

CRANFIELD UNIVERSITY

Alissa M. Cotton

**Engineering Scale-Up and Environmental Effects of the
Calcium Looping Cycle for Post-Combustion CO₂ Capture**

School of Applied Sciences

Doctor of Philosophy

Academic Year: 2012 - 2013

Supervisor: Prof. J.E. Oakey and Dr. K. Patchigolla
August 2013

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ABSTRACT

This thesis has addressed several gaps in the knowledge with regards to the calcium looping cycle for CO₂ capture, including identification of engineering challenges associated with the scale-up of the technology to pilot scale and beyond; assessment of changes in sorbent morphology during the pilot scale capture process; and partitioning of elemental impurities in the limestone between the solid and gaseous phase during the CO₂ capture process.

Hydrodynamic investigations identified the optimum superficial velocities required for the reactor in order to optimise solids entrainment and flux, and to minimise gas bypassing. Estimations made in determining how particle attrition would affect minimum fluidisation velocity confirmed a decrease of approximately 0.09m/s for every 5 % reduction in particle size. Amendments made to the exhaust diameter and position, and the loop seals, improved the pressure balance of the system thus enhancing solids transfer.

Reactor and process modifications, including modification of carbonator temperature, and maintenance of temperature above 420°C in standpipes resulted in improved CO₂ capture %. Increasing bed inventory had a positive effect of CO₂ capture % due to an increased Ca looping ratio. Steam addition also benefitted the carbonation process, due to improved sorbent morphology and therefore CO₂ diffusion into the sorbent. SO₂ was considered to have a detrimental effect on CO₂ capture due to pore pluggage, although burner-derived steam had a positive effect in maintaining capture %.

Gaseous elemental emissions from the process were low for all elements, but concentrations of elements in the solid sorbent phase were influenced by bed inventory, implying that filtering systems may be required in industry for the large masses of sorbent required. Concentrations of elements in the sorbent were identified to be below levels typical of cement, with the exception of Ni, implying that there is potential for spent sorbent to be used in the cement industry with adequate mitigation measures in place.

Keywords: Carbon Capture, Limestone, Elements, Cement

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TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGEMENTS.....	iv
LIST OF FIGURES.....	x
LIST OF TABLES	xvii
LIST OF EQUATIONS.....	xix
LIST OF ABBREVIATIONS	xxi
NOMENCLATURE.....	xxii
1 PHD OVERVIEW	1
1.1 Key Gaps in Knowledge and PhD Objectives	2
1.1.1 Scale-up of Calcium Looping Cycle Technology	2
1.1.2 Trace element emissions from the calcium looping cycle.....	4
1.2 Outline of PhD Thesis	6
1.3 Dissemination from PhD Thesis.....	7
2 INTRODUCTION.....	10
2.1 Climate Change Effects due to Greenhouse Gas Emissions	10
2.1.1 International Agreement on Climate Change: Kyoto Protocol	15
2.1.2 Carbon Capture and Storage Policy.....	17
2.2 CO ₂ Capture Technology Systems	19
2.2.1 Post-Combustion.....	20
2.2.2 Oxy-fuel Combustion.....	21
2.2.3 Pre-Combustion	21
2.2.4 Industrial processes	22
2.3 Financial Issues regarding CO ₂ Capture	23
2.4 Transport	25
2.5 Storage	26
2.6 Existing projects demonstrating CCS chain	26
2.6.1 Sleipner	26
2.6.2 In Salah	27
2.6.3 Weyburn.....	27
2.7 CO ₂ Capture Technologies	27
2.7.1 CO ₂ Separation Methods.....	28
2.7.2 High Temperature Solid Looping Cycles	35
3 FACTORS AFFECTING THE CALCIUM LOOPING CYCLE FOR CO ₂	
CAPTURE	41
3.1 Technical and Economic Aspects	41
3.2 Capture Efficiency.....	43
3.3 Partial Pressure	45
3.4 Effect of Temperature	45
3.4.1 Calcination Temperature	46
3.5 Sintering.....	47

3.5.1 Sintering Mechanism.....	49
3.6 Carbonation Temperature.....	50
3.7 Effect of Repeated Calcination / Carbonation Cycles	50
3.8 Attrition	53
3.9 Effect of Sorbent Size	55
3.9.1 Sulphation	57
3.10 Effect of Steam	59
3.11 Limestone type	62
3.12 Calcium Looping Cycle Technology Scale-Up.....	65
3.12.1 University of Stuttgart, Germany	68
3.12.2 INCAR-CSIC, Oviedo, Spain.....	69
3.12.3 CANMET Energy and Technology Centre, Ottawa, Canada.....	69
3.12.4 Technical University of Darmstadt, Germany.....	70
3.12.5 University of Vienna, Austria	70
3.12.6 Ohio State University, Columbus, USA	70
3.12.7 Tsinghua University, China	71
3.12.8 Industrial Technology Research Institute, Taiwan.....	71
4 HYDRODYNAMICS AND FLUIDISATION	72
4.1 Hydrodynamic Scaling	72
4.2 Flow Regime in a Fluidised Bed Reactor	78
4.3 Pressure Change.....	81
4.4 Particle Residence Time Distribution	83
4.5 Gas Bypassing.....	85
4.6 Solids Circulation Rate	87
4.7 Minimum Fluidisation Velocity	89
5 ELEMENT PARTITIONING FROM LIMESTONE AND IN POWER GENERATION PROCESSES	94
5.1 Introduction.....	94
5.1.1 Regulations	95
5.1.2 Effect of elements on cement properties.....	96
5.1.3 Elemental partitioning in energy processes.....	97
5.2 Limestone Impurities.....	99
5.3 Trace Element Partitioning during Energy Processes.....	102
5.4 Thermodynamic Equilibrium Modelling	108
5.5 Industrial Contaminant Removal Processes	110
5.5.1 Flue Gas Desulphurisation	111
5.5.2 Mechanical (Cyclone) Filters.....	111
5.5.3 Fabric Filters	112
5.5.4 Electrostatic Precipitators.....	112
5.6 Summary	113
6 EXPERIMENTAL METHODOLOGY	115
6.1 Cold Model Design	115

6.2 Cold Model Hydrodynamics Experiments	119
6.2.1 Pressure Profile.....	119
6.2.2 Minimum Fluidisation Velocity	119
6.2.3 Solids Flux.....	120
6.2.4 Gas Bypassing	120
6.3 Pilot Scale Hot Reactor.....	120
6.4 Flue Gas Analysis	124
6.5 Sorbent Properties.....	125
6.6 Sorbent Sampling	125
6.7 Sorbent Analysis	126
6.8 CO ₂ Capture Experimental Procedure	126
6.9 Elemental Sampling	126
6.9.1 General flue gas sampling.....	126
6.9.2 Inductively-Coupled Plasma – Optical Emission Spectroscopy.....	129
6.10 Test programme.....	130
7 RESULTS AND ANALYSIS: COLD MODEL	134
7.1.1 Pressure Balance	134
7.1.2 Minimum Fluidisation Velocity	138
7.1.3 Solids Flux.....	142
7.1.4 Gas Bypassing	146
7.1.5 Cold Model Modifications	152
7.1.6 Calciner Exhaust Position	154
7.1.7 Exhaust Diameter.....	155
7.1.8 Gas Distributors	155
7.1.9 Combination of Modifications	158
7.1.10 Pressure Profile.....	159
7.2 4. Conclusions	161
8 RESULTS AND ANALYSIS: CO ₂ CAPTURE OPTIMISATION	163
8.1 Process Optimisation	164
8.1.1 Carbonator Pressure	166
8.1.2 Effect of particle size	167
8.1.3 Effect of temperature.....	169
8.1.4 Effect of bed inventory.....	172
8.1.5 Calciner Gas Distributors	173
8.1.6 Lower Loop Seal Standpipe Blockage.....	174
8.1.7 Further Reactor Modifications	177
8.1.8 Attrition	180
8.1.9 Comparison of results with other pilot scale reactors	186
8.2 Effect of Steam	189
8.3 Effect of SO ₂	195
8.3.1 Effect of SO ₂ – Single Column Batch Tests.....	195
8.3.2 Effect of SO ₂ – Looping Cycle Experiments	199

8.4 Conclusion	205
9 RESULTS AND ANALYSIS: ELEMENT PARTITIONING	207
9.1 Elemental Content in Raw Limestone Sample	207
9.2 Effect of Bed Inventory	208
9.2.1 ICP-MS analysis	209
9.2.2 Major elements	209
9.2.3 Minor Elements	212
9.2.4 Trace Elements	214
9.2.5 Mass Balance	218
9.2.6 SEM-EDS Analysis	220
9.3 Experimental Elemental Partitioning – Effect of Additional Steam	221
9.3.1 Major Elements	221
9.3.2 Minor Elements	224
9.3.3 Trace Elements	225
9.3.4 SEM-EDS Analysis	227
9.4 Experimental Elemental Gaseous Emissions – Effect of SO ₂ Concentration	228
9.4.1 Single column tests	228
9.4.2 Looping Cycle Tests	235
9.4.3 SEM-EDS Analysis	244
9.5 Statistical Analysis	244
9.6 Comparison of solid element concentrations with those found in cement	246
9.7 Comparison of flue gas elemental concentrations with those of cement works and lime kiln emissions limits	248
9.8 ICP-OES analysis of gas samples	252
9.8.1 Elements detected in Carbonator and Calcliner	252
9.8.2 Elements Detected by ICP-OES in the Carbonator Sample Only ..	254
9.9 Thermodynamic Modelling - Sensitivity Analysis	256
9.9.1 Thermodynamic Modelling – Effect of Sorbent Mass	261
9.9.2 Thermodynamic Modelling – Effect of SO ₂ concentration	263
9.10 Conclusion	268
10 DISCUSSION	270
10.1 Efficiency and Engineering Scale Up of the Calcium Looping Cycle ..	270
10.1.1 Pilot Scale Research	270
10.1.2 Industry	271
10.2 Potential for Sorbent to be Used at the Industrial Scale	271
10.3 Elemental Partitioning and Potential for Sorbent to be Used Within the Cement Industry	273
11 CONTRIBUTIONS TO KNOWLEDGE AND FURTHER WORK	276
11.1 Contributions	276
11.1.1 Reactor	278

11.1.2 Technology.....	279
11.2 Implications of Findings	280
11.3 Further Work.....	280
11.3.1 Reactor.....	280
11.3.2 Technology:.....	281
REFERENCES.....	282
APPENDICES.....	318

LIST OF FIGURES

Figure 2-1 Relationship between atmospheric concentrations of CO ₂ and global temperature [26]	11
Figure 2-2 CO ₂ concentrations derived from EPICA and Vostok ice cores. The red bar at the side indicates the evolution of the Mauna Loa measurements. On this time scale, the 50 years of measurements span less than the thickness of the line, so it appears vertical [27]	12
Figure 2-3 IEA predictions for CO ₂ emissions based on different scenarios of technology and policy implementation [32].....	14
Figure 2-4 IEA statistics for fossil fuel use and CO ₂ emissions a) Trend in CO ₂ emissions from fossil fuel combustion; b) Shares of anthropogenic GHG emissions in Annex 1 countries; c) World primary energy supply [33]	15
Figure 2-5 Overview of Carbon Capture, Transport, and Storage [35]	17
Figure 2-6 Methods of CO ₂ capture from fossil-fuel fired power stations [46]	20
Figure 2-7 CO ₂ separation techniques [66]	28
Figure 2-8 Cryogenic CO ₂ separation [46].....	30
Figure 2-9 Pressure swing adsorption of CO ₂ across a molecular sieve [68].....	31
Figure 2-10 CO ₂ Absorption using a liquid or solid sorbent [61]	32
Figure 2-11 Chemical Looping Combustion (adapted from Eide <i>et al.</i> , 2005 [82]).....	36
Figure 3-1 Calcium looping cycle, comprising calcination of CaCO ₃ in the calciner to produce a high-purity CO ₂ stream for transport and storage, after which CaO is transferred to the carbonator for CO ₂ capture, producing CaCO ₃ which is then cycled back to the calciner.....	42
Figure 3-2 Equilibrium partial pressure of CO ₂ over CaO [11]	45
Figure 3-3 Conversion vs number of cycles for experiments carried out at different calcination temperatures [89]	47
Figure 3-4 a) Fresh fracture surface of a calcined limestone; b) Same limestone after 100 calcination / carbonation cycles. Scale bar 2µm [114]	48
Figure 3-5 Decrease in carbon capture capacity with increasing cycles, at increasing temperatures using La Blanca limestone, for calcination time of 10 minutes, carbonation time of 10 minutes and 650°C temperature, in 10% vol. CO ₂ [117]	49
Figure 3-6 Decrease of carbonate conversion with increasing number of carbonation/calcination cycles [127].....	51
Figure 3-7 Textural transformation of CO ₂ sorbent over many cycles, where CaO is shaded light grey, and CaCO ₃ is shaded dark grey [9].....	52
Figure 3-8 Evolution with the number of carbonation / calcination cycles of the maximum carbonation capacity of CaO [90].....	53
Figure 3-9 Effect of Sorbent Size on CaO Sorption Capacity [89]	56
Figure 3-10 Conversion curves vs. time for different particle size . Limestone: La Blanca, pCO ₂ 0.01 MPa, T _{carbonation} 650°C, T _{calcination} 850°C, for 15 minutes. (Left) cycle 1; (Right) cycles 20. Note that the Y-axis is different for both figures [141].....	56
Figure 3-11 Extent of CaO Deterioration for Two Different Limestone in a Reaction Atmosphere of 2200 ppmv SO ₂ in Air at 900°C [123]	59
Figure 3-12 Partial pressure of water vapour over Ca(OH) ₂ [148]	60

Figure 3-13 Relationship between sorbent morphology and conversion in presence of additional steam [150].....	61
Figure 3-14 Effect on CO ₂ capture capacity of CaO for different limestones [155].....	64
Figure 3-15 Effect of dry flue gas and wet flue gas on CO ₂ capture efficiency [169]....	69
Figure 4-1 Comparison between D_{sl} calculated with Equation 4-7 and D_{sl} fitted individually to the experiments [201]	81
Figure 4-2 a) Pressure profile for a cold model, where FR is fuel reactor and AR is air reactor [184]; b) Pressure profile for a cold model, where 1 -11 is air reactor, 12 outlet from cyclone, 13 top of downcomer and 14-18 fuel reactor [190]	83
Figure 4-3 Residence time in the riser versus solids circulation flux, G, for superficial gas velocity, U, in the range 2.5 to 3.5 m/s [207].....	85
Figure 4-4 CO ₂ tracer gas fraction at inlet and outlet of solid injection nozzle [124].....	87
Figure 4-5 Bed pressure drop versus superficial gas velocity, from which U_{mf} is determined [191].....	91
Figure 4-6 Liquid bridge effect between two equal spheres. a = half particle separation [199]	92
Figure 4-7 Effect of pressure and particle size on U_{mf} values for sand and glass particles [213]	93
Figure 5-1 XRF Elemental Analysis of Kelly Rock Limestone [137].....	101
Figure 5-2 Trace element behaviour during combustion [257].....	104
Figure 5-3 Distribution of Pb, Cd, As and Hg in YM coal and its residue after gasification. 1. Ion exchangeable; 2 . Bound to carbonates and Fe-Mn oxides; 3. Bound to organic matters; 4. Stable form; 5. Released into volatile phase [260]	106
Figure 6-1 Cold model diagram of a 25kW pilot-scale CO ₂ capture rig, comprising an entrained flow carbonator (1), cyclone (2), upper loop seal (3), bubbling fluidised bed calciner (4), lower loop seal (5), calciner gas distributor (6), and carbonator gas distributor (7). Hollow arrows denote gas (Air/N ₂) input locations. Not drawn to scale.	116
Figure 6-2 Comparison of the fluidisation regimes for the hot reactor carbonator (●) and cold model carbonator (◆), and for the hot reactor calciner (▲) and cold model calciner (■), adapted from Bischi <i>et al.</i> , 2011 [279], Lim <i>et al.</i> , 1995 [280], where $U^* = Re.Ar^{-1/3}$	119
Figure 6-3 25kW _{th} pilot scale, calcium-looping cycle reactor for CO ₂ capture, comprising air-fired carbonator, oxy-fired calciner, loop seals and cyclones	121
Figure 6-4 a) Carbonator gas distributor comprising eight nozzles; b) Calciner gas distributor comprising twenty nozzles.....	122
Figure 6-5 Typical temperatures in carbonator and calciner during testing, showing carbonator at approximately 600°C and calciner at approximately 900°C.....	123
Figure 6-6 Elemental analysis of Longcliffe SP52 limestone by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Perkin Elmer 400)	125
Figure 6-7 Sampling train comprising series of bubblers through which carbonator flue gas is passed, to sample elemental composition of flue gas	127
Figure 6-8 ICP-OES components and configuration [234].....	129
Figure 7-1 Effect of increasing carbonator flow on carbonator pressure balance, for 4.5 kg CaCO ₃	135
Figure 7-2 Effect of increasing calciner flow on calciner pressure balance, for 4.5 kg CaCO ₃	136

Figure 7-3 Effect of particle size on pressure drop along carbonator for 4.5kg CaCO ₃	136
Figure 7-4 Comparison of predicted and experimental change in pressure across carbonator length.....	138
Figure 7-5 Effect of particle size on minimum fluidisation velocity, U_{mf} , measured at a height of 0.46m up the reactor length, and compared with results from Ryu <i>et al.</i> , 2007 [191]	139
Figure 7-6 Effect of attrition on theoretical U_{mf} values for initial average particle size of 120 μ m and 188 μ m.....	142
Figure 7-7 Effect of bed inventory on solids flux, for a sorbent bed of 4.5 kg and 6 kg, from carbonator to calciner reactor, compared with work by Bischi <i>et al.</i> , 2011 [286]	143
Figure 7-8 Effect of calciner and carbonator gas velocity, and upper loop seal operation (gas velocity of 0.66 m/s when operated), on solids flux, for a lower loop seal fluidisation velocity of 0.66 m/s	145
Figure 7-9 Effect of increasing carbonator and calciner gas velocity, and influence of lower loop seal operation (gas velocity of 0.66 m/s when operated) on solids flux, for an upper loop seal gas velocity of 0.66 m/s	146
Figure 7-10 Effect of lower loop seal gas velocity on gas bypassing from lower loop seal to calciner, for a carbonator gas velocity of 1.91 m/s, calciner gas velocity of 0.23 m/s and upper loop seal gas velocity of 0.66m/s.....	148
Figure 7-11 Effect of calciner gas velocity and loop seal gas velocity on gas bypassing from lower loop seal to calciner, for a carbonator gas velocity of 1.91 m/s	148
Figure 7-12 Effect of carbonator gas velocity for a calciner gas velocity of 0.16 m/s.	149
Figure 7-13 Effect of calciner and loop seal superficial gas velocities on leakage from upper loop seal to calciner, for a carbonator superficial velocity of 1.91 m/s	150
Figure 7-14 Effect of carbonator gas velocity on bypassing from carbonator to calciner, for a calciner gas velocity of 0.23 m/s, and upper and lower loop seal gas velocities of 0.66 m/s.....	151
Figure 7-15 Effect of calciner gas velocity and loop seal gas velocity of gas bypassing from calciner to cyclone, for a carbonator gas velocity of 1.91 m/s.....	152
Figure 7-16 Extent of loop seal sealing before modification with approximately 0.13 kg solids, and after with approximately 0.6 kg solids.....	153
Figure 7-17 Effect of increase mass of solids in lower loop seal on pressure balance	154
Figure 7-18 Calciner exhaust modification from original 45° angle off standpipe, to 90° angle off reactor.....	155
Figure 7-19 Effect of nozzle and gas distributor on carbonator pressure.....	157
Figure 7-20 Effect of gas distributor type on gas by passing throughout the cold model	157
Figure 7-21 Effect of improved sealing of loop seals, on gas bypassing throughout the cold model, for gas velocities of 1.91 m/s in carbonator, calciner gas velocity of 0.23 m/s and 0.66 m/s in loop seals.....	159
Figure 7-22 Effect of modifications to the cold model on the pressure profile of the system, where ● is lower loop seal, ◆ is carbonator, ■ is upper loop seal, and ▲ is calciner	161
Figure 8-1 a) Typical CO ₂ flow rates into and out of the carbonator reactor, and b) associated CO ₂ capture % based on known CO ₂ input and measured output. Error bars are shown based on variance of results. Standard error bars are provided on graph.....	165

Figure 8-2 CO ₂ capture test with burner and loop seal effects	166
Figure 8-3 Measured carbonator pressure for a continuous and batch test, compared with cold model data.	167
Figure 8-4 Effect of particle size distribution on CO ₂ capture % carried out in pilot scale, batch single column, carbonation experiments carried out as part of this study.	168
Figure 8-5 Comparison of CO ₂ capture capacity of 125-250 μ m and 90-125 μ m PSD limestone.	169
Figure 8-6 Initial tests aimed at achieving appropriate carbonator temperatures, showing effect on CO ₂ capture capacity.....	170
Figure 8-7 Effect of carbonation temperature on CaO conversion in a bench scale reactor [121]	172
Figure 8-8 Effect of bed inventory on % CO ₂ capture efficiency, for bed inventory of 4.5 kg, 6 kg and 13 kg.	173
Figure 8-9 Decrease in plenum pressure as calciner gas distributors are individually unblocked.	174
Figure 8-10 a) Image of solid causing LLS blockage; b) XRD analysis of solid causing blockage, confirming presence of Ca(OH) ₂ shown in green and identified on figure..	175
Figure 8-11 a) Lower loop seal entry and exit pressures for calciner gas flow, before and after LLS standpipe blockage was removed. Note different y axis values and units between graphs.	176
Figure 8-12 Calciner exhaust 90° angle bend blockage during attempted steam tests.	177
Figure 8-13 Improved lower loop seal temperature as a result heated element additions.	178
Figure 8-14 Effect of reactor and process modifications on improved CO ₂ capture efficiency made over a series of tests, with test conditions and modifications outlined in Table 8-1.	180
Figure 8-15 Comparison between attrition effects of single column and looping cycle tests with 4.5 kg bed inventory. Standard error bars are present on both curves	181
Figure 8-16 Comparison of BJH analysis of samples taken from carbonator after single column and looping cycle experiment	182
Figure 8-17 Effect of bed inventory on extent of attrition after looping cycle tests	183
Figure 8-18 SEM analysis of samples taken from carbonator after each test: a) 13 kg bed inventory; b) 6 kg bed inventory; c) 4.5 kg bed inventory; d) unreacted limestone. Magnification 1000x. Average test time 120 minutes	184
Figure 8-19 Comparison of BJH analysis of sorbent samples taken from tests run with increasing bed inventor.....	185
Figure 8-20 Effect of additional steam on CO ₂ capture in single column, batch experiments	190
Figure 8-21 EDS analysis of sorbent after testing to show effect of additional steam	191
Figure 8-22 QXRD analysis of sorbent tested with 0 % and 20 % additional steam ..	191
Figure 8-23 SEM analysis of sorbent sampled after testing in single column, for increasing additional steam concentrations: a) 0 % additional steam; b) 5 % additional steam; c) 10 % additional steam; d) 20 % additional steam. Magnification 3000.....	192
Figure 8-24 PSD analysis of sorbent sampled after tests run with 0, 5, 10 and 20 % additional steam.....	193

Figure 8-25 BJH analysis of sorbent sampled after tests run with 0, 5 10 and 20 % additional steam.....	194
Figure 8-26 Effect of increasing SO ₂ concentration on % CO ₂ capture.....	196
Figure 8-27 BJH analysis showing average pore diameter of sorbent sampled from the reactor after each tests, for 0, 1000 and 2000 ppm SO ₂	196
Figure 8-28 PSD analysis of sorbent sampled from the reactor after each tests, for 0, 1000 and 2000 ppm SO ₂	197
Figure 8-29 EDS analysis of sorbent exposed to increasing SO ₂ concentrations in single column experiments.....	198
Figure 8-30 SEM analysis of sorbent exposed to increasing SO ₂ concentrations in single column experiments: a) 0ppm SO ₂ ; b) 1000 ppm SO ₂ ; c) 2000 ppm SO ₂ . Magnification 1000x.....	199
Figure 8-31 Effect of SO ₂ concentration on % CO ₂ capture during pilot scale calcium-looping.....	200
Figure 8-32 Literature and experimental results of carrying capacity and number of carbonation – calcination cycles in bench scale work [90].....	201
Figure 8-33 BET analysis of sorbent taken from reactor after testing with increasing SO ₂ concentrations.....	202
Figure 8-34 PSD analysis of sorbent sampled from reactor after testing with increasing concentrations of SO ₂	204
Figure 8-35 SEM analysis of sorbent from the carbonator after testing for 0, 1000 and 2000 ppm SO ₂ (a-c), and from the calciner after testing for 0, 1000 and 2000 ppm SO ₂ (d-f). Magnification 3000x.....	205
Figure 9-1 Effect of bed inventory on a) increase of solid major elemental concentrations; and b) decrease of solid major elemental concentrations, for bed inventories of 4.5 kg, 6 kg and 13 kg CaCO ₃ . Note change in y axis values between the graphs.....	210
Figure 9-2 Effect of bed inventory on a) increase of flue gas major elemental concentrations; and b) decrease of flue gas major elemental concentrations for bed inventories of 4.5 kg, 6 kg and 13 kg CaCO ₃ . Note change in y axis values between the graphs.....	212
Figure 9-3 Effect of bed inventory on a) increase of solid minor element concentrations, and b) decrease of solid minor element concentrations, for bed inventories of 4.5 kg, 6 kg and 13 kg CaCO ₃ . Note change in y-axis values between the two graphs.....	214
Figure 9-4 Effect of bed inventory on increase of solid trace elemental concentrations, for bed inventories of 4.5 kg, 6 kg and 13 kg CaCO ₃	215
Figure 9-5 Calcite structure: a) single molecule showing stereometric relationships between atoms; b) alternate calcium cations and carbonate anions, showing each Ca ion bonded to 6 O ions [301].....	216
Figure 9-6 SEM-EDS analysis of solid sorbent taken from the carbonator after testing with increasing bed inventory, for bed inventories of 4.5, 6 and 13kg.....	221
Figure 9-7 Effect of additional steam on a) increase in solid major element concentrations; and b) decrease in solid major element concentrations, for 3 kg bed inventory, and additional steam concentrations of 0, 5, 10 and 20 %. Note change in y axis values between the graphs.....	223
Figure 9-8 Effect of additional steam on flue gas major element concentrations for 3 kg bed inventory and additional steam concentrations of 0, 5, 10 and 20 %.....	224

