75.5</td>
</tr>
<tr>
<td>CO₂ (%) (dry basis)</td>
<td>0</td>
<td>97.4</td>
</tr>
<tr>
<td>O₂ (%) (wet basis)</td>
<td>1.9%</td>
<td>1.5%</td>
</tr>
<tr>
<td>NOx (ppm, wet basis)</td>
<td>~0</td>
<td>5</td>
</tr>
<tr>
<td>SOx (ppm, wet basis)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

AIX.5 Capacity estimation of the simulated unit

This sequential-capture unit is different from conventional units in that fuels are fed in both the FBC and the calciner. The exothermic carbonation reaction generates a large amount of heat in the carbonator. Hence heat exchangers need to be installed in all three reactors to generate steam. The capacity of this plant is therefore estimated based on the total fuel consumption with
Appendix IX A case study based on Option B proposed in Chapter 8

the aid of the rule of thumb for fuel consumption, e.g., ~330 g of standard fuel (~29260 kJ/kg LHV) per kWh for large (e.g. 100~300 MW) pulverized-coal-fired power plants.

For a fuel feed of ~40 t/h in the FBC, as well as 29.4 t/h (with CaO conversion=0.4) in the calciner, the simulated unit is equivalent to a 262 MW fossil-fuel-fired conventional unit.

AIX.6 Sensitivity analysis results:

As sorbent performance is a key factor, sensitivity tests were conducted with variable CaO conversion in the carbonator. The results are shown in Figures AIX.2 and AIX.3. The results show that:

- Increasing CaO conversion leads to a decrease in the CaCO₃ needed, but very gradually after the CaO conversion reaches a certain level, as shown in Figure AIX.2,

- In Figure AIX.3, the total heat available was calculated by adding the heat generated in the FBC and CARBNER and the sensible heat of the CO₂ stream (e.g. 140670 kg/h at 950°C) and of the CO₂-free STACKFLG stream (650°C). If it is assumed that 40% of the total heat can be used to generate electricity (a typical overall thermal efficiency for large PC-fired units). At least ~250 MW of power can be generated, almost the same capacity as for a unit without CO₂ capture based on the same fuel consumption or (or heat). In other words, if 40% overall thermal efficiency can be achieved in a CO₂ capture plant based on this process, the overall power generation per unit mass of fuel consumed is not greatly harmed.

- The total CaCO₃ needed (for both SO₂ and CO₂ removal) in the FBC depends on the sulfur content in the fuel fed to the FBC is shown in Figure AIX.4. Figure AIX.4 shows that the CaCO₃ requirement changes very little because of the much larger amount of CaCO₃ required for CO₂ removal in the carbonator relative to the SO₂ removal. Given
that the molar ratio of carbon to sulfur is very large (e.g. >50) and more sorbents have to be added to the system because only a fraction of the sorbents (e.g. <40%) retains its reactivity to react with CO₂, the sorbent needed for SO₂ removal only accounts for a minor fraction of the total sorbent.

Figure AIX.2 Sensitivity of CaCO₃ feed to average CaO utilization in carbonator for a 262 MW fossil-fuel-fired conventional FBC unit.
Appendix IX A case study based on Option B proposed in Chapter 8

Figure AIX.3 Sensitivity of energy production to average CaO conversion in the carbonator for of a 262 MW fossil-fuel-fired conventional FBC unit.
Appendix IX A case study based on Option B proposed in Chapter 8

Figure AIX.4 Sensitivity of total CaCO₃ needed in FBC on sulfur content in raw fuel fed to the FBC for a 262 MW fossil-fuel-fired conventional FBC unit

AIX.7 Conclusions from case study.

The case study show that a power plant using calcium-based sorbent to capture CO₂ must deal with the following issues:

- The average calcium utilization in the carbonator needs to be maintained at an intermediate level, e.g. 30 to 50%, to appreciably reduce the feed rates of fuel and CaCO₃. A further increase in sorbent performance would not appreciably decrease the feed requirement. From Chapter 7, intermittent hydration using liquid water or even exposure to ambient humid air might help achieve a high level of calcium utilization.
Appendix IX A case study based on Option B proposed in Chapter 8

- A process of this kind would be applicable to high-sulfur fuel in the FBC, as the sorbent needed for desulfurization accounts for only a small fraction of the total sorbent feed. However, for the calciner, the fuel must have a low sulfur content to avoid sorbent deactivation.

- For calcination, it is important to select an appropriate fuel with low sulfur content, to maintain a low level of excess oxygen or to choose alternative ways to provide the heat of calcination.