Figure 9-9 Effect of additional steam on solid minor element concentrations, for 3 kg bed inventory and additional steam concentrations of 0, 5, 10 and 20 %	225
Figure 9-10 Effect of additional steam on solid trace elemental concentrations, for 3 kg bed inventory and additional steam concentrations of 0, 5, 10 and 20 %	226
Figure 9-11 SEM-EDS analysis of solid sorbent taken from the carbonator after testing with increasing additional steam concentrations of 0, 5, 10 and 20 %	228
Figure 9-12 Effect of SO ₂ on a) increase of solid major elemental concentrations; and b) decrease of solid major elemental concentrations for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO ₃ . Note change in y axis values between the graphs	229
Figure 9-13 Effect of SO ₂ concentration on flue gas major element concentrations for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO ₃	230
Figure 9-14 Effect of SO ₂ concentration on solids minor element concentrations for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO ₃	231
Figure 9-15 Effect of SO ₂ concentration on flue gas minor element concentrations for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO ₃	231
Figure 9-16 Effect of SO ₂ concentration on solids trace element concentrations for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO ₃	232
Figure 9-17 Effect of SO ₂ (single column batch tests) on particle size distribution of sorbent samples from carbonator, for SO ₂ concentrations of 0, 1000 and 2000 ppm SO ₂	233
Figure 9-18 SEM-EDS analysis of solid sorbent taken from the carbonator after testing with increasing SO ₂ concentrations of 0, 1000, and 2000 ppm SO ₂	234
Figure 9-19 Effect of SO ₂ on a) increase of solid major elemental concentrations; and b) decrease of solid major elemental concentrations for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 13 kg CaCO ₃ . Note change in y axis values between the graphs	236
Figure 9-20 Effect of SO ₂ on increase of flue gas major elemental concentrations for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 13 kg CaCO ₃	237
Figure 9-21 Effect of SO ₂ on a) increase of solids minor elemental concentrations; and b) increase and decrease of flue gas minor elemental concentrations, for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 13 kg CaCO ₃ . Note change in y-axis values between graphs	238
Figure 9-22 Effect of SO ₂ on increase of solids trace elemental concentrations for SO ₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 13 kg CaCO ₃	239
Figure 9-23 a) Effect of SO ₂ (looping cycle) on particle size distribution of sorbent samples taken from carbonator after testing; b) effect on SO ₂ on cumulative PSD of Italian limestone [295]	241
Figure 9-24 SEM-EDS analysis of sorbent taken from carbonator at the end of each test, for increasing SO ₂ concentration of 0, 1000 and 2000 ppm SO ₂	244
Figure 9-25 PCA analysis suggesting relationships between varying bed inventories of 4.5, 6 and 13 kg, and solids elemental concentrations	246

Figure 9-26 Calculated trace gaseous species (MTDATA) for 4.5 kg, 6 kg and 13 kg sorbent	262
Figure 9-27 Calculated solid Mg-based species (MTDATA) for 4.5 kg, 6 kg and 13 kg bed inventory	263
Figure 9-28 Calculated solid Ca-based species (MTDATA) for 4.5 kg, 6 kg and 13 kg bed inventory	263
Figure 9-29 Calculated trace gaseous species (MTDATA) for 0 ppm, 1000 ppm and 2000 ppm SO ₂	266
Figure 9-30 Calculated solid Mg-based species (MTDATA) for 0 ppm, 1000 ppm and 2000 ppm SO ₂	267
Figure 9-31 Calculated solid Ca-based species (MTDATA) for 0 ppm, 1000 ppm and 2000 ppm SO ₂	268
Figure A-1 Published journal paper Cotton <i>et al.</i> , 2013.....	310
Figure A- 2 Published journal paper, Chen <i>et al.</i> , 2012.	311
Figure A- 3 Accepted journal paper, Cotton <i>et al.</i> , 2013.....	312
Figure A- 4 Submitted journal paper, Cotton <i>et al.</i> , 2013.....	313
Figure A- 5 Published conference paper, Cotton <i>et al.</i> , 2013.	314
Figure A-6 EPA Method 29 Sampling train adapted to investigate metals concentration in the carbonator flue gas.	319
Figure A- 7 PCA Effect of bed inventory: Major elements – Solid Phase.....	320
Figure A- 8 PCA Effect of bed inventory: Major Elements – Gas Phase.....	320
Figure A- 9 PCA Effect of bed inventory: Minor Elements – Solid Phase	321
Figure A- 10 PCA Effect of bed inventory: Trace Elements – Solid Phase	321
Figure A- 11 PCA Effect of additional steam: Major Elements – Solid Phase.....	322
Figure A- 12 PCA Effect of additional steam: Major Elements: Gas Phase	322
Figure A- 13 PCA Effect of additional steam: Minor Elements – Solid Phase.....	323
Figure A- 14 PCA Effect of additional steam: Trace Elements – Solid Phase.....	323
Figure A- 15 PCA Effect of SO ₂ (batch test): Major Elements – Solid Phase.....	324
Figure A- 16 PCA Effect of SO ₂ (batch test): Major Elements – Gas Phase.....	324
Figure A- 17 PCA Effect of SO ₂ (batch test): Minor Elements – Solid Phase.....	325
Figure A- 18 PCA Effect of SO ₂ (batch test): Trace Elements – Solid Phase	325
Figure A- 19 PCA Effect of SO ₂ (looping): Major Elements – Solid Phase	326
Figure A- 20 PCA Effect of SO ₂ (looping): Major Elements – Gas Phase	326
Figure A- 21 PCA Effect of SO ₂ (looping): Minor Elements – Solid Phase	327
Figure A- 22 PCA Effect of SO ₂ (looping): Trace Elements – Solid Phase	327

LIST OF TABLES

Table 2-1 Average Carbon Content of Fossil Fuels [29].....	13
Table 2-2 Summary of EU and UK policy and non-policy support for CCS.....	17
Table 2-3 Economic and efficiency comparison of power stations with and without the three types of CO ₂ capture. Costs for capture include CO ₂ compression to 110 bar (11 MPa) but not storage and transport costs. These are very site-specific, but indicative aquifer storage costs of \$10/t CO ₂ would increase electricity costs for natural gas plants by about 0.4 c/kWh [59]	24
Table 2-4 Sorption Capacities of CO ₂ Sorbents adapted from Dasgupta <i>et al.</i> , 2008 [75]	33
Table 2-5 Summary of CO ₂ separation methods.....	34
Table 3-1 Summary of post combustion capture pilot plant reactors, adapted from Dean <i>et al.</i> , 2010 [11]	66
Table 4-1 Scaling law limitations acknowledged in the literature	75
Table 4-2 Particle properties used in cold model investigations	77
Table 5-1 Indicative best available technique (BAT) emission levels for releases to air for a lime works [230].....	96
Table 5-2 Potential metal impurities of interest from Ca-based CO ₂ capture, and associated operability and durability issues, adapted from Finney <i>et al.</i> , 2010 [234] ...	98
Table 5-3 Trace element emissions from Coal [243]	103
Table 5-4 Typical Retention and Enrichment Factors for Trace Elements in UK coals, for exhaust temperatures of approximately 130°C [258].....	105
Table 5-5 Trace element capture efficiencies: field data (facilities utilizing ESP alone for particulate control) [277]	113
Table 6-1 Component values for the hot reactor and cold model, compared with literature data.....	117
Table 6-2 Comparison of Glicksman's full set of scaling law dimensionless parameter values (from which the Simplified Scaling Laws are derived, and as used in this study), with those achieved by Pröll <i>et al.</i> , 2009 [184]	118
Table 6-3 ICP-OES operating parameters, including temperatures and gas flow rates [234]	130
Table 6-4 Cold Model Test Programme	131
Table 6-5 CO ₂ Capture and Elemental Sampling Programme.....	131
Table 6-6 CO ₂ Capture Tests encompassing process and reactor modifications	132
Table 7-1 Comparison of experimentally and theoretically derived U _{mf} values for cold model.....	140
Table 7-2 Percentage change in U _{mf} as a result of attrition-induced reduction in particle size	142
Table 8-1 Test conditions and modifications made in a bid to improve % CO ₂ capture efficiency.....	179

Table 8-2 Comparison of attrition rate and extent of attrition for Longcliffe limestone, compared with work by Jia <i>et al.</i> , 2007 [132]	185
Table 8-3 Comparison of pilot scale calcium looping reactor at Cranfield, with other pilot scale reactors described in the literature. Adapted from Charitos <i>et al.</i> , 2010 [293], Rodriguez <i>et al.</i> , 2011 [291], and Lu <i>et al.</i> , 2008 [8]	188
Table 8-4 Pore surface area and volume analysis of samples from tests in increasing concentrations of additional steam	194
Table 8-5 Comparison of sorbent pore characteristics for pilot scale looping tests and bench scale batch tests in increasing SO ₂ concentrations, using Longcliffe limestone, adapted from Kavosh (2011) [121]	203
Table 9-1 Identification of major, minor, and trace elements in the limestone powder sample used in the calciner-carbonator reactor	208
Table 9-2 Elements found in samples in concentrations < 0.1 ppm, and not considered in analysis	209
Table 9-3 Mass balance for effect of bed inventory, showing elemental partitioning between solid and gaseous phase.	219
Table 9-4 Chemical composition of 310 stainless steel from which the reactor is made	227
Table 9-5 Mass balance for effect of SO ₂ concentration during looping cycle experiments, showing elemental partitioning between solid and gaseous phase.	243
Table 9-6 Comparison of maximum element concentration in solid sorbent for each test, compared with typical concentration in cement. Those concentrations found to be higher in this study than in typical cement concentrations are highlighted in grey	249
Table 9-7 Comparison of maximum element concentration in flue gas for each test, compared with best available technique emissions limits for a cement works and lime kiln [230] [231]	251
Table 9-8 Modal average and maximum intensities of elements found in both the carbonator and calciner flue gases; all values are count rates per second. Adapted from Finney <i>et al.</i> , 2012 [234]	253
Table 9-9 Modal average and maximum intensities of elements found only in the carbonator flue gases; all values are count rates, not concentrations, and do not taken into account background readings, as no instrument calibration took place. Adapted from Finney <i>et al.</i> , 2012 [234]	254
Table 9-10 MTDATA sensitivity analysis results for 9 elements	259
Table 9-11 MTDATA sensitivity analysis results for 21 elements	260
Table A- 1 % CO ₂ Capture Calculations	316
Table A- 2 Example PSD Analysis Results	317
Table A- 3 Example BJH Analysis Results	318

LIST OF EQUATIONS

Equation 2-1	23
Equation 2-2	25
Equation 2-3	25
Equation 2-4	29
Equation 2-5	31
Equation 2-6.....	38
Equation 2-7.....	38
Equation 2-8.....	38
Equation 3-1	41
Equation 3-2	43
Equation 3-3	44
Equation 3-4.....	44
Equation 3-5	44
Equation 3-6.....	45
Equation 3-7	52
Equation 3-8	53
Equation 3-9.....	54
Equation 3-10.....	54
Equation 3-11.....	57
Equation 3-12.....	57
Equation 3-13.....	57
Equation 3-14.....	57
Equation 3-15	58
Equation 3-16	60
Equation 4-1	73
Equation 4-2	73
Equation 4-3	73
Equation 4-4	73
Equation 4-5	73
Equation 4-6	80
Equation 4-7	80
Equation 4-8	81

Equation 4-9.....	82
Equation 4-10.....	84
Equation 4-11.....	84
Equation 4-12.....	84
Equation 4-13.....	87
Equation 4-14.....	89
Equation 4-15.....	90
Equation 4-16.....	90
Equation 4-17.....	90
Equation 4-18.....	90
Equation 5-1.....	105
Equation 5-2.....	105
Equation 5-3.....	109
Equation 5-4.....	109
Equation 5-5.....	111
Equation 5-6.....	111
Equation 6-1.....	124
Equation 6-2.....	124
Equation 6-3.....	128
Equation 7-1.....	137
Equation 7-2.....	137
Equation 7-3.....	138
Equation 7-4.....	155

LIST OF ABBREVIATIONS

AR	Air Reactor
CCR	Carbon Capture Ready
CCS	Carbon Capture and Storage
DEPG	Dimethly Ether of Polyethylene
EMR	Electricity Market Reform
EOR	Enhanced Oil Recovery
EPS	Emissions Performance Standard
ESA	Electrical Swing Adsorption
FBC	Fluidised Bed Combustor
FBR	Fluidised bed Reactor
FGD	Flue Gas Desulphurisation
FR	Fuel Reactor
GHG	Greenhouse Gas Emissions
IGGC	Integrated Gas Combined Cycle
IPCC	Intergovernmental Panel on Climate Change
LLS	Lower Loop Seal
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MTDATA	Metallurgical and Thermodynamic Databank
NPL	National Physical Laboratory
Ofgem UK	Office of gas and electricity markets United Kingdom
PPM	Parts per million
PSA	Pressure Swing Adsorption
PSD	Particle Size Distribution
RTD	Residence Time Distribution
TSA	Temperature Swing Adsorption
TGA	Thermo-gravimetric Analyser
ULS	Upper Loop Seal
UNFCCC	United Nations Convention on Climate Change
ZECA	Zero Emission Coal Alliance

LIST OF NOMENCLATURE

A	Cross-sectional area of carbonator	m ²
A %	Extent of attrition	%
A ₀	Orifice area	m ²
AA	Average ash mass percentage in coal	%
a _{i,j}	Number of units of component i per species j,	-
A _m	Membrane area	m ²
A _s	Area of sampling probe tip	m ²
C	Salt concentration (g/g)	g/g
CA	Tracer volume fraction	-
%C	% CO ₂ capture	%
C _f	Flow coefficient	-
C _{p_e}	Calciner specific heat	J / kgK
C _{so}	Particle discharge coefficient of an opening under outflow condition	-
d _p	Particle diameter	M
D	Bed diameter	M
D _{sr}	Lateral dispersion coefficient	-
E(t)	Residence time of system	S
E _{CO2}	CO ₂ capture efficiency	%
Env	Non-volatile pollutant emission	kg / yr
EP	Energy penalty	-
EP*	Increase in plant input per unit of product or output	-
E _v	Volatile pollutant emission	kg / yr
F	Retention factor in ash	-
f _a	Free active CaO fraction	mol %

F_{Ca}	Calcium looping ratio between reactors	mol / h
F_{CO_2}	CO ₂ flow to the carbonator	mol / h
f_m	Fractional loss of porosity around CaO micrograins	-
f_w	Fractional loss of porosity adjacent to large pores or grain boundaries	-
G	Acceleration due to gravity $m\ s^{-2}$	ms^{-2}
G	Gibbs energy which is to be minimised by varying the values of the $n_{i,j} = 1, 2, \dots, N$;	kJ
G_r	Local solids flux at a distance r from bed centre	$kg\ m^{-2}\ s^{-1}$
G_s	Mass flux of solid	$kg\ m^{-2}\ s^{-1}$
I_A	Grey-scale luminescence of selected area in fluidised bed	-
I_{max}	Maximum grey-scale luminance of activated solids	-
I_{min}	Maximum grey-scale luminance of non-activated solids	-
J	Flux across a membrane	kmol / s
$k_{,i}$	Reaction rate constant	-
L	Bed length	M
$\log P_{CO_2,eq}$	Equilibrium partial pressure of CO ₂	Bar
M	Dimensionless mass turnover	-
m	Geometric scale based on size of reactor	-
M	Number of components in the system	-
M^*	Total mass load	Kg
M_{+75}	Mass of particles in the bed at time t with size $>75\mu m$	Kg
$M_{+75,0}$	Mass of particles in the bed at initial time with size $>75\mu m$	Kg
M_{den}	Mass of solids in dense phase region	kg

	of riser	
M_{dil}	Mass of solids in dilute phase of carbonator	kg
n_{Ca}	Amount of calcium in carbonator	Mol
N	Number of cycles	-
N	Number of species in the system	-
n_i	Amount in moles of species j present in the system, each chemical substance with different phase designation being considered as a distinct chemical species	Mols
ΔP	Pressure differential	bar
ΔP_{dense}	Pressure loss across dense phase region of riser	N/m^2
ΔP_{dilute}	Pressure loss across dilute phase region of riser	N/m^2
PC_{coal}	Trace element weight fraction in the coal	-
P_i	Permeability value for component i	$kmol.m / s.m^2.bar$
PM	Particulate matter emission	kg / yr.
Q	Volumetric flow rate	m^3/s
$Q_{a,b}$	Flow rate of element a in the incoming or outgoing material stream b	$\mu g/min$
Q_b	Flow rate of material stream	(kg/min for solid stream, l/min for liquid stream)
$R_{,a}$	Attrition rate	1 / h
R	Enrichment factor	-
r_i	Number of moles of component i in the system.	mols
r_{Nage}	Fraction of calcium that has been fully calcined N_{age} times after at least $N_{age}-1$ complete carbonations	-

S_d	Cross-sectional area of a downcomer	m^2
S_o	Area of an opening	m^2
T	Temperature	K (Kelvin) (unless otherwise stated)
t_{res}	Mean residence time of solids	s
t_s	Sample collection time	s
u_0	Superficial gas velocity $m\ s^{-1}$	$m\ s^{-1}$
u_j	Chemical potential of species j, which may be a function of some or all of the species amounts in the same phase, and also depends on temperature, pressure and model of the phase under consideration	-
u_{mf}	Minimum fluidisation velocity	$m\ s^{-1}$
U_t	Terminal settling velocity	$m\ s^{-1}$
V	Fluid flow speed	$m\ s^{-1}$
V_{CO2in}	Total known volume of CO_2 introduced into carbonator	litres
V_{CO2out}	Total known volume of CO_2 exiting carbonator	litres
W_d	Circulation rate of solids per unit area of downcomer	$kg / m^2.s$
W_s	Mass of solids collected	kg
X_{ave}	Maximum average carbonation conversion attainable by solids in the system, equivalent number of full carbonation and calcination cycles for a sorbent to reach its current maximum conversion potential (measured as X_{Nage})	mol %
$X_{CaCO3\ (non-sulphated)}$	Fraction of $CaCO_3$ non-sulphated	-
$X_{CaCO3\ (sulphated)}$	Fraction of $CaCO_3$ sulphated	-
X_{carb}	CaO carbonation conversion	mol %
$X_{deactivated}$	Fraction of X deactivated, i	-
X_{max}	Average CaO CO_2 carrying capacity	mol %

X_N	Carbonation conversion in N^{th} cycle	mol %
X_{Nage}	Maximum carbonation conversion achieved in a full carbonation cycle irrespective of the history of the sorbent in terms of previous calcination–carbonation cycles	mol %
ϵ_{mf}	Bed voidage at minimum fluidisation velocity	-
ϵ_u	Voidage at the bottom of an upflowing bed	-
η / μ	Dynamic viscosity	Pa s
η_{CCS}	Efficiency of a plant employing CCS	-
η_{ref}	Efficiency of a plant with no CCS	-
ϕ	Particle sphericity	-
ρ_c	Calcliner specific density	
ρ_f	Gas density	kg m^{-3}
ρ_s	Particle density	kg m^{-3}
δ	Membrane thickness	m
τ_{active}	Active space time	h

1 PHD OVERVIEW

The aim of this PhD work is to contribute to knowledge with regards to the operational development of an advanced method of CO₂ capture using the calcium looping cycle, and in particular, the engineering scale-up and environmental effects of the process. In order for the technology to be developed further, it is widely acknowledged that more research is required on the scale-up of the technology before it can be implemented on an industrial scale. This work has been carried out on a 25kW_{th}, pilot-scale CO₂ capture reactor, seeking to identify potential challenges that may arise when scaling-up from bench to pilot scale and beyond, and how to overcome these challenges and enhance the capture efficiency of the process. In addition, there is currently minimal research available that has investigated the potential environmental effects in terms of elemental partitioning between solid and gaseous phases, that may arise as a result of the technology implementation. Therefore part of this PhD work has aimed to determine elemental release from the pilot scale calcium looping process, and also the potential for spent sorbent to be used within the cement industry. The work was carried out at Cranfield University, UK, during the period 2010 to 2013, as part of the EPSRC-funded 'UK-China H₂ Production Network' project. The work described in this thesis is both experimentally and computer modelling derived.

Global emissions of anthropogenic CO₂ are increasing and it is widely accepted that these emissions are contributing to increased average global temperature and in turn, climate change. In order to minimise further temperature rise, there are international agreements in the form of the Kyoto Protocol, which outline targets for CO₂ emission reductions. The UK has a legally-binding target to achieve an 80% reduction in CO₂ emissions by 2050, based on 1990 levels [1]. It is widely recognised that technology development and implementation is imperative in order to reduce CO₂ emissions and to prevent greater than a 2°C average global temperature rise above 1990 levels, beyond which the effects on the earth's climate would cause 'net negative impacts in many developed countries' [2].

Carbon capture and storage (CCS) is an emerging technology with the potential to mitigate CO₂ emissions from point sources including power plants and industry. The calcium-looping cycle for CO₂ capture employs the use of calcium-based CO₂ sorbents, such as CaO. These sorbents are gaining widespread interest due to their abundance, low cost, high potential CO₂ capture efficiency, reduced risk to the environment compared with other potential CO₂ sorbents, potential for subsequent SO₂ retention from flue gas, and use within the cement industry [3] [4]. The challenge with the calcium looping cycle however, comes in the form of decay in sorbent capture capacity with increasing numbers of capture cycles, and there are issues for the scale-up of the process for industry implementation.

1.1 Key Gaps in Knowledge and PhD Objectives

An extensive literature review has been carried out (available as subsequent chapters 2 - 5) to identify key gaps in the knowledge with regards to the calcium looping cycle for CO₂ capture. The gaps in the knowledge have directed the research presented here and provide the PhD aims and objectives, which were outlined at the start of the work. These objectives are presented below.

1.1.1 Scale-up of Calcium Looping Cycle Technology

A great deal of work is available in the literature with regards to the calcium looping cycle, particularly research at the laboratory and bench scale. In addition, some pilot scale work has been carried out which has further proven that the calcium looping cycle is a viable technology [5] [6] [7] [8], but it is widely acknowledged that further research needs to be carried out, particularly at the pilot scale, in a bid to understand the issues regarding scale-up of the technology for industry. It has previously been noted that caution is required when discussing the use of thermogravimetric analyser (TGA) data to draw conclusions on large scale facilities, due to issues including temperature gradients and fluid dynamics that may arise on scale-up [9] [10]. In addition, more work is required on sorbent degradation and associated sorbent morphological changes [11]. Further to this, the pilot scale calcium looping reactor at Cranfield University had not previously been operated as a

continuous looping cycle, and therefore operation and development of the reactor was required.

PhD Aim 1

To assess the efficiency of the calcium-looping cycle at the pilot scale, and identify potential engineering scale-up issues which may arise.

PhD Objective 1a

To obtain a better understanding of the hydrodynamics of Cranfield's hot CO₂ capture rig through the design and manufacture of a hydrodynamically-scaled cold model. Identify potential changes to hot reactor through cold model testing.

PhD Objective 1b

To explore the use of hydrodynamic data derived from the cold model for improved CO₂ capture performance to ensure that the capture process in the pilot scale reactor can be optimised.

PhD Aim 2

To assess any changes in sorbent morphology during the pilot scale capture process, including the effects of steam and SO₂, and therefore the potential for limestone and the calcium looping cycle to be used at the industrial scale. Identify engineering challenges which may arise at the pilot-scale.

PhD Objective 2a

To assess the change in limestone morphology under the above conditions, using scanning electron microscope (SEM), energy dispersive X-ray spectrometry (EDS), quantitative X-ray diffraction (QXRD) technology and BET/BJH analysis.

PhD Objective 2b

To assess the effect of SO₂ concentration and steam concentration during carbonation on the CO₂-capture capacity of the sorbent.

PhD Objective 2c

To identify engineering challenges which arise at the pilot scale through running the pilot scale reactor, and compare results achieved with those at the bench scale. Identify mitigation measures where possible.

1.1.2 Trace element emissions from the calcium looping cycle

Limestone is a naturally-occurring material, and thereby often contains other contaminant species in the form of trace elements. The high temperature conditions under which carbonation and calcination occur, present opportunities for elements to be released to the environment, thereby representing a potential source of environmental contamination, in addition to that produced from coal combustion. A study of Dutch coal-fired power stations employing flue gas desulphurisation (FGD) concluded that the predominant source of trace elements in the FGD plants were from the use of limestone [12]. A large amount of research has been carried out on the use of limestone in the calcium looping cycle as a method of CO₂ capture, and on elemental emissions from other thermal conversion processes for solid fuel [13] [14] [15] [16] [17], but it is apparent that no work to date has investigated the elemental partitioning that may result from the use of limestone in the calcium looping cycle. Further, the use of thermodynamic equilibrium data has been widely used to report trace element partitioning during energy conversion processes [15] [18] [16] [19], but again, it is apparent that there is no work available in the literature with regards to thermodynamic equilibrium calculations for the calcium looping cycle. Spent CaO sorbent may be subsequently used in the cement industry, but investigation into the elemental concentration of the sorbent is required as different elements can affect different properties of cement.

PhD Aim 3

To investigate elemental partitioning from the use of limestone in the calcium looping cycle, including potential adverse effects to the environment from gaseous emissions in flue gas, and elemental concentrations in the limestone sorbent, and therefore the potential for spent sorbent to be used within the cement industry.

PhD Objective 3a

To assess experimentally the elemental emissions in the flue gas from the pilot scale calcium looping cycle process, during limestone regeneration.

PhD Objective 3b

To assess experimentally the elemental concentration in the sorbent after having been used in the calcium looping cycle, and compare concentrations with those typical for cement.

PhD Objective 3c

To use thermodynamic equilibrium modelling software to support experimental work and determine equilibrium partitioning of elements.

Therefore, the PhD work is presented in three main components in this thesis, with the first part focusing on the hydrodynamic investigation of the pilot scale reactor through the design, operation and development of a full-scale cold model. The second part comprises work carried out on developing, improving and optimising the CO₂ capture efficiency of the pilot-scale reactor, with particular focus on the effects of additional steam, and SO₂, and the resulting effects on sorbent morphology. The third part of this thesis focuses on the elemental partitioning from limestone use in the calcium looping cycle process, and reports on both experimental and thermodynamic equilibrium modelling work.

1.2 Outline of PhD Thesis

An outline of this thesis with a brief description of the content of each chapter is provided below:

- Chapter 2 presents the background to global climate change, and in turn requirements for the calcium looping cycle;
- Chapter 3 presents details on factors affecting the calcium looping cycle, including temperature and impurities, as well as methods of sorbent degradation;
- Chapter 4 provides information on work available in the literature with regards to hydrodynamic investigations of fluidised beds using cold models;
- Chapter 5 presents a literature review of major, minor and trace element emissions from both coal-power generation processes, and processes employing the use of limestone, as well as outlining the effect that certain elements have on cement properties. It also reviews the use of thermodynamic equilibrium modelling for trace elements, and outlines research carried out to date using such software;
- Chapter 6 provides a description of the 25kW pilot scale CO₂ capture reactor at Cranfield University, and outlines the experimental methodology for cold model hydrodynamic investigations, CO₂ capture experiments, and trace element emissions investigations;
- Chapter 7 provides the results and analysis of hydrodynamic investigations carried out in the cold model, from which the optimum experimental conditions were outlined for the CO₂ capture reactor;
- Chapter 8 provides the results and analysis from the development and optimisation of the calcium looping cycle for CO₂ capture. Reactor modifications are discussed, and a comparison is made where possible with bench scale and other pilot scale work. In addition, results from batch scale tests investigating the effects of additions steam as

presented, as are results from batch and continuous tests investigating the effect of SO₂ on the pilot scale calcium looping process;

- Chapter 9 presents work carried out on experimental and thermodynamic modelling of trace element emissions, and provides a bench mark of experimental results against those emissions limits from cement and lime works. In addition, the elemental concentration of the sorbent is compared with those concentrations typical of those found in cement, in a bid to determine whether spent sorbent may subsequently be suitable for use in the cement industry;
- Chapter 10 provides an overall discussion of the results achieved in this study and their relevance to industry and also policy; and
- Chapter 11 provides the final conclusions, contributions to knowledge, and an outline of further work identified from this PhD.

1.3 Dissemination from PhD Thesis

International journal papers published during the course of the work presented in this thesis are outlined below. The first page of each of these papers is available as Appendix A.

- Cotton, A., Patchigolla, K., Oakey, J.E. (2013) 'Hydrodynamic characteristics of a pilot-scale cold model of a CO₂ capture fluidised bed reactor' *Powder Technology* 235, 1060-1069.
- Cotton, A., Patchigolla, K., Oakey, J.E. (2013) 'Minor and Trace Element Emissions from Post-Combustion CO₂ Capture from Coal: Experimental and Equilibrium Calculations' *Fuel* 117, Part A: 391-407.
- Cotton, A., Finney, K.N., Patchigolla, K., Eatwell-Hall, R.E.A., Oakey, J. Swithenbank, J., Sharifi, V. (2013) 'Quantification of trace element emissions from low-carbon emission energy sources: I. Ca-looping cycle for post-combustion CO₂ capture; and II. Fixed bed, air blown down-draft gasifier' *Chemical Engineering Science*, Accepted manuscript, In Press.

The contributions to international conferences during production of the work presented in the thesis are outlined below.

- Cotton, A., Patchigolla, K., Oakey, J.E. (2013) 'Overview of, and experimental methodology for, sorption enhanced hydrogen production' Proceedings of GHGT-11, Kyoto, Japan, *Energy Procedia* 37 2232-2244.
- Cotton, A., Patchigolla, K., Oakey, J.E. 'Effect of steam and SO₂ on pilot scale, post combustion CO₂ capture' IEAGHG 4th Network Meeting on High Temperature Solid Looping Cycles, August 2012, Beijing, China (oral presentation).
- Cotton, A., Patchigolla, K., Oakey, J.E. 'Modelling Environmental Effects of Calcium-based CO₂ Capture', UKCCSC Early Career Researchers Winter School, January 2012, Cambridge, UK (oral presentation).
- Cotton, A., Kavosh, M., Patchigolla, K., Oakey, J.E. 'Calcium Looping Cycle Technology Developments at Cranfield University', IEAGHG 3rd Network Meeting on High Temperature Solid Looping Cycles, August 2011, Vienna University of Technology, Austria (oral presentation and poster).
- Cotton, A., Kavosh, M., Patchigolla, K., Oakey, J.E. 'Technology Scale-Up Effects of the Calcium Looping Cycle', UKCCSC and Nottingham University EngD Summer School, July 2011, Guwahati, India (oral presentation and poster).
- Cotton, A., Patchigolla, K., Oakey, J.E. 'Engineering Issues for Carbon Capture via Calcium Looping Cycle in a 25kW Reactor', Proceedings of 5th International Conference on Clean Coal Technologies, CCT2011, May 2011, Zaragoza, Spain (oral presentation and proceedings).
- Cotton, A., Patchigolla, K., Oakey, J.E. 'Cold Model Design of a 25kW Pilot Scale Carbon Capture Rig', IEAGHG 2nd Network Meeting on High Temperature Solid Looping Cycles, September 2010, Amsterdam, Netherlands (poster).

The journal paper below has been published during the PhD work, and is peripheral to work carried out for this thesis:

- Chen, H., Zhao, Z., Huang, X., Patchigolla, K., Cotton, A., Oakey, J.E. (2012) 'Novel optimized process for utilization of CaO-based sorbent for capturing CO₂ and SO₂ sequentially' *Energy Fuels* 26, 9, 5596–5603.

2 INTRODUCTION

2.1 Climate Change Effects due to Greenhouse Gas Emissions

It is now accepted that the effects of anthropogenic global warming are the result of an increase in greenhouse gas (GHG) emissions produced primarily from fossil fuel combustion, and these are leading to climate change. Here, climate change is defined by the Intergovernmental Panel on Climate Change (IPCC) as ‘a statistically significant variation in either the mean state of the climate or in its variability, persisting for an extended period (typically decades or longer)’ [20]. GHG emissions are continuing to rise from a value of 280 parts per million (ppm) prior to the industrial revolution at the end of the 18th century [21], to a concentration of approximately 389ppm in 2010 [22] (Figure 2-1). More recently, the month of May 2013 saw CO₂ concentrations of 400 ppm recorded [22].

Carbon dioxide has been identified as a prominent greenhouse gas, and its effects on global warming were first determined by Tyndall (1859) [23], whilst Arrhenius (1896) published the first calculations of global warming as a result of anthropogenic CO₂ emissions [24]. Arrhenius (1896) [24] noted that fossil fuels are a significant source of ‘carbonic acid’ (carbon dioxide), and suggested that variations in atmospheric concentrations of carbon dioxide may contribute to long-term changes in climate. In 1990, it was estimated [25] that of the then current greenhouse gas emissions, CO₂ emissions accounted for 80% of the contribution to global warming, a number which is considered to have since risen to greater than 90%.

CO₂ is a naturally occurring gas that contributes to maintaining the earth’s temperature at a level adequate for life. Solar radiation is emitted as visible light and passes through the earth’s atmosphere, which is then reflected by the earth as lower-frequency infrared radiation. Naturally-occurring greenhouse gases allow visible light to pass through the atmosphere, but prevent infrared radiation from leaving the earth’s atmosphere due to the change in frequency, thus maintaining the temperature of the earth.

The earth's temperature has fluctuated throughout time as a result of natural changes. However, it is believed that the increased concentration of anthropogenic CO₂ in the atmosphere is causing the earth's temperature to increase beyond levels that would occur naturally. The relationship between global atmospheric CO₂ concentrations and global temperature is well documented (Figure 2-1), and data from a variety of sources, including modern day thermometers, as well as longer term data from Mauna Loa, corals, tree rings and Antarctic ice core data (Figure 2-2), identify that the earth's global average temperature has increased to a level beyond that which has previously been experienced over the past one thousand years.

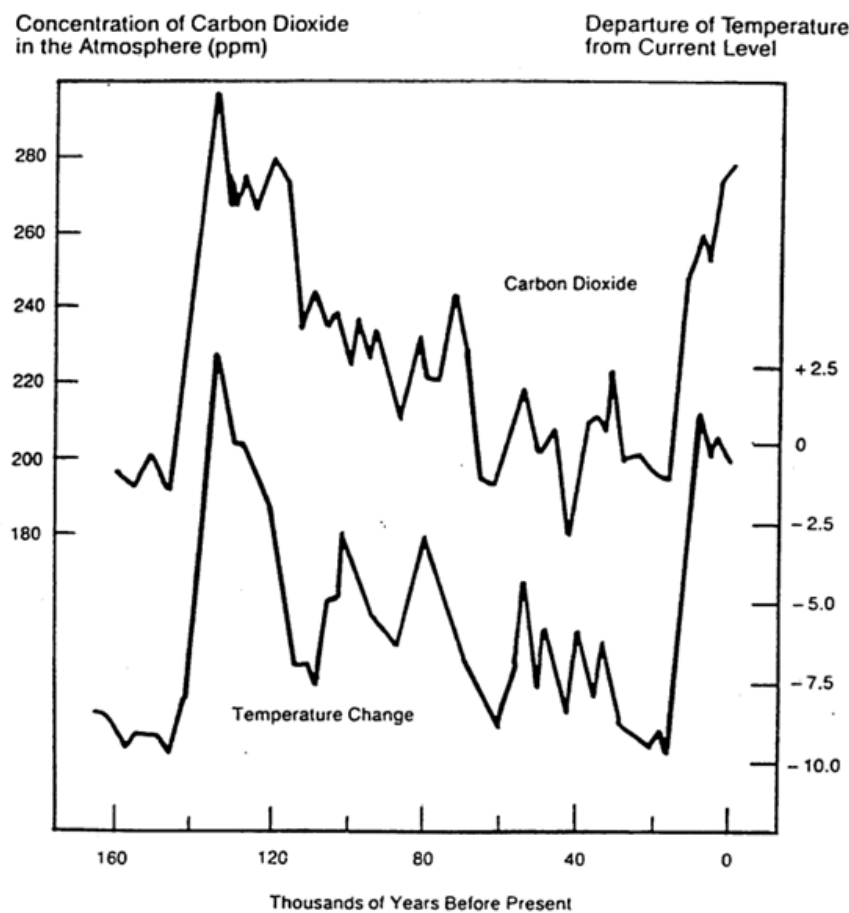


Figure 2-1 Relationship between atmospheric concentrations of CO₂ and global temperature [26].

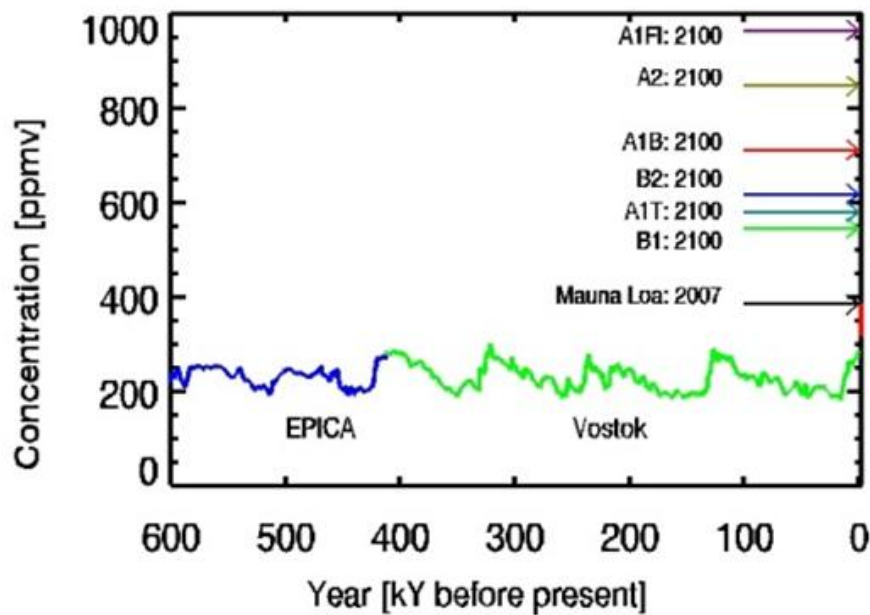


Figure 2-2 CO₂ concentrations derived from EPICA and Vostok ice cores. The red bar at the side indicates the evolution of the Mauna Loa measurements. On this time scale, the 50 years of measurements span less than the thickness of the line, so it appears vertical [27].

It is known that changes in climate as a result of anthropogenic global warming will have environmental and socio-economic implications, including increases in sea level, resulting in widespread inundation of low-lying areas. Further, weather extremes will result in flooding, desertification and drought, leading to crop failures and low water supplies, increases in disease prevalence, extinction of vulnerable species, and human migration, and therefore higher populations in more habitable areas of the world, thus increasing pressure on resources. As well as changes in climate due to atmospheric emissions, other effects of increased atmospheric CO₂ include ocean acidification leading to changes in nutrient cycling and food chains. It is estimated that ocean acidification has increased by approximately 30% since the onset of the Industrial Revolution [28].

Increasing global population, growing economies, and improved quality of living, particularly in non-Organisation for Economic Cooperation and Development (OECD) countries such as China and India which contain large domestic coal

reserves, are driving energy demand and thus CO₂ emissions. The predominant point sources of CO₂ are from large combustion sources such as fossil fuel-fired power stations, as well as cement, iron, steel, pulp and petro-chemical production industries.

Coal is considered a relatively cheap commodity when compared to other non-renewable and renewable energy sources, and is also abundant throughout the world, of which it is estimated that China has approximately one-third of the world's coal reserves. Coal is however the most carbon-intensive of the fossil fuels [29] [30] [31] (Table 2-1).

Table 2-1 Average Carbon Content of Fossil Fuels [29].

Fossil Fuel	Average Carbon Content (Metric Tonnes Carbon per Terajoule, T/TJ)
Coal	25.4
Oil	19.9
Natural Gas (Methane)	14.4

The IEA forecast that by 2030 approximately one third of energy emissions will come from coal, with the growth of coal use in non-OECD countries being a particular issue.

The IEA has made a number of predictions for global temperature rise, based on projected policy and technology implementation. By 2035, if current energy-use trends are followed, a 'catastrophic 6°C' global temperature rise may occur. However, this temperature increase could be minimised to a 2°C rise, if technologies and policies are implemented to reduce CO₂ emissions to the atmosphere (Figure 2-3) [32].

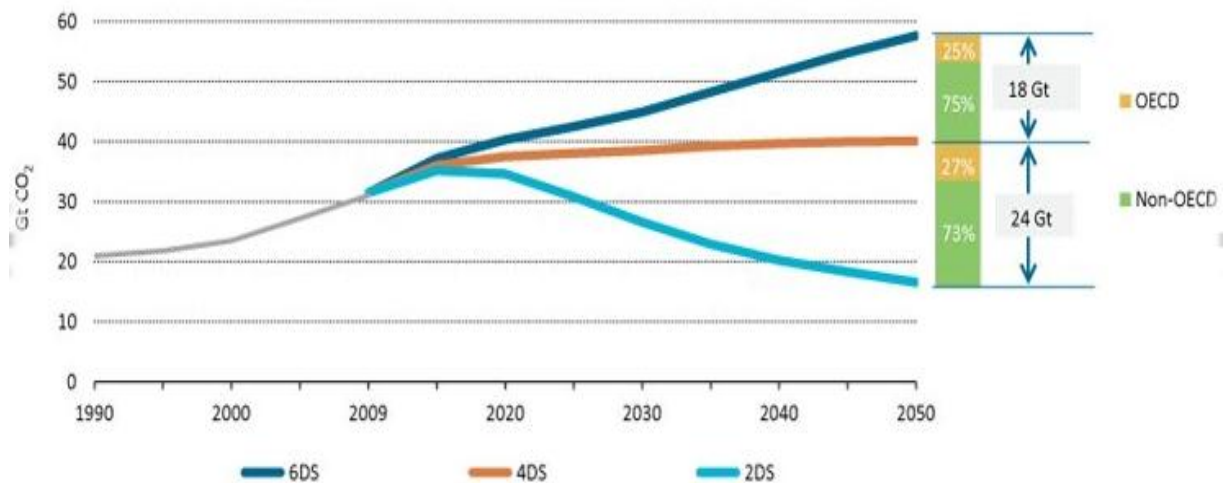


Figure 2-3 IEA predictions for CO₂ emissions based on different scenarios of technology and policy implementation [32].

IEA data provided as Figure 2-4 [33] outlines that CO₂ emissions reached over 28 Gt in 2006 (Figure 2-4a), and that energy production accounted for 83% of anthropogenic greenhouse gas emissions in Annex I (developed and 'economies in transition') countries in 2006, from which 94% of the GHG emissions were CO₂ (Figure 2-4b). Globally, fossil fuels currently account for over 80% of global energy production, and global fossil fuel consumption doubled between 1971 and 2007, as did the use of renewable energy, although in 2007, renewable energy still only accounted for 18% of world energy supply (Figure 2-4c). These factors combined ensure that anthropogenic CO₂ emissions are continuing to rise.

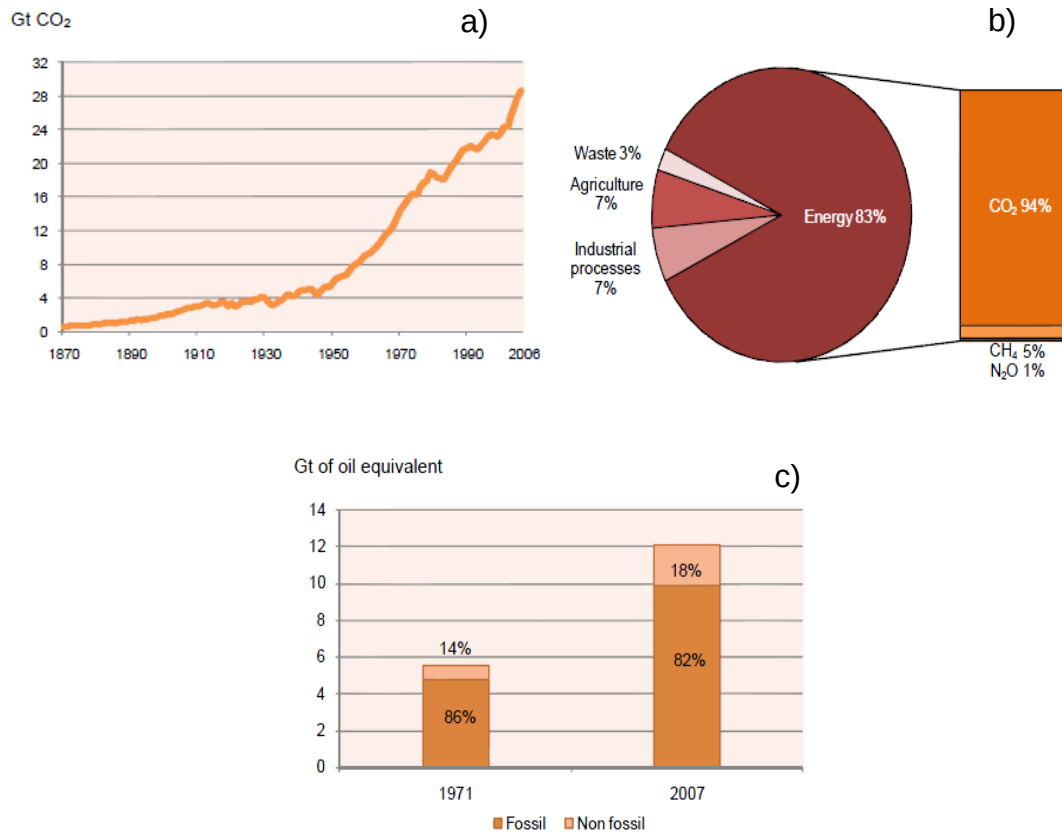


Figure 2-4 IEA statistics for fossil fuel use and CO₂ emissions a) Trend in CO₂ emissions from fossil fuel combustion; b) Shares of anthropogenic GHG emissions in Annex 1 countries; c) World primary energy supply [33].

2.1.1 International Agreement on Climate Change: Kyoto Protocol

The United Nations Framework Convention on Climate Change (UNFCCC) (1992) is an international treaty aimed at 'stabilising greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system'. The Kyoto Protocol (1997) [20] is an update of the original treaty and outlines the legally-binding reductions in GHG (including CO₂) emissions that the 37 industrialised member states must adhere to, for which average targets were a 5% reduction on 1990 levels, between 2008 and 2012. The UK has a legally binding target through the Climate Change Act 2008 [1] to achieve 80% reduction in CO₂ emissions by 2050, based on 1990 levels.

The mitigation measures to be employed in order to accord with the protocol can be classified into three separate groups:

1. Reduce energy use;
2. Increase energy efficiency and therefore reduce carbon intensity; and
3. Technology implementation to enhance carbon sinks e.g. CCS.

A reduction in energy use is likely to be difficult to employ, given the increasing global population and improvements in quality of life aspired to, particularly in non-OECD countries. One quarter of the world's population is thought to have no access to electricity, and therefore if this number is to improve, energy use will have to increase [34].

The second option of improving energy efficiency requires new technology and implementation of renewable energy sources. However, this is both costly, and also renewable energy sources alone are unlikely to meet the predicted increase in future energy demand. Across the majority of the world, fossil fuels, of which coal in particular, are cheaper in price and more abundant than renewable energy sources, therefore use of, and reliance on fossil fuels is projected to rise.

The third mitigation option of technology implementation for carbon sinks, such as the use of carbon capture and storage (CCS), is considered the most achievable and the fastest option to reduce anthropogenic CO₂ emissions to the atmosphere.

Carbon Capture and Storage

CCS is an emerging technology, which has the potential to remove CO₂ emissions from large, point combustion sources, such as power stations, in a bid to reduce releases of point-source, anthropogenic CO₂ emissions to the atmosphere. The process comprises three main steps, namely the capture of CO₂ emissions from industrial flue gas; compression of the CO₂ up to approximately 8 MPa depending on technology used, and subsequent transportation via pipeline or ship; and storage in a permanent sub-surface site (Figure 2-5).

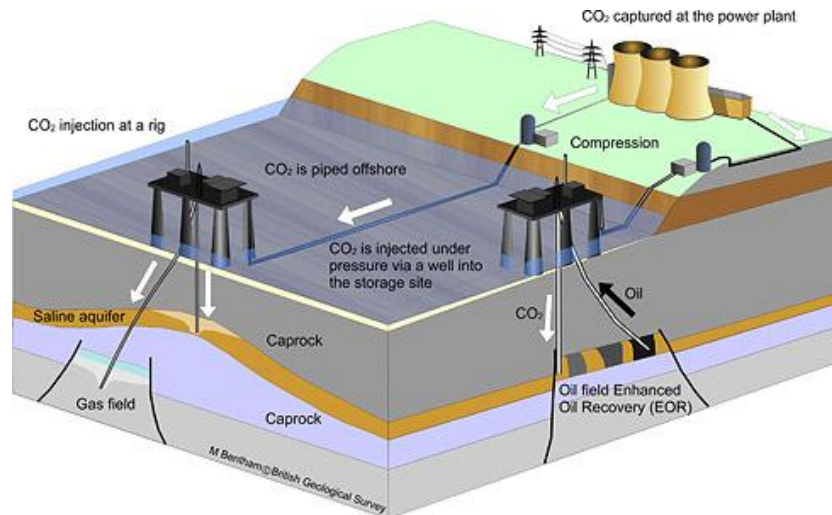


Figure 2-5 Overview of Carbon Capture, Transport, and Storage [35].

2.1.2 Carbon Capture and Storage Policy

CCS is recognised as a viable technology to reduce greenhouse gas emissions from industry. European Union (EU) and UK policy and support for low carbon technology, including CCS implementation, is outlined in a number of policy documents, a summary of which is provided as Table 2-2.

Table 2-2 Summary of EU and UK policy and non-policy support for CCS.

Policy	Support for CCS
EU Directorate-General for Climate Action 2010 [36]	Emissions Trading System - prices carbon emissions, so stimulating the development of technologies which avoid them NER300 funding programme - provides funding for large-scale demonstration of low carbon energy technologies Strategic Energy Technology Plan (SET Plan) - aims to accelerate development and deployment of cost-effective low carbon technologies through research, development and demonstration of low carbon technologies.
UK Electricity Market Reform: Policy Overview 2012 [37]	Outlines need for decarbonisation, security and affordability of energy supply. States gas will play an important long term role in energy supply, and coal-fired power stations to only be built with CCS.
UK Energy Act 2011 [38]	Outlines measures to improve energy efficiency and energy security, and enable low-carbon technologies.
UK Electricity Market Reform	Introduces Carbon Floor Price to reduce uncertainty, and encourage investment in low carbon technology. States

White Paper (2011) [39]	no new coal-fired power stations are to be built without CCS, and anticipates that following electricity market reform (EMR), CCS will be widely deployed on existing and new fossil fuel power plants. Emissions Performance Standard (EPS) set at 450g CO ₂ /kWh introduced to enforce this. CCS included in £110 billion the UK Office of Gas and Electricity Markets (Ofgem) has estimated is required for decarbonisation of electricity, and associated EMR.
UK Overarching National Policy Statement for Energy Infrastructure (EN-1) (July 2011) [40]	States all commercial scale (at or over 300 MW) combustion power stations (including gas, coal, oil or biomass) have to be constructed Carbon Capture Ready (CCR); and new coal-fired power stations are required to demonstrate CCS on at least 300 MW of the proposed generating capacity.
UK Energy Act 2010 [41]	Introduces new CCS incentive to support construction of four commercial-scale CCS demonstration projects in the UK and the retrofit of additional CCS capacity to these projects should it be required at a future point. Requires UK Government to prepare regular reports on progress made on decarbonisation of electricity generation in Britain, and development and use of CCS.
UK Energy Act 2008 [42]	Updates energy legislation to reflect the availability of new technologies, such as CCS.
Climate Change Act 2008 [1]	Legally binding target of at least an 80% cut in greenhouse gas emissions by 2050 based on 1990 levels, to be achieved through action in the UK and abroad. Further to this, a reduction in emissions of at least 34% is required by 2020.
UK Energy White Paper (2007): Meeting the Energy Challenge [43]	States coal will play a significant role in global electricity generation for foreseeable future, and identifies CCS as a potential measure to help the UK achieve requirements of Climate Change Act 2008). Promotes further research into CCS, and its employment at commercial-scale.
UK Energy White Paper 2003: 'Our Energy Future: Creating a Low-Carbon Economy' [44]	Identifies CCS as a potential measure to help UK achieve requirement of Climate Change Act 2008, and in turn promotes further research into the technology.
Non-Policy Support for CCS:	
UK CCS Commercialisation Programme	UK Government allocated £1billion funding for development of first commercial-scale CCS project to support practical experience in design, construction and

Competition [45]	operation of CCS. This will enable private sector electricity companies to build CCS-equipped fossil-fuel power stations in the future, without Government capital subsidy, and at an electricity market price that is competitive with other low carbon generation technologies.
International Panel on Climate Change: Special Report on Carbon Capture and Storage [46]	Outlines that new and emerging CCS technology can 'significantly reduce CO ₂ capture costs and associated energy requirements', but states research is required into technical details for emerging technologies, including pilot-scale testing, and the environmental issues associated with CO ₂ capture and other contaminants in the systems.
Stern Review on the Economics of Climate Change [47]	Identifies CCS as a promising low-emission energy technology, for use within the power, cement and petrochemical industries.