- Heat exchangers are needed in the carbonator and at the downstream end of the calciner to utilize the sensible heat, and improve the overall thermal efficiency.

- A detailed economic study is needed to provide further information on the viability of alternative CO₂ strategies.
Table AIX.4 Calculation results for all streams in Figure VIII.1 (with CaO conversion to CaCO₃ is assumed as 0.4 in the CARBONER block)

| Stream ID | AIR | BACK | CACO3 | CACOF | EED | CAO | CAOCC | CAOCCO | CO2 | DRAN1 | DRAN2 | FLUE1 | FLUE2 | FLUE3 | FLUE4 | FUEL1 | FUEL2 | INJULN | ER | INCALC | CO2 | OUTCAL | RESOLDS | STACHF | STASHF |
|-----------|-----|------|-------|-------|-----|-----|-------|-------|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|
| Temperature | 300 | 849.96 | 950 | 950 | 950 | 849.96 | 950 | 850 | 850 | 850 | 15 | 15 | 15 | 15 | 300 | 850 | 850 | 850 | 850 | 850 | 850 | 850 |
| Pressure bar | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Mass Frac | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Mass Frac | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Mass Flow kg/h | 28.6085 | 98.1914 | 318.37 | 444.05 | 249.838 | 245514 | 14253.4 | 16045 | 5156.388 | 319327 | 320895 | 425655.08 | 322329 | 58784.11 | 40000 | 29277.93 | 40000 | 29277.93 | 40000 | 40000 | 29277.93 | 40000 | 29277.93 | 40000 |
| Volume Flow cu/m | 47.2908 | 29.9704 | 108.46 | 163596 | 74.712 | 74.2806 | 632142 | 435027 | 1.577867 | 10.8484 | 10.25915 | 10.24976.9 | 10.24976 | 713009.42 | 638431 | 21.72904 | 21468.56 | 17012.46 | 88001.07 | 400311.23 | 237.6171 | 31.54776 | 713701.3 |
| Enthalpy GJ/hr | 28.6085 | 98.1914 | 318.37 | 444.05 | 249.838 | 245514 | 14253.4 | 16045 | 5156.388 | 319327 | 320895 | 425655.08 | 322329 | 58784.11 | 40000 | 29277.93 | 40000 | 29277.93 | 40000 | 40000 | 29277.93 | 40000 | 29277.93 | 40000 |
| Density kg/m³ | 0.60542 | 327.258 | 2944.1 | 2714.31 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 | 3306.2 |
| Mass Flow kg/hr | 28.6085 | 98.1914 | 318.37 | 444.05 | 249.838 | 245514 | 14253.4 | 16045 | 5156.388 | 319327 | 320895 | 425655.08 | 322329 | 58784.11 | 40000 | 29277.93 | 40000 | 29277.93 | 40000 | 40000 | 29277.93 | 40000 | 29277.93 | 40000 |
| CO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| NO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| SO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| H2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CL2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| HCL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| C | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| N2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| H2O | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| O2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CAO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CASO4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| ASH | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Fuel | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Appendix IX.A case study based on Option B proposed in Chapter 8
APPENDIX X PRELIMINARY TEST RESULTS FOR Li₄SiO₄ CARBONATION AND SULPHATION

AX.1 Preparation method of Li₄SiO₄

The preparation method was the same as described in the literature (Kato, 2001; Kato et al., 2002a; 2002b). High-purity Li₂CO₃ (5 grams) and SiO₂ (quartz) (2.03 grams), supplied by Fisher Scientific were blended in a molar ratio of 2:1. Li₂CO₃ particles are less than 30 µm and SiO₂ particles are less than 50 µm. The mixture was ground in a mortar in order to achieve a good mixing. The mixture was then maintained at 1000°C for 8 h in a sealed oven exposed to ambient air. The agglomerated product was then ground mildly before being tested.

The following reaction proceeds to produce Li₄SiO₄,

\[
2\text{Li}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Li}_4\text{SiO}_4 + 2\text{CO}_2 \quad \Delta H_{298K} = 225.7 \text{ kJ/mol} \quad (AX.1)
\]

AX.2 Carbonation test

The Gibbs free energy of the reaction of Li₄SiO₄ carbonation or reaction (AX.2) is shown in Figure AX.1 generated by use of the database of HSC 4.0.

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3 \quad \Delta H_{298K} = -141.9 \text{ kJ/mol} \quad (AX.2)
\]

It is seen that at atmospheric conditions, temperatures higher than 720°C favour calcination in the presence of 100% CO₂ at 1 atm pressure.