The policy and published reports outlined above demonstrate the support for CCS and confirm its role in reducing CO₂ emissions, but acknowledge that further work is required for industrial implementation of the technology.

2.2 CO₂ Capture Technology Systems

There are three routes for CO₂ capture from fossil-fuel power stations, in addition to industrial CO₂ removal processes (Figure 2-6). These comprise post-combustion, pre-combustion, and oxy-fuel capture, and are described in further detail below.

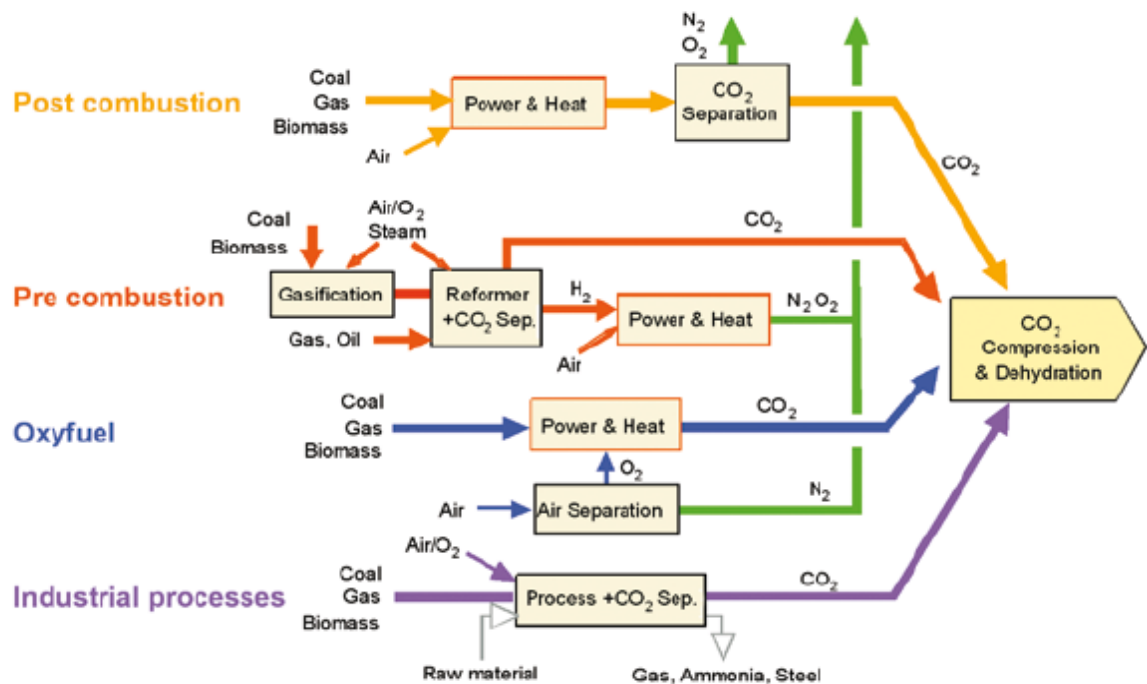


Figure 2-6 Methods of CO₂ capture from fossil-fuel fired power stations [46].

2.2.1 Post-Combustion

Post-combustion CO₂ capture treats flue gases that result from the combustion of a fuel in air, producing a flue gas containing approximately 3-15 % CO₂ (depending on whether natural gas or coal is used as fuel) as well as H₂O, N₂, SO_x, NO_x and particulates as other products. The heat resulting from the fuel combustion is used within a steam turbine to generate electricity. The resultant CO₂-containing flue gas is passed through a chemical sorbent, from which CO₂ is removed from the gas, compressed, and transported to a sub-surface storage reservoir. The CO₂-depleted flue gas with typically 80% CO₂ removed [48], is released to the atmosphere. The sorbent may typically be a solvent such as amines, including monoethanolamine, or more recently it has been suggested that CaO can be used for this step in a process known as calcium looping [9]. The low pressure (~0.1 MPa) at which the flue gas is at following post-combustion CO₂ capture represents a technical challenge, due to the requirement for compression of the captured CO₂ to allow it to be piped to a storage site. However, the key benefit of this method of capture technology is

that it can be retrofitted to existing power plants, thereby eliminating the requirement for expensive new-builds [49].

2.2.2 Oxy-fuel Combustion

Oxy-fuel combustion requires the burning of a fuel in nearly-pure oxygen rather than air, resulting in a flue gas comprising predominantly CO₂ (80-98 % depending on fuel and system used [50]) and H₂O, due to the absence of air, and hence N₂. This approach therefore represents an opportunity for near-100% CO₂ capture. If fuel is burnt in pure oxygen, the flame temperature can be excessively high for that required in a power station, but the CO₂ and/or H₂O-rich flue gas can be recycled to the combustor in order to moderate the temperature. The CO₂ is generally cooled to around 50°C and compressed to approximately 3 MPa for processing [51]. Oxygen is usually produced by low temperature (cryogenic) air separation and novel techniques to supply oxygen to the fuel, such as membranes and chemical looping cycles are being developed. The use of oxygen alone for combustion means that boiler sizes can be reduced, and NO_x control equipment is not required [52]. However, a key issue with the technology is ensuring that there is minimal air influx which would reduce the efficiency of the process, meaning that an air separation unit is required which increases the financial cost of the technology. In addition, high concentrations of SO₂ in the exhaust gas stream may cause equipment corrosion, and furthermore the technology is the least mature of the three capture options [52]. Oxy-fuel for pulverised coal combustion is considered to have similar costs and efficiencies to post-combustion capture [52] [53].

2.2.3 Pre-Combustion

Pre-combustion CO₂ capture comprises gasification of coal or some other hydrocarbon feedstock, or reforming of natural gas in oxygen or air, to create a synthetic gas ('syngas') comprising CO and H₂. In a 'water-gas shift reaction' the CO produced is reacted with steam in a catalytic reactor to produce CO₂ and more H₂, from which the CO₂ content may typically be 15-60 %, at a pressure of 2-7 MPa [50]. CO₂ can then be separated from the gas stream using a chemical or physical sorbent, such as a metal oxide or a membrane, to

produce a pure CO₂ stream for transport and storage. The pure stream of H₂ produced may be used for fuel cells or other applications, or in a turbine for electricity production. This process cannot be retro-fitted to existing power plants and is therefore primarily suitable for Integrated Gas Combined Cycle (IGCC) plants.

As CO₂ and other pollutants are removed prior to combustion, precombustion capture is considered to have potential to be the most efficient and cost-effective of the three capture technologies, particularly with the further development of IGCC plants [54] [55], and it is considered that the energy requirements for precombustion may be half of that required for post-combustion capture. However, in addition to the relatively low availability and high capital cost of IGCC plants [56], the efficiency of H₂-burning turbines is generally lower than that of natural gas-burning turbines, the water gas shift reaction incurs an energy penalty due to high temperatures required, and efficiency losses may be lost during gasification of solid or liquid fuels, although it is anticipated that future technology improvements will improve these efficiency losses [53].

2.2.4 Industrial processes

The cement industry is the second highest CO₂ emitting sector behind the power sector, with total worldwide emissions of 932 MtCO₂ yr⁻¹ [46]. Due to the reasonably high concentrations of CO₂ (15-30 % volume) in the flue gas from cement plants, post combustion capture is considered suitable CO₂ capture technology, particularly as it could be retrofitted to existing plants. Oxy-fuel combustion capture is also considered a viable alternative [46].

Natural gas typically contains at least 4% volume CO₂, which although is a lower concentration than many other industries, still represents an ideal opportunity for CO₂ capture due to the large quantities of natural gas produced each year, with global demand at 3,284 billion m³ in 2010 [57]. Chemical solvents, physical solvents and membranes are typically used for CO₂ removal from natural gas (gas sweetening), with two demonstration CO₂ capture plants,

Sleipner and In Salah (Section 2.6.1 and 2.6.2 respectively), both capturing and storing CO₂ from natural gas production [46].

Iron and steel production represents an opportunity for oxy-fuel firing with CO₂ capture, by feeding the blast furnace with pure O₂ and recycled top gas instead of conventional air. Furthermore, pre-combustion capture could be used to convert a fossil fuel to H₂ from which CO₂ could be captured, and the H₂ could be used to reduce the iron ore. It is anticipated that capture rates of 90-95 % could be achieved [46].

2.3 Financial Issues regarding CO₂ Capture

CO₂ capture requires an additional input of energy in order for the capture process to occur, and therefore increases the cost of energy production. As a result of this, the capture of CO₂ is generally the most costly part of the CCS process, and therefore for investors, the part that carries most risk. The cost of capture depends upon a number of factors including, the fuel used and associated price fluctuations, capture technology and maturity, concentration of CO₂ in the flue gas stream, CO₂ sorbent (discussed in further detail in Section 2.71.), and location of the power plant. Table 2-3 below outlines an economic and efficiency comparison of gas- and coal-fired power stations, with and without the three different types of capture technology. In order to carry out economic comparisons of the capture technologies, the term ‘Cost of CO₂ avoided’ is used, which takes into account the cost per mass of CO₂ that is captured, and compares for a plant with no capture, and with capture technology (Equation 2-1) [58].

$$\text{Cost of CO}_2 \text{ Avoided} = \frac{(\text{COE})_{\text{capture}} - (\text{COE})_{\text{ref}}}{(\text{CO}_2/\text{kWh})_{\text{ref}} - (\text{CO}_2/\text{kWh})_{\text{capture}}} \quad \text{Equation 2-1}$$

Efficiency is also an important indicator when comparing technologies: the more efficient a process, the fewer resources required, and the lower the cost. Table 2-3 identifies that for coal-fired plants, oxy-fuel and post-combustion capture have the higher thermal efficiencies at 35.4 and 34.8 % Lower Heating Value (LHV) respectively, whilst in terms of Cost of CO₂ avoided, pre-combustion

capture has the lowest cost, followed by post-combustion capture with values of 23 and 34 \$/t CO₂ respectively.

Table 2-3 Economic and efficiency comparison of power stations with and without the three types of CO₂ capture. Costs for capture include CO₂ compression to 110 bar (11 MPa) but not storage and transport costs. These are very site-specific, but indicative aquifer storage costs of \$10/t CO₂ would increase electricity costs for natural gas plants by about 0.4 c/kWh [59].

Technology	Thermal efficiency (%) (LHV)	Capital cost (\$/kW)	Electricity cost (c/kWh)	Cost of CO ₂ avoided (\$/t CO ₂)
Gas-fired plants				
No capture	55.6	500	6.2	–
Post-combustion capture	47.4	870	8.0	58
Pre-combustion capture	41.5	1180	9.7	112
Oxy-combustion	44.7	1530	10.0	102
Coal-fired plants				
No capture	44.0	1410	5.4	–
Post-combustion capture	34.8	1980	7.5	34
Pre-combustion capture	31.5	1820	6.9	23
Oxy-combustion	35.4	2210	7.8	36

In terms of energy penalties, and therefore plant efficiency, a number of studies have been carried out to ascertain the reduction in power plant output as a result of employing CCS, which has been done based on the use of Equation 2-2 [60].

$$EP = 1 - (\eta_{CCS} - \eta_{ref})$$

Equation 2-2

Where EP is energy penalty, η_{CCS} is the efficiency of a plant employing CCS, and η_{ref} is the efficiency of a plant with no CCS.

Rubin *et al.*, 2007 [60] provides an alternative equation (Equation 2-3) to define energy penalty, based on change in net plant heat rate, or efficiency (η), but also taking into account resource and environmental implications. This therefore could be considered to be a more accurate method of measurement by taking into account life cycle analysis of the electricity production process with inherent CCS.

$$EP^* = \frac{EP}{(1-EP)} = (\eta_{CCS} - \eta_{ref}) - 1$$

Equation 2-3

Where EP^* is the increase in plant input per unit of product or output.

2.4 Transport

Transport of CO_2 from point source of capture to sub-surface reservoir is required. Pipeline is considered the most efficient and economical method of transport, although transport by ship is also feasible when volumes are small, or the distance is too long (over 1000-1500 km [61]) for pipelines to be economical. For pipeline transport the captured CO_2 is typically compressed to a pressure of 8MPa or above at room temperature, so that it is at dense phase (i.e. liquid), which makes transport more efficient and requires smaller pipelines than if it were to be transported as a gas [46]. It is anticipated that for the UK in particular, redundant natural gas pipelines could be used to transport CO_2 from capture sources to North Sea sub-surface storage reservoirs.

Transport via ship is considered to be similar to that of the ship transport of liquefied petroleum gas (LPG), for which there is considered a wealth of experience. The preferred conditions under which CO_2 would be transported by ship is in liquid phase at a temperature lower than ambient, and pressures higher than atmospheric. The design parameter is around -54°C per 0.6 MPa to

-50 °C at 0.7 MPa for transporting a CO₂ volume of approximately 22,000 m³ [46].

Transport of CO₂ by pipeline has been widely carried out, particularly in the US where CO₂ has been extensively used for enhanced oil recovery (EOR). There were approximately 6000 km of CO₂ pipelines in the US in 2008, a figure which is considered to have increased since [62].

2.5 Storage

Storage of CO₂ takes place in sub-surface reservoirs several kilometres beneath the surface, in areas which have specific geology to ensure CO₂ does not migrate from the original storage site. Generally, CO₂ will be injected into saline aquifers or exhausted oil and gas fields, which comprise a porous rock overlain by a layer of impermeable rock (caprock). Overtime, the CO₂ will move through the porous rock where it will become trapped within the pores, in a process known as 'residual storage'. Some CO₂ may dissolve in surrounding water, causing density to increase and the water to sink, thus trapping the CO₂ in what is known as 'dissolution storage'. Over time mineral storage may also occur whereby the CO₂ irreversibly reacts with a metal oxide rock formation to form stable metal carbonates. Therefore, within a storage site, there may be several chemical reactions which take place over time, resulting in the trapping and permanent storage of CO₂.

2.6 Existing projects demonstrating CCS chain

There a number of demonstration projects which have been capturing, transporting and storing CO₂ for a length of time. A summary of a selection of these projects is provided below, which demonstrate that the CCS process has been successful to date.

2.6.1 Sleipner

The Sleipner gas field located off the Norwegian coast in the North Sea was one of the world's first capture and storage demonstration sites. The natural gas produced from the field contains up to 9% CO₂, which must be reduced to 2.5%

for commercial reasons. Norwegian taxes made it more economically viable for the CO₂ to be stored, rather than released to the atmosphere. Therefore, the excess CO₂ is removed from the natural gas using amine technology, and is injected into, and stored within a deep saline aquifer approximately 1km beneath the sea bed. It has been active since 1996, and has to date stored 8-9 Mt CO₂, from which no leakage has been identified.

2.6.2 In Salah

CCS at In Salah, Algeria has been in operation since 1994, and captures and stores CO₂ produced from on-site natural gas production. Amine technology is used for the capture process, and the CO₂ is compressed to approximately 185 bar in order to inject it into the low permeability sandstone storage aquifer. Three million tons of CO₂ have so far been stored securely. In 2007, monitoring data suggested migration of a CO₂ plume and subsequent leakage from an old appraisal well drilled in 1980, and lacking well integrity, leading to temporary suspension of injection. Estimates suggest leakage of less than 1 tonne CO₂ occurred, and the well from which the leak occurred was fully decommissioned and injection and storage was successfully recommenced [63].

2.6.3 Weyburn

Beulah, North Dakota is the site of a coal gasification plant and has been employing CCS since 2000. Rectisol (physical solvent) is used to separate the CO₂ from the feed gas stream, which is then transported via a 330 km pipeline to Weyburn, Canada where it is used for Enhanced Oil Recovery (EOR). Despite suggestions that leakage was occurring from the storage site, allegations of which were subsequently learned to be unfounded, monitoring has shown that the geological storage site is suitable for long-term CO₂ storage [64].

2.7 CO₂ Capture Technologies

Post-combustion CO₂ capture is considered the most advanced, and widely demonstrated of the three capture technologies. The reason for this is that the technology is widely established in the natural gas industry, in removing CO₂

and H₂S impurities from the natural gas [65]. Further, post-combustion capture technology is the only CO₂ capture technology which can be retrofitted, perhaps making it currently the most attractive for demonstration projects as not as much financial investment is required. There are a number of technologies available to separate CO₂ from flue gas in capture systems, and these are described in further detail below.

2.7.1 CO₂ Separation Methods

There are a number of techniques that are used and being developed to separate CO₂ gas from an industry flue gas. As shown in Figure 2-7, these can be categorised into membrane, cryogenic, adsorption, and absorption technology. In addition, the use of micro-algae for CO₂ capture has also been investigated.

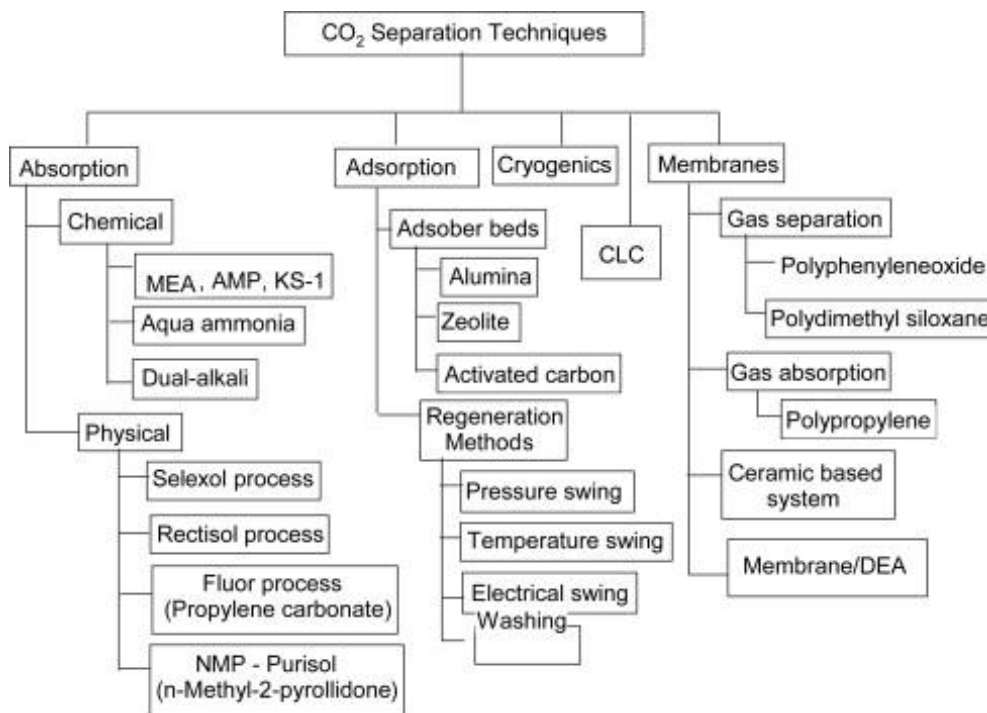


Figure 2-7 CO₂ separation techniques [66].

2.7.1.1 CO₂ Separation with membranes

Membranes used for CO₂ capture are usually specially manufactured to allow the selective permeation of particular gases, such as CO₂, generally driven by a pressure difference, based on Fick's Law (Equation 2-4) [67].

$$J = \frac{P_i}{\delta} A_m \Delta P$$

Equation 2-4

Where J is the flux across the membrane (kmol/s), P_i is the permeability value for component i ((kmol.m/ (s.m².bar)), δ is membrane thickness (m), A_m is the membrane area (m²), and ΔP (bar) is the pressure differential between the feed side and permeate side.

Membranes are usually ceramic, metallic or polymeric, and allow adsorption of certain molecules on the surface, which then diffuse through to the other side of the membrane, where it is then desorbed under different conditions. Due to the high pressures required, these systems are considered costly in post-combustion capture systems due to the low pressure and low concentration at which CO₂ is produced. The technology has not been used commercially for CCS, although it has been used widely for CO₂-recovery from natural gas processing [67].

2.7.1.2 Cryogenic separation

Cryogenic separation of CO₂ involves the flue gas being converted to liquid form through a series of steps involving compression, cooling and expansion. Once in liquid form, it can be distilled in a distillation column, thus separating out the individual components present in the original gas e.g. CO₂ and N₂ (Figure 2-8). Refrigerated separation can also be used to remove impurities from gases, and also for removing CO₂ from syngas that has undergone shift conversion of CO to CO₂. Cryogenic separation is generally used for high purity (>90 %) CO₂ stream, and therefore is more appropriate for pre-combustion or oxyfuel combustion than post-combustion.

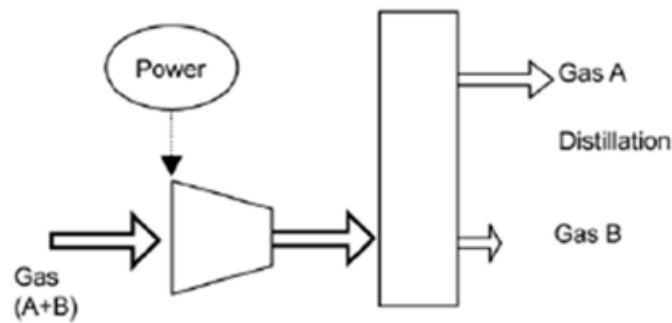


Figure 2-8 Cryogenic CO₂ separation [46].

2.7.1.3 Adsorption

CO₂ is adsorbed onto the surface of an adsorbing agent, such as a zeolite or activated carbon, otherwise known as ‘molecular sieves’. Following adsorption, the pressure or temperature of the vessel is changed to release a high purity CO₂ gas stream for capture, and to regenerate the sorbent, in a process known as Pressure Swing Adsorption (PSA) (Figure 2-9) or Temperature Swing Adsorption (TSA). PSA is generally the focus of research due to the shorter time frames required when compared to TSA which requires longer cycle times to heat sorbent particles for regeneration [46]. A relatively new concept with regards to adsorption is the use of electricity in releasing CO₂ from adsorption materials, in what is known as Electric Swing Adsorption (ESA). An electric current is applied to the CO₂-containing gas column, thus producing thermal energy to release the CO₂ in a process similar to TSA. ESA however requires an input of energy to produce the current, whereas in TSA, the heat is provided from waste gases. ESA technology is considered suitable for natural gas-fired power plants, due to the lower CO₂ concentrations typically present in the flue gas (approximately 5 %).

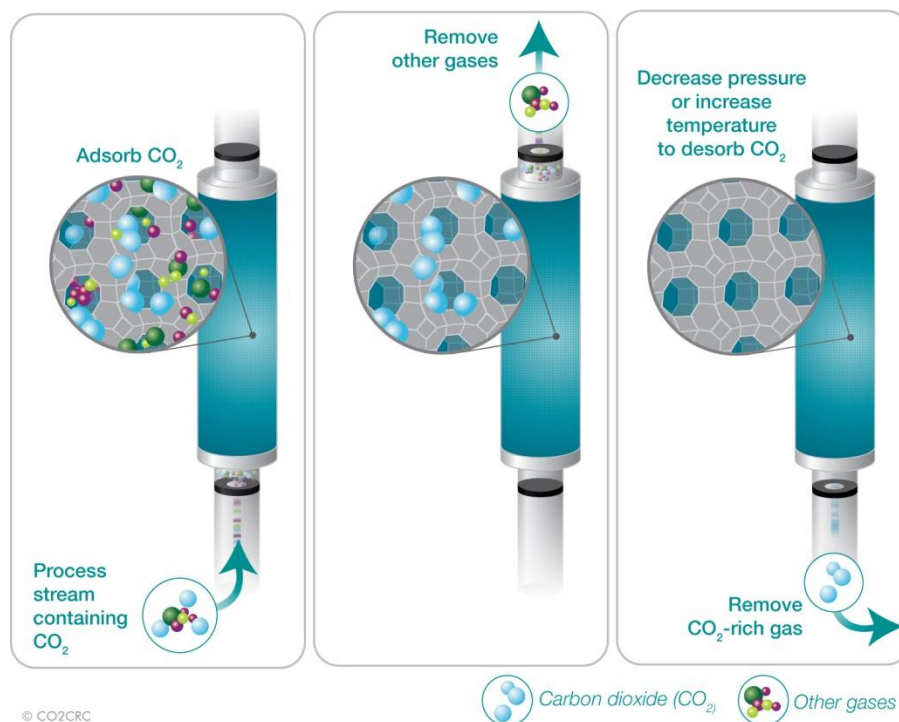


Figure 2-9 Pressure swing adsorption of CO₂ across a molecular sieve [68].

2.7.1.4 Biological - Microalgae

In addition to the capture technologies outlined in Figure 2-7 above, the use of microalgae for CO₂ capture has also been considered. The biological process of photosynthesis (Equation 2-5) takes place in plants and algae, and utilises photosynthesis to fix CO₂ to biomass.



Due to their high efficiency at absorbing light, research has been carried out on the use of microalgae to ‘capture’ CO₂, although it has been noted that such a process would be considered carbon recycling, and not mitigation because at some point in time the CO₂ will be returned to the atmosphere as part of the natural carbon cycle [69]. Results to date suggest that algal CO₂ fixation rates equivalent to 114 tons CO₂/year [70] have been achieved in so-called bioreactors. Despite research into the technology for the past 50 years, the technology is still considered to be in the early stages of maturity [71], and impurities present in flue gases including SO_x may have negative effects on the microalgal communities due to acid formation.

2.7.1.5 Absorption

In the process of absorption, the CO₂-containing gas stream is passed over a liquid or solid sorbent, which absorbs the CO₂. The process differs from adsorption in that the CO₂ is absorbed into the whole volume of the sorbent, rather than just onto the surface as is the case with an adsorption process. Absorption processes are generally cyclic as the sorbent is transferred to another vessel, where due to changes in temperature or pressure, a pure stream of CO₂ is released. This allows the sorbent to be regenerated, and it is then transferred back to the original vessel for repeated CO₂ sorption cycles (Figure 2-10).

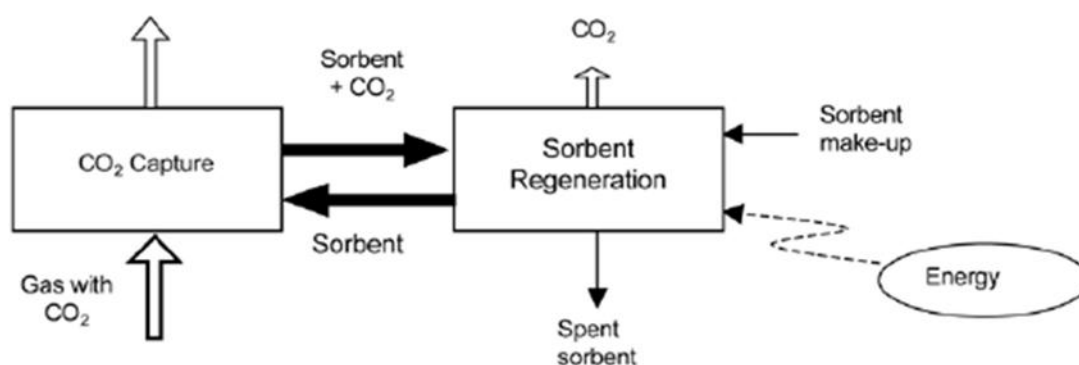


Figure 2-10 CO₂ Absorption using a liquid or solid sorbent [61].

The use of chemical solvents as CO₂ sorbents is probably the most mature of the CO₂ separation technologies, and is the one that is currently used within demonstration capture plants in the UK, including at SSE's Ferrybridge power station. Absorption using solvents may be a chemical process through the use of amines, which depends on acid-neutralisation reactions, and is suitable for low concentrations of CO₂. Amines can be grouped into primary, secondary, tertiary or quaternary depending on the number of alkyl groups attached to the nitrogen atom in the molecular structure. Typically, primary (e.g. monoethanolamine (MEA)) and secondary amines (e.g. methyldiethanolamine (MDEA)) are used for CO₂ capture. There is some concern about the potential environmental impacts from the use of some amines. MEA has a high biodegradability and therefore poses little environmental risk, however, other amines used within capture plants, such as MDEA and piperazine, have low

biodegradability and high ecotoxicology, and therefore if emitted to the air have the potential to degrade to form nitrosamines which are classified carcinogens [72]. Research is on-going into this issue to determine the extent of risks posed from amine use [73].

Absorption of CO₂ from flue gases may also occur using a physical solvent (e.g. N-Methyl-2-Pyrrolidone (Purisol®), Methanol (Rectisol®), Propylene Carbonate (Fluor Solvent) and Dimethyl Ether of Polyethylene Glycol (DEPG) (Selexol)), which function based on Henry's Law, with absorption occurring at low temperatures and high pressures. This is suitable for CO₂ at higher concentrations and pressures, and is therefore most suitable for use in pre-combustion carbon capture technologies where the CO₂ may be at concentrations of 35-40 % and at 20 bar or more [74]. Furthermore, the use of metal oxide sorbents, such as CaO, is an emerging technology requiring further research before it can be implemented at the commercial scale. However, it has been suggested that CaO has by far one of the highest sorption capacities available (Table 2-4), making it a promising sorbent for CCS. Furthermore, it is widely available, is proving to be efficient at CO₂ capture and is low in cost.

Table 2-4 Sorption Capacities of CO₂ Sorbents adapted from Dasgupta *et al.*, 2008 [75].

CO ₂ Sorbent	Capacity (g/kg)	Basis
MEA	60	Solubility – 15.3 wt %
Silica gel	13.2	303 K, 0.4 mm silica gel particle
Activated carbon	88	293 K, specific area – 1393 m ² /g
CaO	393	50 % conversion

A summary of the advantages and disadvantages of the aforementioned CO₂ separation methods is provided in Table 2-5.

Table 2-5 Summary of CO₂ separation methods.

CO ₂ Separation Technology	Advantages	Disadvantages	Existing Application
Membranes	Industrial experience of technology as currently used for natural gas separation.	Low separation capacity requiring gas streams to pass over membrane more than once, requiring higher energy input. Technology is not well developed in the CCS field.	Natural gas separation.
Cryogenic	CO ₂ is converted to liquid form, ready for transport.	Energy input required for refrigeration process is excessively high for dilute CO ₂ streams.	Nitrogen and oxygen production from air.
Adsorbents	Some adsorbents, particularly CaO and activated carbon are low in cost [76]. Mature technology due to commercial use in natural gas processing.	CO ₂ capture capacity of adsorbents is generally lower than other separation methods. Energy input required for PSA and ESA.	Natural gas separation.
Biological – Microalgae	Algae have rapid growth rates. Industrial experience as used in other industries. Biomass could be converted to a liquid fuel.	Technology is not well developed in the CCS field. Considered to be ‘CO ₂ recycling’ rather than mitigation. Pond area of 50-100 km ² estimated to be required for 500 MW power plant [77].	Biofuel production and wastewater treatment [78].
Absorbents	High CO ₂ capture capacity (>90 %). Generally low in cost. Most mature of separation technologies.	High energy input required for sorbent regeneration. Potential environmental issues with solvent degradation.	Natural gas separation.

2.7.2 High Temperature Solid Looping Cycles

High temperature solid looping cycles are a method of CO₂ absorption, as described in section 2.7.1.5 and shown in Figure 2-10, and comprise two (or more) reactors between which a solid sorbent is cycled, transferring with it heat, and CO₂ or O₂. A fuel such as coal-derived syngas is burnt to release CO₂ and H₂O. CO₂ is separated from the gas stream using the sorbent, which is then transferred to a second vessel where due to a temperature increase, CO₂ is released for subsequent transport and storage. Fluidised beds are ideal contacting devices for systems that require effective heat transfer, but demand large circulation rates of solid sorbents to match large CO₂ flows, such as that produced in a power plant. The gases in the two reactors do not come into contact, thus allowing efficient CO₂ capture.

2.7.2.1 Chemical Looping Combustion (CLC)

Chemical looping combustion is a form of solid looping that uses metal oxides (e.g. iron oxide, nickel oxide or copper oxide) as an oxygen carrier to facilitate fuel combustion [79]. Syngas (H₂, CO, C_xH_y) is combusted in the fuel reactor using oxygen from a metal oxide, which in turn is reduced, producing CO₂. For the majority of metal oxides, this oxidation reaction is exothermic, except in the case of copper for which oxidation is endothermic [80].

The reduced metal is then transported to the air reactor where it is oxidised in an exothermic reaction, before it is cycled back to the first reactor to once again undergo reduction for further fuel combustion (Figure 2-11) [81].

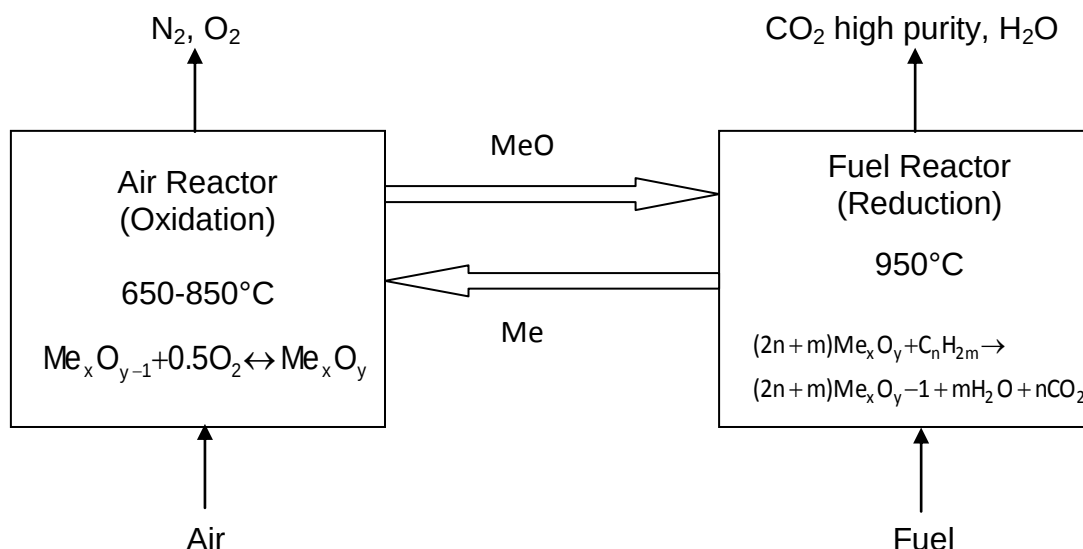


Figure 2-11 Chemical Looping Combustion (adapted from Eide *et al.*, 2005 [82]).

Research is being undertaken on a variety of metals to determine the optimum for oxygen transport, and also the cyclical process of chemical looping. Research has so far focused mainly on nickel oxide testing at the laboratory and bench scale, although some work has been done to date on iron and copper oxides [83] - [86]. A key issue with chemical looping combustion is the production of enough sorbent for use within a pilot scale plant. Research to date has mainly focused on laboratory and bench-scale reactors, which use relatively small amounts of sorbent. However, sorbent masses in the region of tens of kilograms are required for pilot scale operation. Furthermore, consideration of health and safety aspects of producing particular sorbents, such as nickel oxide, is required.

2.7.2.2 Calcium Looping Cycle

The calcium looping cycle is a method of CO₂ capture, comprising the use of limestone-derived CaO as a CO₂ sorbent within a fluidised bed. It has been the subject of significant interest within the research community over recent years after first being proposed by Shimuzu *et al.*, 1999 [31]. The technology has been demonstrated at the pilot scale for use as post-combustion CO₂ capture, using a number of fuels [6] [5] [87] [88]. Limestone-derived sorbent is considered to be cost effective, efficient and abundant, and there is also the potential for sorbent released from the cyclic process to be used within the

cement manufacture industry, which currently emits 5% of global CO₂ emissions from stationary sources. Dean *et al.*, 2011 [11] suggest that the cement manufacturing process produces 0.6 – 1.0 kg CO₂ per tonne of cement produced, of which approximately 80 % is from limestone calcination [11]. However, this figure is considered to be underestimated by approximately 1000 times, and should actually be in the region of 600 – 1000 kg (0.6 - 1.0 tonnes) CO₂ per tonne of cement. It is considered that the energy required within the cement works could be reduced by 50 %, assuming that spent sorbent is removed from the calciner and is therefore predominantly CaO [9]. Therefore, CO₂ capture via the calcium looping cycle is an attractive option for CO₂ capture from industrial point sources [3] [89]. The direct use of CaO from calcium looping would remove the requirement for the cement industry itself to generate CaO from CaCO₃, thus reducing CO₂ emissions from both the power, and cement manufacture industries [3].

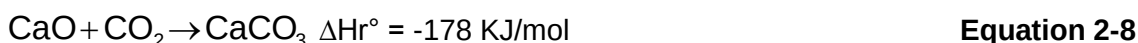
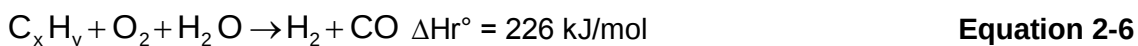
2.7.2.3 Calcium Looping Cycle for Post Combustion Capture

The majority of research carried out on the calcium looping cycle has focused on post combustion CO₂ capture, and is also the focus of this PhD work. The calcium looping cycle process (Figure 3-1) comprises the separation of CO₂ from combustion-derived flue gases, by passing the CO₂-containing flue gas through a fluidised bed of lime (CaO) in a reactor known as a carbonator, whereby at a temperature of approximately 600-650°C (depending on the CO₂ partial pressure), CaO reacts with and thus captures the CO₂ to form CaCO₃. The gas which exits the carbonator is CO₂-depleted, and the CaCO₃ is then transferred to a second reactor, known as the calciner, where due to an increase in temperature to approximately 900-950°C, the CaCO₃ decomposes, releasing CO₂ for compression, transport and storage. CaO is reformed and is then transferred back to the carbonator for further cycles of CO₂ capture [90].

The carbonation reaction is exothermic whilst the calcination reaction is endothermic, thus requiring energy input. The reactors are separate; meaning no gaseous exchange occurs between the two, ensuring the efficiency of the process is optimised.

2.7.2.4 Calcium Looping Cycle for Pre Combustion Capture

Recently, work has been carried out on combining shift and carbonation reactions, in a bid to enhance CO₂ capture from the gasification process. In the process, coal is gasified or methane is reformed, to produce a syngas comprising CO and H₂ (Equation 2-6). In a separate reactor, steam is then added to the CO and H₂ to facilitate the water-gas shift reaction, to produce CO₂ and more H₂ (Equation 2-7). In the same reactor, the addition of CaO allows carbonation (Equation 2-8) to occur, thus removing CO₂ and leaving a stream of H₂ for electricity production, or storage in fuel cells. The primary benefit to this process is that the presence of a CO₂ acceptor in the reactor removes the equilibrium limits of the water-gas-shift reaction in accordance with Le Chatelier's Principle, thus allowing greater H₂ production with enhanced purity, at lower temperatures. Also, due to the inherent CO₂ capture, there are no additional separation costs, and the process has been successfully run at laboratory scale without the additional requirement for a shift catalyst as is currently the case with conventional methane reforming [91].



There have been a number of recent developments on this technology, which was first patented in 1931 by Gluud and Keller [11], but has regained interest due to the global requirement for 'low carbon' energy, and increasing demand for H₂.

2.7.2.5 Zero Emission Coal Alliance (ZECA) Process

Variations on the process include the Zero Emission Coal Alliance (ZECA) process, first developed by the Los Alamos National Laboratory in the US [92]. The scheme overall results in the formation of 2 extra moles of H₂ for each 2 moles of H₂ used during coal methanation, and the H₂ for methanation is recycled from the H₂ stream remaining after processing of the gas. However,

the process therefore uses half of the H_2 produced, and hence has a higher fossil fuel requirement than coal gasification in steam/oxygen. It has been acknowledged that further work is required on combining the reforming/shift reactions and on the in situ capture of CO_2 at appropriate temperatures and pressures [9] [93]. In addition, it was observed that although the process has potentially higher efficiencies than conventional hydrogen production methods, there are a number of significant barriers to the overall ZECA process, including the development of a Solid Oxide Fuel Cell (SOFC) that can operate at higher temperatures than is currently possible, to provide heat for the calciner and that is tolerant to sulphur compounds [94]. In addition, it is required that either calcinations can take place at high pressures with rapid sorbent degeneration, or to repeatedly pass a large volume of hot solids through a big pressure difference. Despite this they conclude that modification of the system to overcome these technical barriers may help realise the ZECA concept. Process efficiency was originally estimated in the 'order of 70%' efficiency as proposed by Ziock *et al.* 2001 [92] although subsequent independent revisions suggest lower efficiencies of approximately 50% vs LHV [95].

2.7.2.6 Hydrogen Production by Reaction-Integrated Novel Gasification (HyPr-RING) Process

Lin *et al.*, 1999 [96] proposed a method for the production of hydrogen from water and hydrocarbons, known as the 'hydrogen production by reaction-integrated novel gasification' (HyPr-RING) method. This technique also integrates gas production and separation, and the associated endothermic and the exothermic reactions, to produce H_2 in one step. However unlike the ZECA process, the combined processes were undertaken by Lin *et al.*, 1999 [96] at high temperatures ($650^\circ C$) and high pressures of between 12 – 105 MPa. High pressure steam is used to hydrate the CO_2 sorbent into $Ca(OH)_2$, in order to recover CaO reactivity, so that the exothermic hydration and carbonation reactions provide sufficient energy for the endothermic gasification reaction [97]. Excess steam is required thus increasing energy requirements and costs, and the process is only considered to produce 91% H_2 . Lin *et al.*, 2004 [98] identified that the high temperatures and long holding times used in the process

increase the potential for interactions between the coal and the sorbent, thus reducing the CO₂ capture ability of the sorbent. In addition, it has been recognised that both the ZECA and HyPr-Ring process must operate at extremely high pressures to produce H₂, and are therefore do not currently appear to be economically feasible [99].

2.7.2.7 GE Process

The GE Process comprises three reactors, a carbon transfer loop, and an oxygen transfer loop. Coal is gasified in the first reactor to produce CO, H₂, and CO₂ which is removed by a CO₂ sorbent. In the second reactor gasification is completed, oxygen transfer material is reduced and the remaining carbon is oxidised. Thus the CO₂ sorbent is regenerated and a stream of pure CO₂ is released. In the third reactor oxygen transfer material is re-oxidised, producing oxygen-depleted air suitable for a gas turbine [100]. The process is considered to be fuel-flexible (i.e. coal and biomass), however, it has been acknowledged that efficiencies of up to only 80% can be obtained [97].

2.7.2.8 Alstom Process

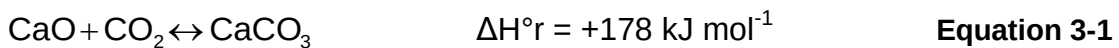
The Alstom Process consists of three loops, within which Ca-based sorbents, including calcium sulphide, are used to transfer both oxygen and heat. Coal is gasified to produce CO which is then converted to CO₂ and H₂ by the water-gas-shift reaction [97]. CO₂ is then removed from the reaction process using CaO as a CO₂ sorbent. The product gas may be hydrogen, syngas, or CO₂, depending on the process configuration.

3 FACTORS AFFECTING THE CALCIUM LOOPING CYCLE FOR CO₂ CAPTURE

This chapter presents a literature review of the factors influencing the calcium looping cycle for CO₂ capture. It firstly provides a review of the technical and economic factors influencing the technology. An overview of the physical and chemical factors affecting capture efficiency is then provided, followed by a summary of the details on pilot scale reactors that have been operated to date, including results achieved and challenges that have arisen upon scale up of the technology.

3.1 Technical and Economic Aspects

The calcium looping cycle utilises fluidised bed technology, whereby a particulate bed is fluidised using a gas within a reactor. In this case the particulate bed comprises the CO₂ sorbent, and the fluidising gas comprises CO₂-containing flue gas. The calcium looping cycle makes use of the reversible carbonation reaction, and the subsequent CO₂ capture and release process is therefore cyclic (Figure 3-1). The equilibrium carbonation – calcination reaction is provided by Equation 3-1, whereby carbonation is exothermic and calcination is endothermic.



The reactors for carbonation (carbonator) and calcination (calciner) are separate, meaning that there is no gaseous exchange between the two, ensuring the efficiency of the process is optimised.

The carbonation reaction can be considered in two parts: an initial fast, kinetically-controlled stage; followed by a slower diffusion-controlled stage, which occurs once the product layer has reached a critical thickness [101], making it harder for CO₂ gas diffusion into the pore network, and in turn, react with CaO. Further detail on this is provided in Section 3.7.

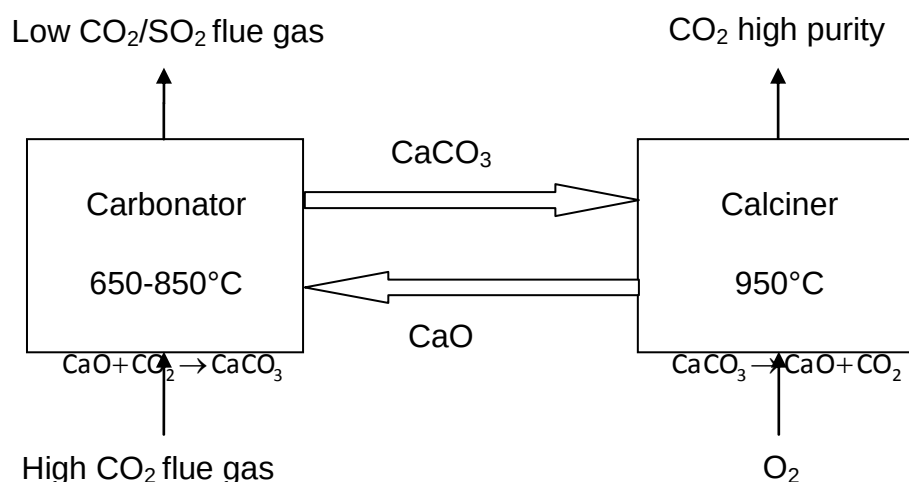


Figure 3-1 Calcium looping cycle, comprising calcination of CaCO_3 in the calciner to produce a high-purity CO_2 stream for transport and storage, after which CaO is transferred to the carbonator for CO_2 capture, producing CaCO_3 which is then cycled back to the calciner.

This process is considered particularly appropriate for use within power generation processes, due to the fact that the technology is relatively mature and potentially scalable to accommodate the large flow rates of flue gas which require processing – a typical 500 MW power station produces flue gas at a rate of 800 kg/s [102]. This would in turn require a typical total CaCO_3 feed rate of 939.5 kg/s [103], which ideally would be reduced to improve process efficiency, thus requiring higher flow rates between the carbonator and calciner reactors. With regards to post combustion capture, it can be retrofitted to existing power plants, removing the requirement for expensive new build and is therefore currently considered the optimum technology for calcium based CO_2 capture.

The calcium looping cycle is considered to offer a reduced energy penalty of approximately 6-8 energy percentage points when compared to other post combustion capture systems, such as amine-based capture which has an energy penalty of 9.5 – 12.5 % [11]. The high temperatures at which the process is carried out means that thermal energy can be recovered to drive a steam turbine or for heat transfer from one reactor to another. The energy penalty could be further reduced by integration with the cement industry, where spent CaO sorbent is sent for cement production, reducing the requirement for

the cement industry to calcine limestone, which is responsible for 50 % of CO₂ emissions from cement manufacturing [9].

The calcium looping cycle process is considered to be capable of removing more than 90 % CO₂ from new power station flue gas streams, and this has been demonstrated at the pilot scale level [7] [8] [104] [105].

With regards to the economics of the calcium looping cycle, several studies have investigated this, of which MacKenzie *et al.*, 2007 [106] suggested a cost of US\$ 19.75 per metric ton CO₂ captured, based on a Canadian power station, which compared positively with that of amine based capture, estimates for which figures vary between US\$ 32.5 – 80 (figures converted to 2006 USD from Canadian dollars, using mean exchange rate of 1.2 for June 2006).

Abanades *et al.*, 2007 [107] predicted a cost of \$15.5 / ton CO₂ avoided for an oxy-fuel carbonator of 86 % efficiency, whilst Romeo *et al.*, 2009 [103] suggest a cost of less than \$20 / ton CO₂ avoided, with purge rate and sorbent cost playing a key role in determining how much below this figure the cost varies.

3.2 Capture Efficiency

The capture efficiency of the calcium looping cycle can be calculated by closing a mass balance for the system. This can be described in terms of carbonate conversion i.e. conversion of CaO to CaCO₃ (Equation 3-2) [7].

$$X_{\text{carb}} = \frac{F_{\text{CO}_2} \cdot E_{\text{CO}_2}}{F_{\text{Ca}}} \quad \text{Equation 3-2}$$

Where X_{carb} is CaO carbonation conversion (mol %), F_{CO_2} is CO₂ flow to the carbonator (mol/h), E_{CO_2} is CO₂ capture efficiency (%), F_{Ca} is calcium looping ratio between reactors (mol/h).

In an industrial situation, fresh sorbent feed will be required to maintain an acceptable capture capacity due to decay in sorbent activity with increasing cycles, as a result of sintering and sulphation for example. Rodriguez *et al.*, 2010 [104] provided an equation for the average capture capacity of sorbent (Equation 3-3).

$$X_{ave} = \sum_{N_{age}=1}^{N_{age}=\infty} r_{N_{age}} X_{N_{age}}$$

Equation 3-3

Where X_{ave} is maximum average carbonation conversion attainable by solids in the system, equivalent number of full carbonation and calcination cycles for a sorbent to reach its current maximum conversion potential (measured as $X_{N_{age}}$), $r_{N_{age}}$ is fraction of calcium that has been fully calcined N_{age} times after at least $N_{age}-1$ complete carbonations, $X_{N_{age}}$ is maximum carbonation conversion achieved in a full carbonation cycle irrespective of the history of the sorbent in terms of previous calcination–carbonation cycles.

Abanades *et al.*, 2004 [108] proposed the concept of f_a , which provides the average particle reaction rate for a given limestone at constant temperature and CO_2 concentration (Equation 3-4):

$$f_a = X_{max} - X_{carb}$$

Equation 3-4

where X_{max} is average CaO CO_2 carrying capacity (mol %) and X_{carb} is CaO carbonation conversion (mol %)

As noted by Charitos *et al.*, 2010 [6] the carbonation conversion is dependent on the ratio of moles of CaO in the carbonator, to moles of CO_2 entering the carbonator, known as space time. However, it is acknowledged that not all of the sorbent in the carbonator is available for reaction; some may already be carbonated, and some may not be able react in the fast reaction regime. Therefore the term active space time can be considered for capture efficiency (Equation 3-5):

$$\tau_{active} = \frac{n_{Ca} f_a}{F_{CO_2}}$$

Equation 3-5

Where τ_{active} is active space time (h), n_{Ca} is amount of calcium in carbonator (mol), f_a is free active CaO fraction (mol %), and F_{CO_2} is CO_2 flow to the carbonator (mol/h).