An experimental test was performed in the atmospheric thermogravimetric reactor. The carbonation temperature was chosen as 650°C with 100% CO₂. The calcination temperature was 800°C in 100% N₂. Each sorption stage lasted 6 minutes.
Figure AX.1 Ellingham plot for the reaction (AX.2) with isobaric lines for partial pressure of CO₂.

Figure AX.2 presents the cyclic CO₂ capture performance over 15 cycles by plotting the mass increase due to reaction (AX.2) divided by the initial total mass of the sorbent. A very stable, ~16 wt% gain during carbonation was observed in this study. Kato et al. (2002a) reported a gain of ~25 wt% upon carbonating a sorbent at 500°C in 20% CO₂ and balance N₂ where their sorbent was prepared in the same manner as in this work. If the starting solids were all Li₄SiO₄, i.e. the solid-state reaction (AX.1) went to completion, then the conversion of reaction (AX.2) was calculated to have reached ~ 45% over each of the 15 cycles on a molar basis. This intermediate conversion and the lower wt% obtained in this test implies that there might be a
Appendix X Preliminary test results for Li$_4$SiO$_4$ carbonation and sulphation

fraction of Li$_2$CO$_3$ and SiO$_2$ which remained unconverted because of either non-ideal mixing or solid-state reaction kinetics.

Figure AX.2 Cyclic CO$_2$ capture performance and subsequent SO$_2$ capture. Test conditions: carbonation-650°C, 100% CO$_2$; Calcination-800°C, 100% N$_2$; Sulphation-850°C, 2900 ppm SO$_2$, 3% O$_2$, balance N$_2$.

Our test is compared with the literature test in Figure AX.3 where the data in Figure AX.2 are repotted with the mass increase in the 1st cycle taken as 100. The small fluctuation of the curve in this work is probably due to experimental errors. Note, however, that in the test of Kao
Appendix X Preliminary test results for Li$_4$SiO$_4$ carbonation and sulphation

et al. (2002) the preparation method was somewhat different in that pelletization step was performed in the presence of an inorganic binder. Also the test conditions in that case were: carbonation at 600°C in 20% CO$_2$/balance N$_2$, 1 h for each sorption; calcination at 800°C in 100% N$_2$ for 1 hr. Figure AX.3 shows a large difference between the two tests, indicating that more work is needed to understand the effects of preparation method and test conditions.

Figure AX.3 Comparison of cyclic CO$_2$ capture ability with literature test.

As our lithium silicate sorbent showed very good reversibility over 15 cycles and the Li-based sorbents need much lower temperature for regeneration, it appears that this Li-based sorbent is likely to be a better CO$_2$ sorbent. As indicated in Figure AX.1, to achieve efficient carbonation at combustion temperatures (e.g. 850°C), pressurized conditions would be required.
Appendix X Preliminary test results for $\text{Li}_4\text{SiO}_4$ carbonation and sulphation

AX.3 Sulphation test

It is also important to know whether this sorbent is reactive to $\text{SO}_2$ and whether there is a negative effect of $\text{SO}_2$ on $\text{CO}_2$ capture as found for the calcium-based sorbents tested in this thesis project. Since the sulphation reactivity of $\text{Li}_4\text{SiO}_4$ is very scarce in the literature, a sulphation test was carried out with the Li-based sorbent after the 15 cycles of carbonation and calcinations. The sulphation test, performed with 2900 ppm $\text{SO}_2$, 3% $\text{O}_2$ and the balance $\text{N}_2$ at 850°C, gave 21.3 wt% increase due to $\text{SO}_2$ capture over 140 minutes test (see Figure AX.2). The overall test history plotted in Figure AX.4, indicates that sulphation was far from being finished after 140 minutes, suggesting that this sorbent may also be a good $\text{SO}_2$ sorbent. This implies that its good reactivity to $\text{SO}_2$ capture may influence its cyclic $\text{CO}_2$ capture. Further tests are clearly needed to clarify the application of this sorbent to FBC systems.

![Diagram](image)

Figure AX.4 Test history for cyclic $\text{CO}_2$ capture and $\text{SO}_2$ capture. Test conditions: carbonation-650°C, 100% $\text{CO}_2$; Calcination- 800°C, 100% $\text{N}_2$; Sulphation-850°C, 2900 ppm $\text{SO}_2$, 3% $\text{O}_2$, balance $\text{N}_2$. 

319