3.3 Partial Pressure

The partial pressure of CO₂ determines whether or not sorption of CO₂ (carbonation) occurs. This is affected by temperature and pressure, and can be calculated from Equation 3-6 using experimental data with temperature above 1170 K and CO₂ pressures above 101 kPa [109]. If partial pressures are greater than equilibrium pressures, then carbonation will be favoured; conversely if partial pressures are lower than equilibrium pressure, then calcination will be favoured (Figure 3-2).

$$\log P_{\text{CO}_2, \text{eq}} = 7.079 - \frac{8308}{T}$$

Equation 3-6

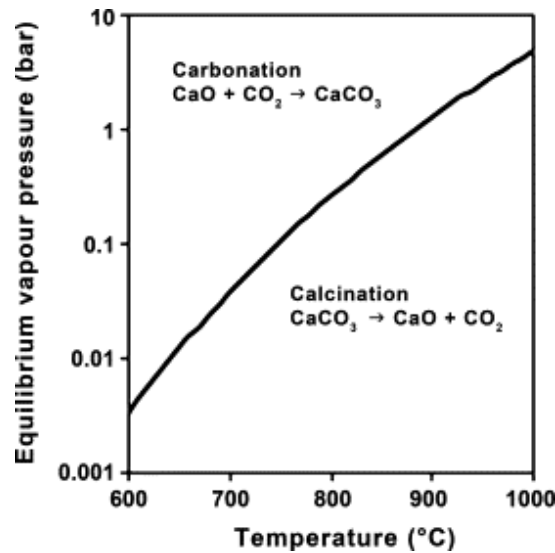


Figure 3-2 Equilibrium partial pressure of CO₂ over CaO [11].

3.4 Effect of Temperature

As mentioned, one of the key benefits of the Ca-based CO₂ capture over other post combustion capture methods is the relatively low efficiency penalty on the overall power generation process. However, energy demand for the process is high due to the heat input required for the endothermic calcination reaction, to maintain the temperature of solids when transferring between the calciner and carbonator, and to provide heat for fresh feed solids. A number of studies [89] [110] have looked into the effects of temperature on the calcium looping cycle

process, with experiments being carried out at a range of temperatures, from 400°C to the region of 950°C.

3.4.1 Calcination Temperature

A high calcination temperature is considered desirable to achieve a rapid calcination rate, and thereby reduce the residence time of the sorbent in the calciner. This in turn allows a smaller size reactor to be used, reducing costs and improving efficiency. Further, an increased temperature will increase the CO₂ equilibrium pressure and therefore reduce the required flow of gas and optimise CaCO₃ conversion, but a compromise is however required due to the increase of sorbent sintering at higher temperatures. Calcination is generally carried out at a temperature of 800-1000°C [110], although research has shown that maximum deterioration due to sorbent sintering can occur at 850°C and minimum at 750°C [91], with Lu *et al.*, 2008 [8] noting that calcination in a pilot scale reactor began at ~700°C, and was quickly completed once the temperature had gone beyond 900°C.

Results from calcination reactions carried out at 800°C and 850°C identified that as calcination temperature increased, sorbent durability decreased at a rate of 5% and 2% at 850°C and 750°C respectively. The addition of 50% H₂O did however retard the deterioration rate to approximately 3% at 850°C [91], although this volume is considered slighter higher compared to what would be produced in coal-gas streams in industry. Similarly, fixed bed thermogravimetric analysis (TGA) calcination reactions carried out at increasing temperatures from 920-1100°C, identified a sharp drop in conversion above 950-1000°C, attributed to sintering mechanisms causing an increase in sorbent decay (Figure 3-3) [89] [111].

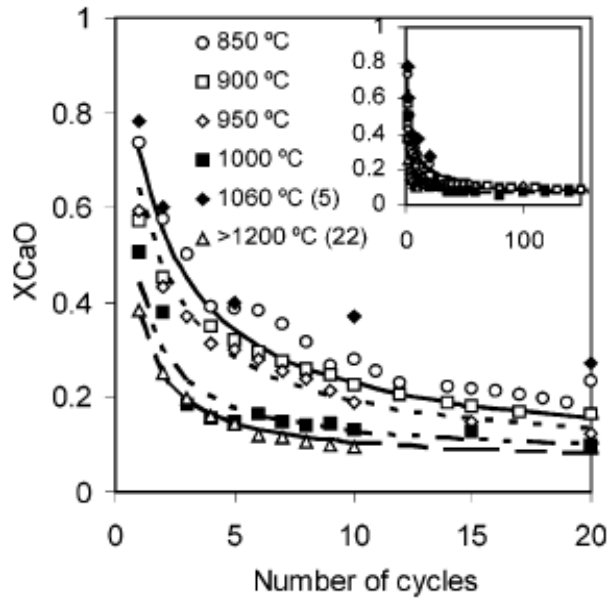


Figure 3-3 Conversion vs number of cycles for experiments carried out at different calcination temperatures [89].

3.5 Sintering

The high regeneration temperatures required during calcination can cause sintering of sorbent particles and it has been observed that carbonation time has little effect on particle sintering, but it is calcination during which sintering predominantly occurs, as well as at higher partial pressures of steam and CO_2 [112] [89]. In addition to high calcination temperatures, sintering is enhanced by repeated cycles of carbonation/calcination, and extended calcination times. Sintering refers to 'changes in pore shape, pore shrinkage and grain growth that particles of CaO undergo during heating' [9], and similarly has been described as 'the bonding of adjacent surfaces of particles by heating' [113]. Figure 3-4 [114] shows limestone before and after 100 carbonation/calcination cycles, following which sintering can clearly be observed.

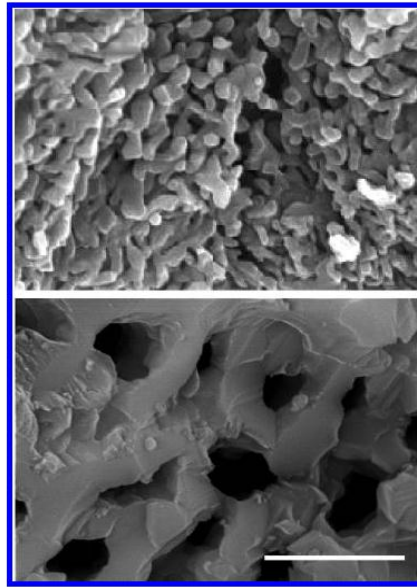


Figure 3-4 a) Fresh fracture surface of a calcined limestone; b) Same limestone after 100 calcination / carbonation cycles. Scale bar 2 μ m [114].

Numerous studies have observed this effect [89] [112] [113] [115] [90] with results concluding that sintering is greatly enhanced over temperatures of 950-1000°C [89], with the ‘Tammann’ temperature of 1154°C being identified as the temperature over which sintering is significant [116]. González *et al.*, 2008 [117] went to the extent of discarding proposed calcination experiments at temperatures of 1150°C due to the poor initial results obtained (Figure 3-5).

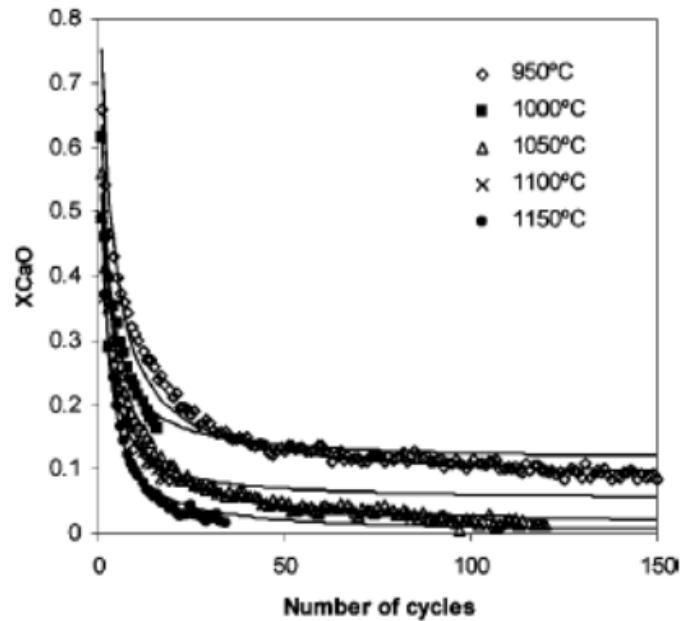


Figure 3-5 Decrease in carbon capture capacity with increasing cycles, at increasing temperatures using La Blanca limestone, for calcination time of 10 minutes, carbonation time of 10 minutes and 650°C temperature, in 10% vol. CO₂ [117].

Despite the general agreement that sintering greatly reduces carbon capture efficiency above temperatures of approximately 1150°C, Curran *et al.*, 1967 [118] successfully carried out a high calcination conversion at a high temperature of 1060°C in continuous mode.

3.5.1 Sintering Mechanism

In terms of sintering mechanisms, it has been suggested that a decline in activity as a result of sintering may result from the formation of an interconnected CaO network which ‘acts as a refractory support and determines sorption performance’ [119]. Similarly, Weimer *et al.*, 2008 [4] suggests small grains and voids form larger grains and voids, resulting in a reduction of the free surface area of the CaO over which diffusion occurs. Schmalzried (1974) [120] proposed a three-stage mechanism, whereby firstly contact area between grains increases but porosity remains unchanged. Secondly, material moves towards pores from grain boundaries and coupled ions (Ca²⁺, O²⁻) move

towards grain boundaries. Finally, large pores are formed at the expense of smaller pores, and grain boundaries act as sources and sinks for ions [121].

3.6 Carbonation Temperature

Carbonation can occur at a range of temperatures, which are dictated by the partial pressure of CO₂, above or below which CaCO₃ formation cannot occur. The effect of carbonation temperature has been extensively investigated, with the optimum temperature considered to be approximately 650-700°C based primarily on TGA experiments [111] [122] [123]. However, pilot scale experiments suggested that decreasing carbonation temperature to 580-600°C provided the optimum CO₂ capture due to an improvement in thermodynamics caused by the temperature difference across the length of the bed [8]. A similar result was found by Fang *et al.*, 2009 [124] who identified that an optimum carbonation temperature of 600 – 680 °C resulted in CO₂ capture of 95% in a 10kW pilot scale reactor. Similarly, Charitos *et al.*, 2010 [7] in a pilot scale 10kW reactor identified an optimum capture efficiency of 93 % for a carbonator temperature of 625 °C, which decreased to approximately 90 % and 77 % capture at temperatures of approximately 655 and 705 °C respectively. This again is explained in terms of equilibrium, in that increasing carbonator temperature increases equilibrium CO₂ concentration, causing equilibrium capture efficiency to decrease. This is described by Equation 3-6 [109].

Product layer diffusion of the carbonation reaction in a pilot scale facility was investigated, from which it was identified that at high temperatures (>850°C), initial reaction rates are not dependent on CO₂ partial pressure, but after long runs, conversion becomes a first order reaction rate with respect to CO₂ pressure, suggesting a change in the transport system i.e. diffusion. Grain growth too appears to be temperature dependent [125].

3.7 Effect of Repeated Calcination / Carbonation Cycles

The process of limestone looping is dependent upon the reversibility of the carbonation reaction, and therefore the number of cycles that the sorbent undergoes is crucial to the efficiency of the process. The carbonation reaction is

typically described as an initial fast kinetically-controlled stage, followed by a slower diffusion-controlled stage, which occurs once the product layer has reached a critical thickness [101], making it harder for CO_2 gas diffusion into the pore network, and in turn, react with CaO . Numerous research studies have shown that sorbent efficiency decreases with the number of calcination/carbonation cycles undertaken, particularly within the first 10 cycles (Figure 3-6), but the degree of decrease in efficiency becomes less with increasing cycles [31] [126] [122] [90].

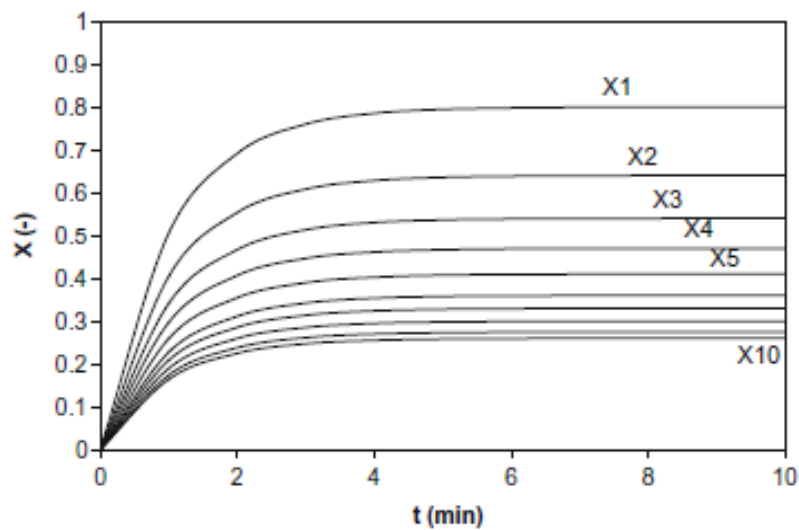


Figure 3-6 Decrease of carbonate conversion with increasing number of carbonation/calcination cycles [127].

Decrease in efficiency is attributed primarily to sintering of the sorbent after repeated heating which is associated with pore closure [113]. It has been noted that closure of pores is not entirely irreversible, and that loss of surface area by sintering is not as important as that of the pore closure mechanism [116]. Bathia and Perlmutter (1983) [128] as cited in [129] however suggest that different reaction rates during the fast carbonation stage may in fact achieve the same final conversion at the end of the fast carbonation period, and concluded that the fast carbonation was associated with pores <10 nm. It has been suggested that in contrast to calcination, whereby porous calcium oxide is formed in place of calcium carbonate, the calcium carbonate that forms on the surface of calcium oxide during carbonation occupies a larger molar volume, and as such

once a layer of carbonate has formed on the surface (including the internal surface areas) a product layer has formed which can grow over pores and impede CO₂ transport throughout the sorbent (Figure 3-7) [9]. Once the product layer has formed a critical thickness, estimates in the literature of which vary between 22nm [116] and 55nm [114], the free surfaces of the CaO are no longer available to react, greatly reducing the surface area of the sorbent, and thus the reaction becomes a slower diffusion-controlled reaction. Therefore, carbonation can be considered to be a two-phase process, with a fast, chemically-controlled reaction phase, followed by a slower, diffusion-controlled reaction phase. Abanades and Alvarez (2003) [129] derived the following Equation 3-7 to describe the loss in microporosity with every cycle, which was found to correlate well with data obtained.

$$X_N = f_m^N (1 - f_w) + f_w$$

Equation 3-7

Where X_N is carbonation conversion in the Nth cycle, f_m is fractional loss of porosity around CaO micrograins, f_w is fractional loss of porosity adjacent to large pores or grain boundaries.

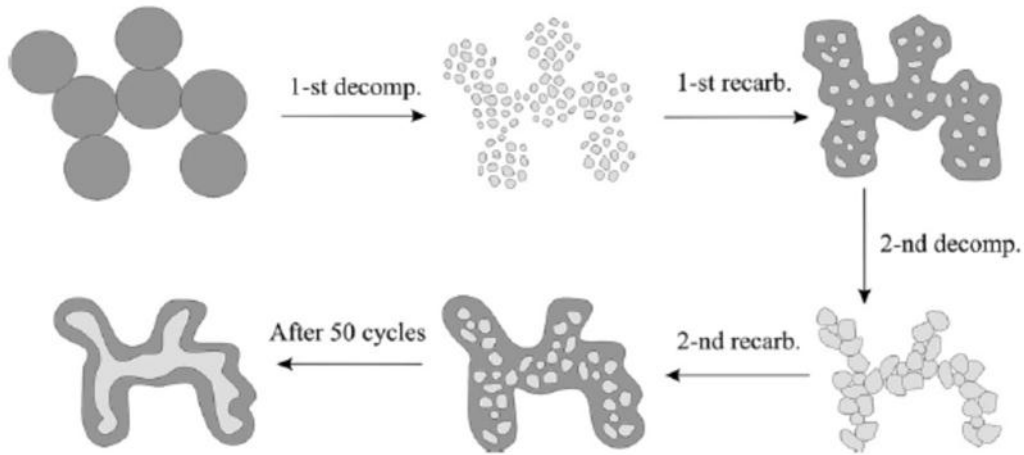


Figure 3-7 Textural transformation of CO₂ sorbent over many cycles, where CaO is shaded light grey, and CaCO₃ is shaded dark grey [9].

The rate approach to the decay asymptote was delayed by extending the carbonation reaction duration time which had a regenerative effect on sorbent conversion due to the formation of additional pore volume and reactive surface

area on the release of the larger amount of CO₂, and this has also been observed in fluidised beds [130]. Florin and Harris [101] [131] noted that the decay asymptote represents an equilibrium between 'loss of surface area and pore volume due to sintering; and an increase in surface area and pore volume due to mass transfer associated with solid-state diffusion during carbonation, which evolves with subsequent release of CO₂'.

Decrease in capture efficiency with increasing cycles based on TGA and fixed bed data, has been shown to fit the following Equation 3-8 [90] (Figure 3-8) [129]:

$$X_{c,N} = f^{N+1} + b \quad \text{Equation 3-8}$$

Where N = number of cycles, f = 0.782 and b = 0.174.

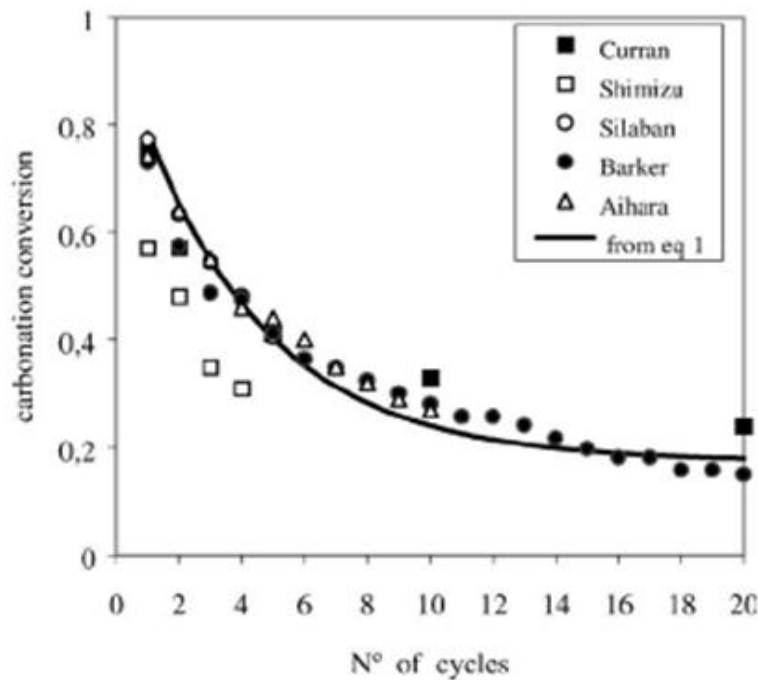


Figure 3-8 Evolution with the number of carbonation / calcination cycles of the maximum carbonation capacity of CaO [90].

3.8 Attrition

Attrition is defined as the 'wearing down over time by friction' and is a common process that takes place in fluidised bed reactors due to high velocities and

number of particle impacts. It has been observed during both bench and pilot scale tests that during the first calcination cycles, limestone has a high attrition rate which reduces with increased cycling [132] [133] [88], with suggestions that the continued rate of attrition upon cycling is considered to be more of a significant problem upon scale-up [9] [8].

Jia *et al.*, 2007 [132] devised equations (Equation 3-9 and Equation 3-10) based on those by Vaux *et al.*, 1978 [134], relating to attrition rate, and extent of attrition in circulating fluidised bed conditions, where only the finest particles (<0.75µm) will be lost, and the larger particles will accumulate in the bed:

$$\text{Attrition rate, } R_a = \frac{-1}{M_{+75}} \frac{dM_{+75}}{dt} \quad \text{Equation 3-9}$$

$$\text{Extent of attrition, } A (\%) = -100 \int_0^t R \, dt = -100 \ln \frac{M_{+75,0}}{M_{+75}} \quad \text{Equation 3-10}$$

Where M_{+75} and $M_{+75,0}$ are the mass of particles in the bed at time t and initial time respectively with size >75µm.

Various mechanisms for attrition are suggested in the literature, which are somewhat dependent on the morphology of the sorbent. Jia *et al.*, 2007 [132] suggests attrition of Havelock limestone is due to jagged peaks formed during crushing, being ‘cleaved off’ during the first cycles, but the attrition mechanism observed in Cadomin limestone is similar to that of a plate shattering, resulting in a particle size distribution shift resulting in smaller size fractions. Chirone *et al.*, 1991 [135] presented a combination of four mechanisms that could result in sorbent attrition during combustion, namely, primary fragmentation; secondary fragmentation; fragmentation by uniform percolation; and abrasive attrition, whilst Scala *et al.*, 2007 [136] suggests that the subsequent processes of chipping, splitting and disintegration are a major factor in attrition.

Particle diameter in limestone appears to reach an asymptote after approximately 10 carbonation / calcination cycles, which is the same approximate duration after which decay in sorbent activity also reaches an

asymptote, suggesting particle size and sorbent decay are linked [122]. Other work however has identified that attrition generally occurs during the first 40h, after which particle size remained almost constant for up to 140h of circulation [88] [134]. This has important implications, in that material collected from the cyclones during the initial start-up process could be re-fed back into the system to minimise process waste, if the material was of an appropriate particle size.

Manovic *et al.*, 2010 [137] suggest that the distribution of SiO₂ impurities in limestone may act to affect surface areas, thus enhancing sintering and decreasing sorbent capacity. Contrastly, depending on the form in which SiO₂ is present, the impurity may act as a scaffold, thus acting to reduce attrition. Reactivation of sorbent with steam was found to increase particle size and porosity, thus acting to reverse attrition effects [122].

Capture costs have been calculated to increase from 15.8 to 17.5 €/ton CO₂ if a less attrition resistant limestone is used [138].

3.9 Effect of Sorbent Size

Large limestone particle sizes may result in reduced reaction rate, particularly during calcination, due to inefficient mass transfer of CO₂ from the reaction front within the sorbent to the particle perimeter [9], and this may occur for particles as small as 63 µm [139]. Laboratory scale investigations have shown there to be a moderate effect in terms of sorbent particle size on sorbent CO₂ capture capacity [140] [137]. Grasa and Abanades (2006) [89] however observed that sorbent size did not influence sorption capacity, but did affect the reaction rate of the initial fast carbonation period (Figure 3-9).

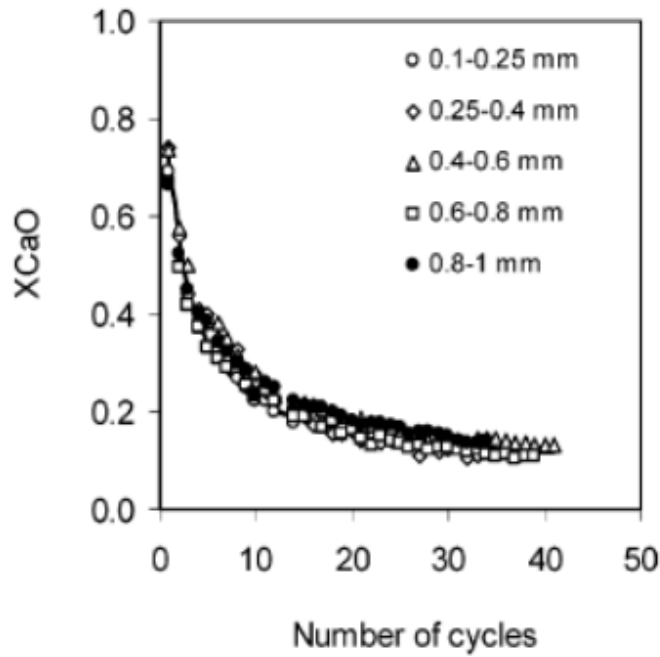


Figure 3-9 Effect of Sorbent Size on CaO Sorption Capacity [89].

They later carried out further TGA tests and concluded that only modest differences in CaO conversion were observed, and that small differences in time were required to reach 50% conversion [141] (Figure 3-10).

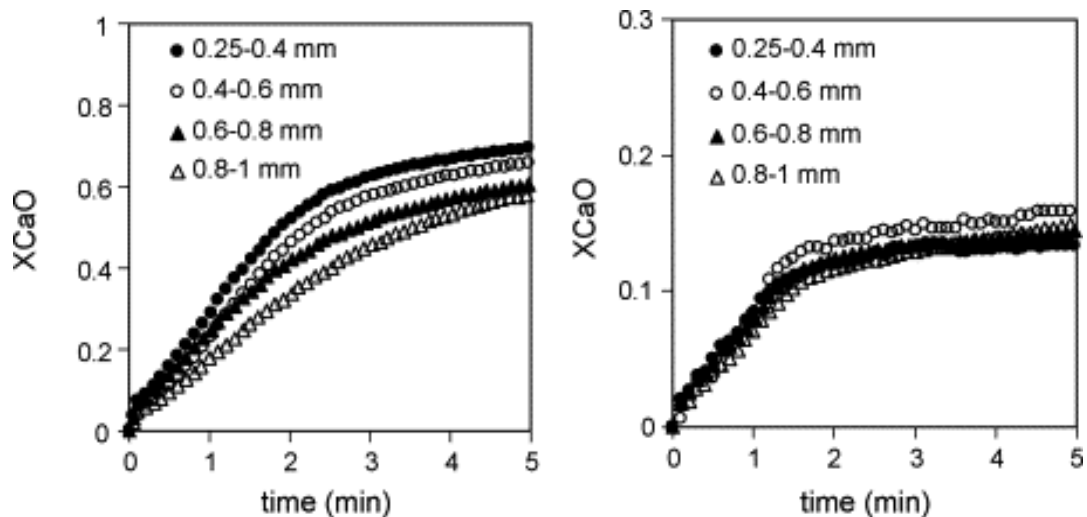


Figure 3-10 Conversion curves vs. time for different particle size . Limestone: La Blanca, $p\text{CO}_2$ 0.01 MPa, $T_{\text{carbonation}}$ 650°C, $T_{\text{calcination}}$ 850°C, for 15 minutes. (Left) cycle 1; (Right) cycles 20. Note that the Y-axis is different for both figures [141].

Florin and Harris (2009) [101] investigated the carbonation characteristics of pure CaO derived from nano-sized CaCO_3 in a TGA. It was demonstrated that

because of the small size of the particles, they therefore had an exceptionally high surface area, and this was the factor which led to the sorbent obtaining a high residual conversion capacity of ~20%, higher than previously quoted with larger particles.

3.9.1 Sulphation

Sulphur is naturally present in coal, primarily forming SO₂ on combustion (Equation 3-11), which in turn reacts with CaO to form CaSO₄ and CaS (Equation 3-12), the production ratio of which is temperature dependent [142]. The products of CaS oxidation can be CaSO₄, SO₂ and CaO (Equation 3-13 and Equation 3-14), whilst CaSO₄ can be reduced to SO₂ and CaO under reducing conditions i.e. in the dense region of a circulating fluidised bed combustor [143]. It is considered that SO₂ is released in the reducing dense region of the regenerator, however, the SO₂ will form CaSO₄ in the oxidising lean phase of the CFB due to the large excess of CaO available [4].



Research at the laboratory and bench scale [123] [4] [112] has shown that SO₂ and the resulting CaSO₄ formation contribute to the deactivation of CaO. Sulphation causes blocking of larger CaO pores formed during cyclic carbonation-calcination, which could otherwise react with CO₂ to form CaCO₃. CaO conversion to CaSO₄ has been shown to increase with increasing number of calcination/carbonation cycles that the sorbent has previously undergone [123] [144]. This phenomenon has been attributed to a change in the pore structure of CaO and increased pore sealing, thus allowing the formation of the CaSO₄ shell, approximately 1-3 μm [123] that prevents O₂ diffusion to the unreacted CaS. Sun *et al.*, 2007 [112] investigated effects of SO₂ on sorbent activity in a TGA, and found that SO₂ presence inhibited capture, but that the

CO₂ / SO₂ ratio was important in determining sorbent reversibility. Manovic *et al.*, 2007 [145] found that samples from a pilot scale reactor which were reactivated in steam for 15 minutes, subsequently achieved 75-85 % sulphation conversion in a TGA, compared to 35-40 % sulphation for the original samples. CO₂ capture was also in the region of approximately 50 %, compared to approximately 40 % for the original samples.

Grasa *et al.*, 2008 [123] provided Equation 3-15 based on TGA work, to describe CaO deactivation due to SO₂.

$$X_{\text{deactivated},i} = [X_{\text{CaCO}_3 \text{ (non-sulphated)}} - X_{\text{CaCO}_3 \text{ (sulphated)}}]_i \quad \text{Equation 3-15}$$

for $i = 1$ to N

Sulphation is however thought to reduce the extent of attrition experienced by sorbents, albeit at the risk of reduced CO₂ capacity. Therefore partial sulphation has been proposed as a method to both remove sulphur from flue gas, and reduce attrition [132], although other work suggests that this may only be suitable for some limestone types due to the different extents of loss of carrying capacity experienced by different limestones when subjected to sulphation (Figure 3-11) [123]. Further, it has been shown that SO₂ is able to react with CaO that has been sufficiently deactivated so that it can no longer react with and capture CO₂ [146]. This may have beneficial implications for industry requirements to reduce SO₂ emissions [123], whilst reducing the quantities of spent sorbent produced.

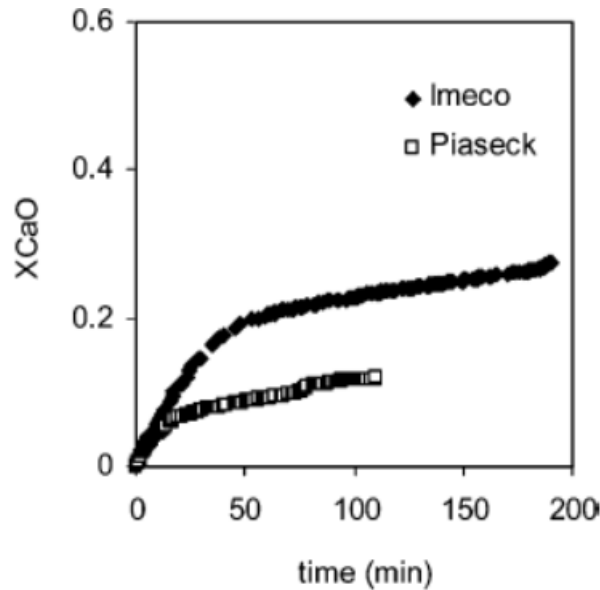


Figure 3-11 Extent of CaO Deterioration for Two Different Limestone in a Reaction Atmosphere of 2200 ppmv SO₂ in Air at 900°C [123].

Thus, CaO deactivation has been shown to increase with SO₂ concentration for a variety of limestone types, although limestone type can strongly influence deactivation time (Figure 3-11) [123]. Ridha *et al.*, 2012 [147] investigated the use of CaO pellets prepared with a kaolin-derived Al(OH)₃ binder, and the same pellets treated with 10% acetic acid. They found that CO₂ capture capacity of both sorbents calcined in SO₂ was eliminated after 2-3 cycles, implying sorbent modification is not effective against SO₂ effects.

The use of the solid purge resulting from the calcium looping cycle process has the potential to be used in the cement industry, which would enhance both the energy and economic efficiency of the process. However, it has been noted that the presence of CaSO₄ in the purge must be limited for cement production [4].

3.10 Effect of Steam

Recent investigations into the calcium looping cycle have focused on methods to improve sorbent capture capacity. Hydration with steam is considered one of the most economical means of doing so and explanations for the beneficial effects vary. Depending on the reactor temperature, hydration of CaO with steam will result in Ca(OH)₂ formation at temperatures below approximately

420°C [148]. Above 420°C, the partial pressure is such that Ca(OH)_2 formation is not thermodynamically favourable, and so CaO remains (Equation 3-16) (Figure 3-12).

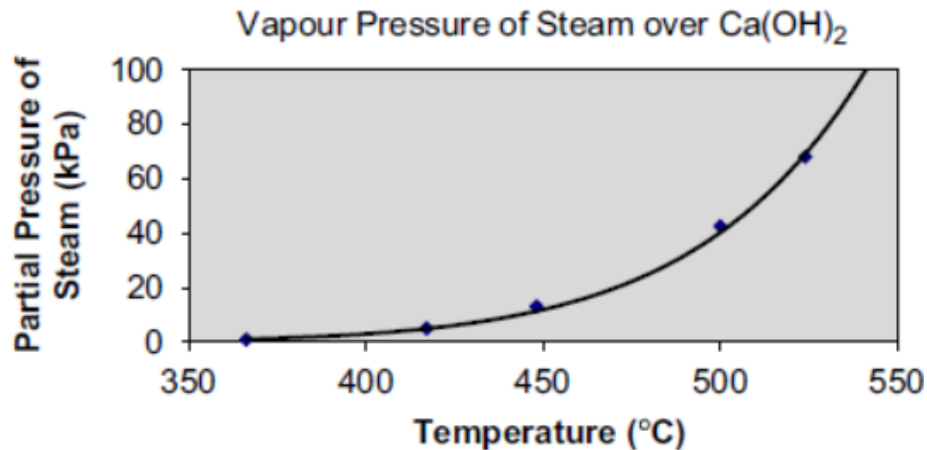
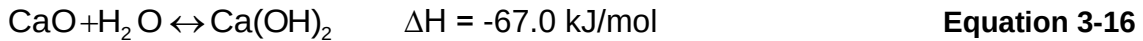


Figure 3-12 Partial pressure of water vapour over Ca(OH)_2 [148].

Arias *et al.*, 2010 [149] suggest that steam addition during calcination causes CaO to swell on hydration to form Ca(OH)_2 , thus exposing a larger fraction of CaO for CO_2 sorption once the Ca(OH)_2 has been decomposed in the relevant reactor. Donat *et al.*, 2012 [150] reported on bench-scale results from the addition of 0, 0.1, and 10% steam, and concluded that presence of steam during carbonation and calcination had a beneficial effect on CO_2 capture. Steam addition during carbonation retains finer pores, and thus reduces diffusion resistance through the carbonate layer, whereas steam addition during calcination acts to enhance sintering, thereby producing larger pores and a more stable pore structure, therefore allowing greater CaO conversion (Figure 3-13). The combination of these effects results in a synergistic effect [150]. Furthermore, the addition of steam during calcination may act to reduce required temperatures in the calciner, and thus reduce energy demand and cost, although steam production in itself is expensive.

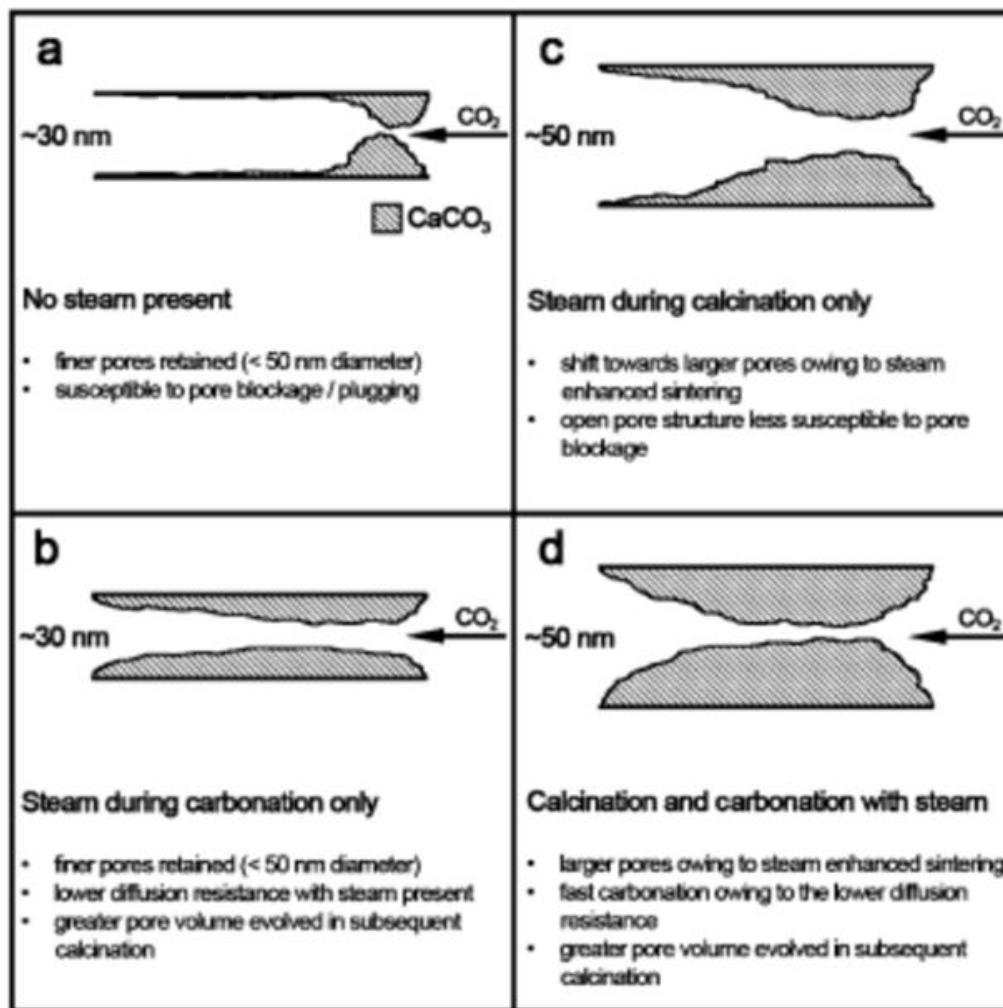


Figure 3-13 Relationship between sorbent morphology and conversion in presence of additional steam [150].

Addition of steam would require reactor pressures to be increased to ensure that sorbent hydration can occur and does not result in Ca(OH)_2 formation, and thus lower temperatures may in turn be required [9]. This would be beneficial for the energy efficiency of the calcium looping process.

Work on pilot scale hydration of spent sorbent resulted in sorbent with improved morphology and reduced the amount that remained unreacted, and improved results were obtained from the carbonator compared to the calciner [151]. Further work in the same pilot plant using a Polish limestone confirmed that with 17% steam, CaO conversion increased from 16.1 % to 29.7 % for the initial carbonation cycle, and the overall capture duration was longer than the same

reaction without additional steam [152]. Investigations by the same author concluded that steam promotes carbonation via enhancement of solid state diffusion into the sorbent product layer. This was also confirmed in bench scale work using Longcliffe limestone, which noted a synergistic effect for steam in both carbonation and calcination [150]. Kavosh (2011) [121] also confirmed from benchscale work using Longcliffe limestone that steam addition during calcination enhanced the sorbent capture capacity and reduced bed temperature requirements. Further Materić *et al.*, 2010 [153] identified that hydration of sorbent in a TGA reduced the decay rate of limestone by increasing the rate of diffusion-controlled carbonation. They noted repeated hydration cycles may increase attrition rates in fluidised beds due to crack formation. Conversely, Arias *et al.*, 2012 [154] found that 20% steam had a negligible effect on fast carbonation rates in a TGA, results of which were attributed to smaller masses of sorbent used compared to other studies where beneficial effects of steam were realised.

These studies lead to the conclusion that steam reduces sorbent decay in capture capacity by increasing the time during which fast diffusion can occur during carbonation, before the transition to slow diffusion occurs, thereby increasing the time for which the sorbent is still active in CO₂ capture.

3.11 Limestone type

Research has been carried out into how and whether carbonation capacity is affected by the type of sorbent. There is discrepancy in the literature as to whether the difference in carbon capture decay of natural limestone-based sorbents is important for sorbent selection, with some work suggesting this is the case, particularly for systems with low purge rates [89].

Grasa and Abanades (2006) [89] tested six different natural limestones and one dolomite, and identified that all sorbents decayed in a similar way, and as a result sorbent selection should be based upon factors other than capture capacity along with cycling. This too has been suggested by other research on whether limestone type is critical in capture capacity [129].

This however is challenged by Salvador *et al.*, 2003 [10] who observed that the capture capacity of Havelock limestone was greater than for Cadomin limestone, and also noted that unlike the Havelock results, the Cadomin data did not appear to level off, suggesting that in fact limestone type may be a critical factor in maximum capture capacity. In the same work, capture capacity of three different limestone types were compared in a fluidised bed combustor (FBC) and a thermogravimetric analyser (TGA). Results showed that there was negligible difference between the CO₂ capture capacities of the limestones in the TGA, whereas results from the FBC showed consistently higher capacity for Havelock limestone over Cadomin limestone. This same pattern of results was also observed when limestone was doped with Na₂CO₃ and NaCl. Given that much of the earlier work researching CO₂ capture has been undertaken using TGA's, the equipment and methodology used in research may have important implications on results when assessing CO₂ capture capacity, and comparing results from different scale processes may not be straightforward.

Dolomite has been identified to be a superior sorbent over limestone [155] (Figure 3-14) attributed to an increased pore volume due to the presence of MgO from the oxidation of magnesium carbonate (MgCO₃). MgO has a higher melting point than CaO, and therefore is less prone to sintering [9].

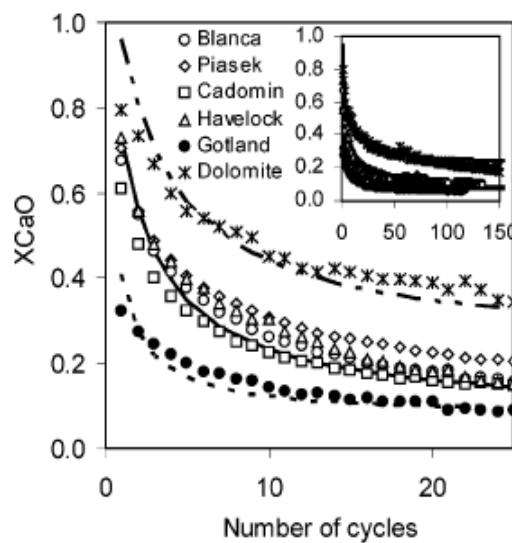


Figure 3-14 Effect on CO₂ capture capacity of CaO for different limestones [155].

Synthesised calcium-based sorbents were compared with natural limestone and dolomite for the combined water gas shift - carbonation reaction in a bench-scale atmospheric-pressure, fixed-bed reactor. The synthetic sorbents were considered superior in terms of carbon capture compared to naturally occurring limestone, over a cyclic-reaction of five cycles [156]. Naturally occurring limestones tested for carbon capture were unable to react completely due to pore pluggage and pore-mouth closure [99] [157]. However, production costs of synthetic sorbents compared to natural sorbents are higher, meaning that synthetic sorbents need to have sufficient capture efficiency for at least 10,000 cycles in order to make them economically viable [108]. The stoichiometric CO₂ capture capacity of CaO sorbent is 78.6 wt% (i.e. 44/56) meaning that even when CaO conversion is low, CaO is generally considered comparable to most synthetic sorbents proposed for CO₂ capture [4]. CaO derived from CaCO₃ has a faster initial rate of reaction than crystalline CaO, attributed to a network of pores created upon calcinations [116].

Barker (1973) [116] confirmed that CaO derived from CaCO₃ has a faster initial rate of reaction than crystalline CaO, and presumes that this is due to a network of pores created upon calcination. K₂CO₃ (Hydrotalcite (HTC)) has been widely tested as a sorbent, and work has shown that although it has high stability over a large number of cycles (>6000 cycles), its adsorption capacity was generally

lower compared with natural sorbents, thus restricting its potential as a sorbent at the industrial scale. In addition, its rate of reaction compared to calcium-based sorbents was also lower [158] [126].

Doping methods have recently been suggested for improving sorbent performance. Li *et al.*, 2009 [111] used acetic acid to improve the carrying capacity of dolomite to 60% after 20 cycles, compared to 26 % for unmodified dolomite. Al-Jeboori *et al.*, 2013 [159] doped limestones with HCl, HBr, HNO₃ and HI. Doping with 0.167 mol % of HBr caused an increase in carrying capacity from approximately 10% (undoped) to 25 % after 13 cycles, and caused an increase in pore diameter, attributed to the increased carrying capacity. Manovic *et al.*, 2008 [160] investigated effects of doping limestone with Na₂CO₃ and Al₂O₃ for which increasing Na was found to decrease activity, whilst increasing Al had a positive effect on sorbent activity. Salvador *et al.*, 2003 [10] found that NaCl doping of limestone in TGA experiments had a positive effect on sorbent performance, but this result was not replicated in a fluidised bed combustor. Rice husk ash addition was investigated in a twin bed fixed reactor. Combined rice husk ash /CaO appeared to have a higher carbonate conversion, and better anti-sintering behaviour after several cycles, when compared to SiO₂/CaO or diatomite /CaO [161].

Finally, Abanades *et al.*, 2004 [162] carried out a cost review of the various sorbents available for carbon capture, and concluded that despite its decay in activity, limestone is the most economical and abundant sorbent currently available.

3.12 Calcium Looping Cycle Technology Scale-Up

As mentioned, the calcium looping cycle for post combustion CO₂ capture has been successfully demonstrated in numerous laboratory and bench scale reactors, and also in a small number of pilot scale reactors. It is well recognised that further scale-up of the technology is required [163]. A summary of the pilot scale reactors is provided in Table 3-1(adapted from Dean *et al.*, 2010 [11]), and the findings from pilot scale research to date, including those challenges identified associated with technology scale up, are outlined below.

Table 3-1 Summary of post combustion capture pilot plant reactors, adapted from Dean *et al.*, 2010 [11].

Research Institute	Reactor Capacity	Calciner Technology	Carbonator Technology	Other Features	Inlet CO ₂ concentration (vol %)	Gas Distributor Type	Method of Solids Transfer Between Reactors
University of Stuttgart [6] [7]	10 kW _{th}	CFB 12.1 m high, 0.071 m ID	BFB 0.114 m ID	Gas Velocity 4 - 6 m/s Residence Time (calciner) 1-5 mins	11-15 %	-	Cone valve and loop seal
	200 kW _{th}	CFB 10m high	CFB 10m high	Cone valve for solids transfer	10-15%		
INCAR-CSIC, Oviedo, Spain [104]	30 kW _{th}	CFBC 6.0 m high, 0.1m ID	CFB 6.5 m high, 0.1 m ID	Gas Velocity 1.1-3.5 m/s Residence time (calciner) 1-5 mins	3-25 %	Air from a blower, CO ₂ from a dewar - no gas distributor required [88]	Fluidisation of loop seal
CANMET Energy and Technology Centre, Ottawa, Canada [8]	75 kW _{th}	CFBC 5m high, 0.1m ID	BFB 5m high, 0.1m ID	Gas Velocity 82.5 slpm	15-16 %	Distributor plate for air and CO ₂	'L' valve and solenoid ball valve

Darmstadt Technical University [164]	1 MW _{th}	CFBC	CFB 8.66m high, 0.59m ID	-	-	Air fan for air and CO ₂	Fluidisation of loop seal
University of Vienna [165]	100 kW _{th}	CFBC	CFB gasifier/ carbonator	CaO catalyst reduced tar formation and lowered required temperatures	10 % (mol)	-	-
Ohio State University [166]	120 kW _{th}	Rotary kiln	Entrained flow bed	Hydration reactor key in reactivating sorbent	12.5 %	-	-
Tsinghua University [124]	10 kW _{th}	1m high, 0.117 ID	1m high, 0.149m ID	Calciner fluidised with air	12% - 13%	Distributor plate with wind caps	Downcomers
Industrial Technology Research Institute, Taiwan [167]	1 kW _{th} 1.9 MW _{th} proposed	BFB 2.5m high, 0.1m ID	Moving bed 0.9m long, 0.05m ID	Batch mode operation required carbonator and calciner temperature of 600-700 °C Pilot plant proposed with Hualian Peace cement plant	15 %	-	-

3.12.1 University of Stuttgart, Germany

The University of Stuttgart operates a 10 kW dual fluidised bed, comprising a 12.4 m high and 0.071 m diameter riser (operating as the calciner), and a 0.114 m diameter bubbling fluidised bed (operating as the carbonator), which has to date achieved 93 % CO₂ capture [7]. Solids transfer is controlled by a cone valve located between the two reactors, and the carbonator is fluidised with synthetic CO₂ and N₂, whilst the calciner and loop seals are fluidised with air. Key findings from the work include that an increased calcium looping ratio of 16 results in an increased capture efficiency of almost 100 % because there is a lower carbonated bed fraction, compared to a ratio of 4, which results in a capture efficiency of 55 %. Increasing space time (ratio of moles of CaO, to CO₂ per hour in the gas feed) too increases capture efficiency because there is an increase in bed inventory for a constant molar inlet flow of CO₂.

Stuttgart also operates a 200 kW_{th} calcium looping reactor, which has achieved over 90 % CO₂ capture. It was recognised that redesign of loop seals when compared to the 10kW reactor, was required to achieve required looping ratios and stable operation, given the presence of 2 CFBCs and 2 cone valves [168]. They have identified that operation with wet flue gas achieves capture values closer to that of equilibrium than with dry flue gas, for temperatures between 580 and 680 °C, implying that wet flue gas enhances carbonation (Figure 3-15). In the same reactor, sorbent loss due to attrition has been calculated to be low at 3 % of bed weight/hour [169].

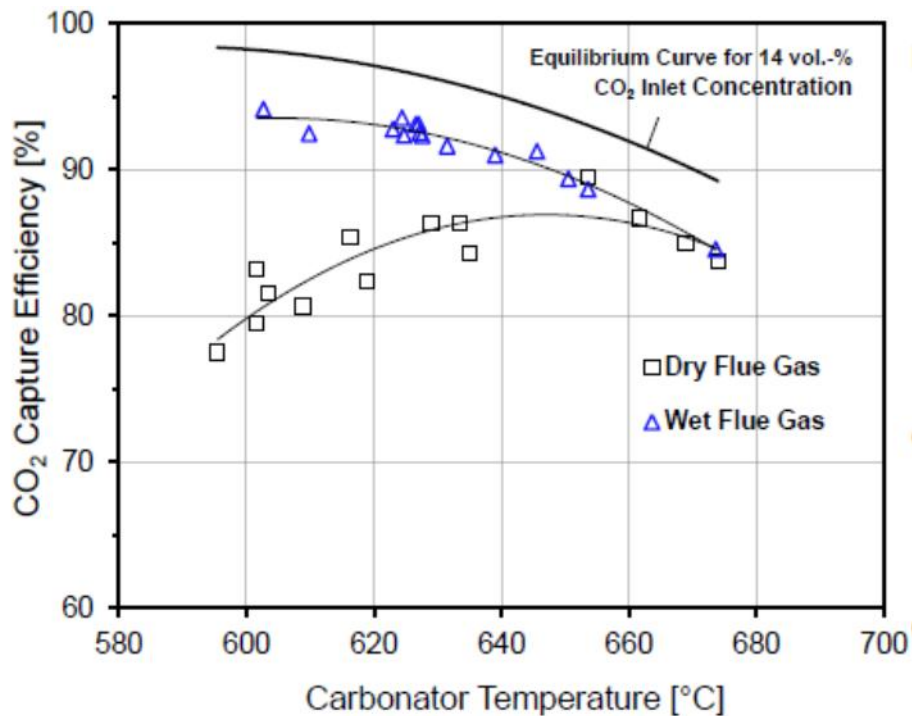


Figure 3-15 Effect of dry flue gas and wet flue gas on CO₂ capture efficiency [169].

3.12.2 INCAR-CSIC, Oviedo, Spain

INCAR-CSIC operates a 30 kW_{th} dual fluidised bed, of which the carbonator riser is 6.5 m high and the calciner is 6.0 m high, and both are of 0.1 m diameter [5]. Loop seals control solids transfer between reactors. A number of challenges reported with reactor operation include inefficient operation of original cyclones, resulting in insufficient solids inventory and therefore high capture efficiencies for only short periods of time. Riser height was also increased from the original 3.2 m to 6.5 m, improving solids circulation rates and bed inventory, and therefore stability of capture efficiency at over 70 %, and close to 90 % [5].

3.12.3 CANMET Energy and Technology Centre, Ottawa, Canada

Canmet operates a 75 kW_{th} dual fluidised bed reactor, with a bubbling fluidised bed riser and circulating fluidised bed combustor, both of 5.0 m height and diameter 0.1 m. A computer operated solenoid valve controls solids flow from calciner to carbonator, whilst an 'L' valve controls solids transfer from cyclone to carbonator. A high CO₂ capture efficiency of over 90 % was recorded for the

first cycles, which decreased to over 75 % after 25 cycles. Attrition of the CO₂ sorbent was found to be a limiting factor in the process performance, with 30% of bed capture by cyclones after 3 cycles. Attrition appeared to continue at a high level with increasing cycle numbers. It was recognised that optimisation of the process requires further investigation [8].

3.12.4 Technical University of Darmstadt, Germany

A 1 MW circulating fluidized bed reactor has been built and operated at Darmstadt University. The carbonator CFB is 8.66 m high, and 0.59 m internal diameter, whilst the calciner CFB is 11.3 m high and 0.4 m internal diameter. Preliminary batch experiments acknowledged that burner nozzle design required further work, as the required pressure was not being obtained due to reduced gas flow from operation of only one reactor [164]. Looping tests identified that 80 % CO₂ absorption was achieved in the carbonator.

3.12.5 University of Vienna, Austria

The University of Vienna has developed the 'adsorption enhanced reforming' process for steam gasification of biomass. A dual fluidized bed system comprises a 100 kW_{th} gasifier and carbonator combination, of which the gasifier is 3 m high and 0.108 m diameter. The process has demonstrated H₂ production from biomass in concentrations of 70 % mol (dry). The simultaneous sorption of CO₂ appears to suppress tar formation from the process. The process has also been successfully demonstrated at an 8 MW_{th} plant in Guessing, Austria, where H₂ concentrations of 50 % were achieved.

3.12.6 Ohio State University, Columbus, USA

Ohio State University has developed the Calcium Looping Process which comprises three components, namely the carbonator, calciner and hydrator. The process has been successfully demonstrated in a 120kW_{th} reactor. Coal combustion flue gas is introduced to an entrained flow carbonator, where at a temperature of approximately 450-650°C carbonation and sulphation of CaO / Ca(OH)₂ takes place, and also dehydration of Ca(OH)₂. The sorbent is then transferred to a rotary kiln calciner for sorbent regeneration between 900-

1300°C, after which CaO is then transferred to a hydrator for sorbent reactivation. Results from the reactor have confirmed >90 % CO₂ removal, and 100 % SO₂ removal at a Ca:C ratio of 1:3. CaO activity dropped to one-third of its original prior to hydration, after which activity was increased back to its original value. Ca(OH)₂ was identified to have the highest reactivity, leading to low Ca:C ratio and residence time. CaSO₄ produced in the carbonator is stable below temperatures of 1450°C, therefore a solids purge of 2-10 % is required to prevent all sorbent forming CaSO₄. Further, the small Ca(OH)₂ particle size of 3 µm may be difficult to maintain in an industrial scenario, taking into account attrition and sintering effects.

3.12.7 Tsinghua University, China

Tsinghua University operates a 10 kW_{th} dual bubbling fluidized bed reactor, comprising a carbonator of 1 m height and 0.149 m internal diameter, and a calciner of 1 m height and internal diameter of 0.117 m. A CO₂ capture capacity of approximately 95 % has been achieved in the reactor with a CaO conversion of approximately 70.4 % in the carbonator. Sorbent fragmentation and attrition were considered to be important issues for the reactor, where after 7 hours of operation the particle size distribution (PSD) was reduced from 0.2 - 1.0 mm, to 0.16 - 0.42 mm.

3.12.8 Industrial Technology Research Institute, Taiwan

The Industrial Technology Research Institute (ITRI), Taiwan operates a 1 kW_{th} CO₂ capture reactor comprising a 2.5 m high, 0.1m ID bubbling fluidized bed carbonator and a 0.9m long, 0.05m ID moving bed calciner. CO₂ capture efficiencies of 99% have been achieved in the reactor to date. The Institute has also developed a 1.9 MW scale pilot plant in collaboration with Taiwan's Hualien Peace cement plant.

4 HYDRODYNAMICS AND FLUIDISATION

High temperature fluidised bed reactors are generally constructed from stainless steel, thereby making it virtually impossible to observe the fluidisation processes taking place within the bed and thus not allowing visual inspection to ensure that the process is working efficiently. Cold models are therefore considered an alternative in order to determine the hydrodynamics of hot fluidised beds, due to the fact that they are cheap to design, construct, operate and modify, whilst at the same time providing reliable information on hydrodynamics providing appropriate scaling criteria are observed. Understanding the hydrodynamics of a system is important in determining where modifications may be made to maximise the efficiency of a CO₂ capture system employing fluidised bed technology. Further, where it may be required to convert the system to accommodate such modifications, cold models allow this to be done so at low costs and within smaller time scales than for hot reactors. Understanding hydrodynamics is vital for reactor design and scale-up, plant operation and optimisation [170].

4.1 Hydrodynamic Scaling

Differences in temperature and pressure between hot and cold models affect gas density, viscosity, and the gas flow rate, thus affect the hydrodynamics of such systems. A number of scaling laws are available in the literature, which permit geometrically-similar fluidised beds with other varying properties, to be scaled so that they are hydrodynamically-comparable. Fitzgerald (1984) [171] identified that in flow modelling, if the four dimensionless groups of the continuity equations and momentum balance for gas and solid phases have the same numerical values in two geometrically similar fluidised beds of otherwise different properties (particle size, particle density, gas viscosity etc) then both beds are hydrodynamically similar.

The scaling laws most widely used throughout the literature in order to scale hot fluidised beds to produce prototype cold models are those of Horio *et al.*, 1986

[172] and of Glicksman (1984) [173] and Glicksman *et al.*, 1993 [174]. Glicksman (1984) [173] derived a full set of scaling laws (Equation 4-1) based on the fluid and particle continuity and motion equations of Anderson and Jackson (1967) [175].

$$\frac{u_0^2}{gL}, \frac{\rho_s}{\rho_f}, \frac{\rho_f u_0 L}{\mu}, \frac{\rho_f u_0 d_p}{\mu}, \frac{L_1}{L_2}, \frac{G_s}{\rho_s u_0}, \phi, \text{PSD} \quad \text{Equation 4-1}$$

Glicksman *et al.*, 1993 [174] then went on to provide the set of reduced scaling laws (Equation 4-2), derived from the original full set of scaling laws.

$$\frac{u_0^2}{gL}, \frac{\rho_s}{\rho_f}, \frac{u_0}{u_{mf}}, \frac{L_1}{L_2}, \frac{G_s}{\rho_s u_0}, \phi, \text{PSD} \quad \text{Equation 4-2}$$

where Reynolds number is in intermediate region i.e. $0.4 < \text{Re} < 500$

In the viscous limit, the simplified set can be reduced further (Equation 4-3), as it is considered that gas phase inertia is negligible compared to viscous forces, so the particle-gas density ratio can be emitted.

$$\frac{u_0^2}{gL}, \frac{u_0}{u_{mf}}, \frac{L_1}{L_2}, \frac{G_s}{\rho_s u_0}, \phi, \text{PSD} \quad \text{Equation 4-3}$$

Glicksman noted that the scaling laws of Horio *et al.*, 1989 [176] (Equation 4-4 and Equation 4-5) were identical to the viscous limit of Glicksman's full set of scaling laws [173] at low Reynolds numbers, from which the simplified scaling laws were derived.

$$U_2 - u_{mf2} = \sqrt{m(U_1 - u_{mf1})} \quad \text{Equation 4-4}$$

$$u_{mf2} = \sqrt{m \cdot u_{mf1}} \quad \text{Equation 4-5}$$

where u_1 and u_2 = superficial gas velocity of reactors 1 and 2 respectively (ms^{-1}); U_{mf1} and U_{mf2} = minimum fluidisation velocity of sorbent reactors 1 and 2 respectively (ms^{-1}); and m = geometric scale based on size of reactor.

It was observed that where a cold scale model is operated with air at ambient pressure and temperature, the fluid density and viscosity will be significantly different between the two gas conditions. When the Reynolds number (based on particle diameter and fluid properties [177]) is small, fluid inertial effects are unimportant and the number of non-dimensional parameters can be reduced by omitting the fluid density. At high Reynold's numbers, the fluid viscosity is deemed unimportant. This was also demonstrated in work carried out on bubbling fluidised beds [178], concluding that Glicksman's simplified scaling laws are suitable for the viscous limit when Re_p is less than 30, but when Re_p has a value greater than 30, Glicksman's full set of scaling laws are required [179].

A number of modifications based on these laws have been explored in the literature [180] [178] [181]. Anderson and Jackson [175] originally suggested that the dimensionless measure of particle shape should be matched for non-spherical particles, in agreement with Glicksman who too proposed that particle sphericity should be set as an identical parameter in order to simplify the scaling process. To simplify this concept further, other work [179] [180] sought to incorporate sphericity with other dimensionless groups, instead of treating it as a separate entity.

Louge (1987) [181] investigated Glicksman's simplified scaling laws for circulating beds, and added the ratio of particle and gas mass flow rates per unit area (i.e. loading) to Glicksman's dimensionless parameters. In contrast to later work carried out by Horio *et al.*, 1989 [176], further scaling laws were proposed which did not include gas and particle flow rates per unit area [179].

Numerous studies have demonstrated the utility of the scaling laws, although there are several studies which acknowledge that aspects of the scaling laws are not wholly accurate, thus limiting the effectiveness of the scaling process under certain circumstances. These limitations are summarised in Table 4-1.

Table 4-1 Scaling law limitations acknowledged in the literature.

Scaling Law Limitation	Reference(s)	Cold Model	Hot Reactor	Reactor Application
Volume increase which occurred during methane combustion in a hot model could not be accurately represented in the cold model of the system, but overall the cold model study provided useful information on the fluid dynamic behaviour.	Kronberger <i>et al.</i> , 2005 [182]	0.55L	2.2m high, 10kW	Chemical looping combustion (CLC)
Scaling laws do not take into account effects from inter-particle forces, primarily because of the difficulty in measuring them. There is some agreement that inter-particle forces are an important factor in scaling, and influence fluidised bed dynamics.	Knowlton <i>et al.</i> , 2005 [183]	n/a	n/a	n/a
	Pröll <i>et al.</i> , 2009 [184]	1:3 scale 0.46x0.46m	4.1m air riser, 3m fuel riser, 120kW	CLC
	Fitzgerald <i>et al.</i> , 1984. [171]		1.83x1.83m	Fluidised bed combustor
	Yang <i>et al.</i> 2000 [185]	3m high, 0.3m i.d.	n/a	Fluidised bed gasifier
Gas/solid-wall friction and solid acceleration effects are not accounted for. To accommodate this, Issanger <i>et al.</i> , (1999) modified Chang and Louge's momentum equation for one-dimensional acceleration by adding terms for friction.	Boukis <i>et al.</i> 2007 [186]	Full scale	2m riser, 0.5m combustor	Circulating fluidised bed
	Pröll <i>et al.</i> 2009 [184; 187]	1:3 scale	4.1m air riser, 3m fuel riser, 120kW	Chemical Looping Combustor

Scaling Law Limitation	Reference(s)	Cold Model	Hot Reactor	Reactor Application
It is generally necessary to change the sorbent size and/or density in cold models to achieve the same dimensionless numbers in the hot and cold reactor. Further, for scaling to be successfully applied, the flow regime and the particle Geldart Group should be the same in both sizes of beds (Knowlton <i>et al.</i>, 2005). However, it is widely accepted that Group B particles are more difficult to scale up than Group A particles, because bubbles grow too much larger sizes with Group B particles, and hence slug more readily.	Knowlton <i>et al.</i> , 2005 [183]	n/a	n/a	n/a
Scale models only provide a true representation of the prototype if the assumption that 'no quantities not included in the dimensionless groups are important' is satisfied.	Grace and Taghipour (2004) [188]	n/a	n/a	Fluidised beds

Despite reservations on the scaling accuracy, it is considered that the use of scaling laws remains the most efficient, cost effective method of determining the hydrodynamics of a hot fluidised bed system, and it is generally accepted that certain aspects of the dimensionless parameters may be ‘relaxed under extreme conditions’ in order to compromise and make cold model gas and sorbent selections easier [185].

In order to account for the changes in density between the hot conditions of the reactor, and ambient conditions of the cold model, the density of the solids used can be increased to achieve similarity of the density ratio included in the scaling laws. A summary of the particle properties used for cold model work in the literature is provided in Table 4-2.

Table 4-2 Particle properties used in cold model investigations.

Particle	ρ_s (kg m ⁻³)	ρ_s (hot): ρ_s (cold)	dp (μm)	U_{mf} (m s ⁻¹)	Reference
CaCO ₃	2500	0	93	0.72	Fitzgerald <i>et al.</i> , 1984 [171]
Sand	2650	2.2	385	0.07	Ramirez <i>et al.</i> , 2007 [189]
	2600	2.01	150	0.32 (u)	Johansson <i>et al.</i> , 2003 [190]
	2575	-	106-212	0.018	Ryu <i>et al.</i> , 2007 [191]
Bronze powder	8730	2.72	54	4.25 (u)	Pröll <i>et al.</i> , 2009 [184]
	8900	-	180	0.11	Kehlenbeck <i>et al.</i> , 2004 [192]
	8750	3.5	110-150	0.5 (u)	Bolhar-Nordenkamp <i>et al.</i> , 2002 [193]
Glass beads	2550	0	67.5	0.74 (u)	Kronberger <i>et al.</i> , 2005 [182]

Particle	ρ_s (kg m ⁻³)	ρ_s (hot): ρ_s (cold)	dp (μ m)	U_{mf} (m s ⁻¹)	Reference
	2530	-	109	-	Chang <i>et al.</i> , 1992 [179]
	2600	3.7	200-240	-	Foscolo <i>et al.</i> , 2007 [194]
	2540	0.94	88.3 -112.3	0.014 – 0.028	Glicksman <i>et al.</i> , 1993 [174]
Zirconium dioxide (ZrO ₂)	5700	3.16	142 / 230	2.31 / 3.21 (u)	Charitos <i>et al.</i> , 2010 [6]
Plastic grit	1440	-	234	-	Chang <i>et al.</i> , 1992 [179]
	1400	0.52	99.5 / 144.5	0.0085 / 0.0155	Glicksman <i>et al.</i> , 1993 [174]
Steel grit	7400	-	67	-	Chang <i>et al.</i> , 1992 [179]
Copper particles	9000	3.6	500	0.53	Fitzgerald <i>et al.</i> , 1984 [171]
	8822	3.7	122	0.044	Foscolo <i>et al.</i> , 2007 [194]
Steel particles	7250	2.7	26 / 49.5 / 57.7	0.0075 / 0.014 / 0.015	Glicksman <i>et al.</i> , 1993 [174]

4.2 Flow Regime in a Fluidised Bed Reactor

Solids flow within fluidised beds has been studied in numerous past research papers, and has been described as a number of convective currents occurring in different regions of the bed, and induced by rising bubbles [195] [196]. Flow is generally formed of a dilute upward solids flow in the core driven by bubble activity, with a higher concentration, downward solids flow in the emulsion region near the walls [197] [198] [195]. Charitos *et al.*, 2010 [6] suggested that there are three regions of operation in a cold model of a circulating fluidised bed (CFB): a region of stable riser operation; bordered by a slugging region at lower velocities; and a region of unstable riser operation at higher velocities, although it was noted that this observation could be due to lower operation temperatures in a cold model compared to a reactor at temperature.

Solids exchange is known to occur between the 'countercurrent' (i.e. upward and downward) phases, although Abanades and Grasa (2001) [195] suggest that an exchange of solids between 'cocurrent' phases (i.e. flow in the same direction) from adjacent convection currents does occur, but driven by the same mechanism as counter current exchange. In their development of a counter-current backmixing model, which proved to adequately describe axial and lateral mixing of fluidised beds, they suggest that counter current solids exchange is always greater than concurrent solids flow. Solids velocities in fluidised beds have been identified to be lower than those for bubble velocities [195] [199].

de Diego *et al.*, 1995 [197] noted that solid flux downward through the annulus decreased with height in the riser, and annulus thickness decreased with height in the riser and with an increase in superficial gas velocity for each solid and particle size. Issanger *et al.*, 1999 however observed that at high solids flux and density conditions, a more homogenous flow regime is formed, starting from the bottom of the reactor and gradually working upwards.

Cold model studies of CFBs have identified that global solids circulation is relatively little influenced at all by operating conditions in the fuel reactor, but rather it is the air reactor conditions which has the greatest influence [182] [184] [194]. Increasing gas velocity in the FR affected the pressure profile of the FR, and increased the solid holdup in the AR by pushing more solids through the lower loop seal [184].

It is suggested that particle size affects hydrodynamic stability in fluidised beds. Glicksman *et al.*, 1984 [173; 174] included particle diameter within their full set of scaling laws, and Kronberger *et al.*, 2005 [182] concluded that increasing fluidisation velocity and decreasing particle size improved particle mixing, and reduced the prominence of less active zones in the bed.

Kunni and Levenspiel (1991) [196] suggest that complete solids mixing through a fluidised bed occurs because those particles close enough to a moving bubble, are drawn into its 'wake' and thus complete mixing occurred where there was motion. An equation to describe this concept was developed, which was further modified by Shi and Fan (1984) [200] to estimate the lateral dispersion coefficient, D_{sr} (Equation 4-6).

$$\frac{D_{sr}}{(U-U_{mf})h_{mf}} = 0.46 \left[\frac{(U-U_{mf})d_p \rho_f}{\mu_f} \right]^{-0.21} \left[\frac{h_{mf}}{d_p} \right]^{0.24} \left[\frac{\rho_s - \rho_f}{\rho_f} \right]^{-0.43} \quad \text{Equation 4-6}$$

Grasa and Abanades [201] used this equation to fit the experimental data of lateral solids mixing observed in a gas-solid fluidised bed (Figure 4-1). Phosphor material comprising SrAl_2O_4 with traces of Eu and Dy as a coating on particles, was used to observe and trace particle movements [201] [202]. The solids were activated with a UV source and emitted visible light for several minutes. Part of the bed had the coating, allowing the mixing process to be tracked. The experiment was recorded with a video camera for image quantitative analysis and the tracer concentration was directly proportional to the luminescence in the images (Equation 4-7). The concentration profiles obtained were used to determine lateral dispersion coefficients and were found to fit well with Equation 4-6 proposed by Shi and Fan [200].

$$CA = \frac{I_A - I_{\min}}{I_{\max} - I_{\min}} \quad \text{Equation 4-7}$$

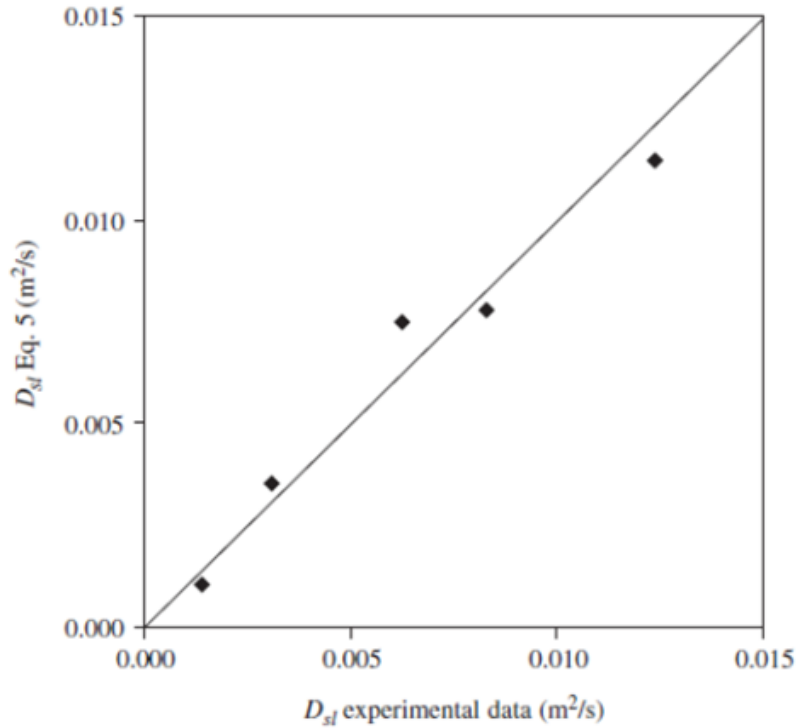


Figure 4-1 Comparison between D_{sl} calculated with Equation 4-7 and D_{sl} fitted individually to the experiments [201].

Temperature change across a bed can also provide information regarding solids movement. Werther (1999) [198] suggested that thermocouples located along a riser can provide information on solids mixing, for example, an unexpected increase in temperature may result from particle agglomeration. Kunii and Levenspiel (1991) [196] derived the following equation to link thermal conductivity of a fluidised bed and the mobility of solids [196] [201] (Equation 4-8):

$$k_l = D_{sl} C_{pe} \rho_e \quad \text{Equation 4-8}$$

where C_{pe} and ρ_e are the calciner effective values of specific heat and density respectively; D_{sl} is the solids lateral diffusion coefficient in the bed.

4.3 Pressure Change

Pressure change measurement along a reactor length can be used to determine a variety of characteristics of fluidised bed reactors (FBRs), including quality of fluidisation, bubble formation and bubble motion [171]. Once fluidisation has

occurred within a FBR, solids are suspended in solution by the upward drag force of the moving gas. Therefore the pressure drop of the gas is approximately equal to the weight of the solids minus buoyancy per cross-sectional area of the bed, as denoted by Equation 4-9, from which the height of the fluidised bed can be calculated [198]:

$$\Delta P = (\rho_s - \rho_f)c_v g \Delta h \quad \text{Equation 4-9}$$

At a given gas velocity, it has been observed that pressure drop increases with increasing solids flux, and likewise, for a given solids flux, pressure drop increases with increasing superficial gas velocity. In addition, the properties of various particles have an impact upon the system hydrodynamics, and hence pressure drop, predictions of which were made using a modified version of the Ergun equation [110].

Pressure drop across cold models is generally measured with the use of pressure transducers across the reactor length. Once steady state has been achieved, pressure drops across the cold model can be measured for a particular length of time [6] [110]. It has been noted that there appears to be a height above the distribution plate at which pressure fluctuations are regular, and below which are random, which may be caused by bubble formation or coalescence [171], and therefore care should be taken in interpreting these results.

Pressure profiles of a cold model identified exponential decay of pressure, and therefore solid concentrations, with height in the fuel reactor. In the air reactor however, decay was linear suggesting high solids concentration over the whole height (Figure 4-2a) [184]. Johansson *et al.*, 2003 [190] carried out preparatory tests on a cold model and identified that the pressure change between the fuel reactor and the rest of the system should be as small as possible in order to minimise gas bypassing (Figure 4-2b). Despite this, the pressure in the fuel reactor should be higher than in the cyclone, but lower than in the air reactor, to ensure solids movement in the appropriate direction. It was noted that pressure in the fuel reactor could be controlled by changing the outlet cross-sectional area [190].

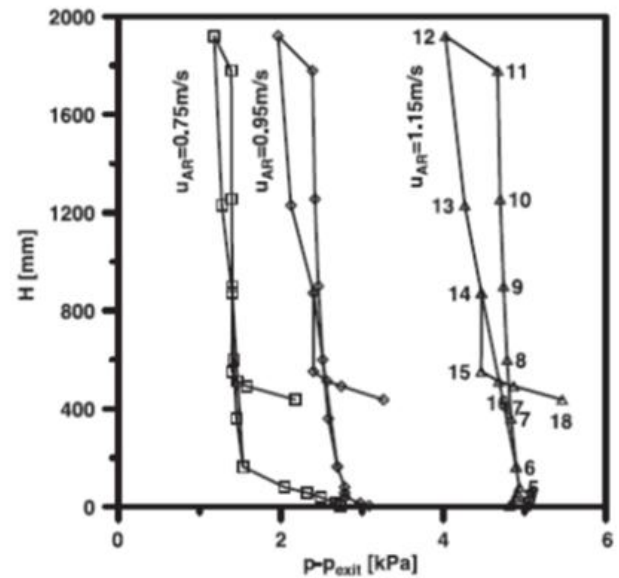
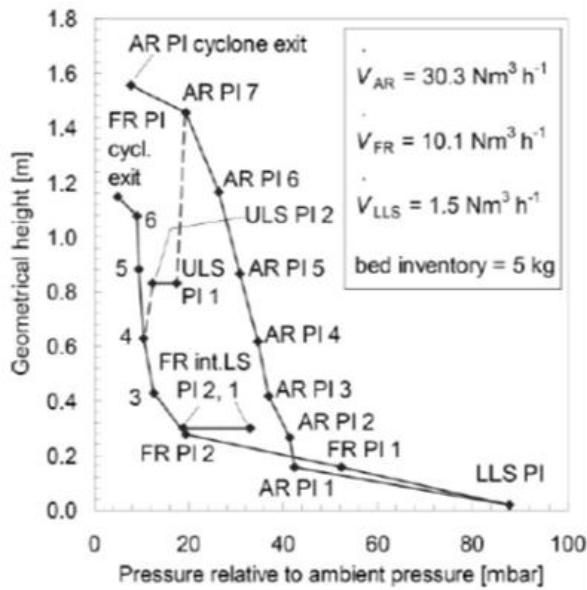


Figure 4-2 a) Pressure profile for a cold model, where FR is fuel reactor and AR is air reactor [184]; b) Pressure profile for a cold model, where 1 -11 is air reactor, 12 outlet from cyclone, 13 top of downcomer and 14-18 fuel reactor [190].

4.4 Particle Residence Time Distribution

Particle residence times (PRT) and PRT distribution (PRTD) throughout a CFB can provide important information on mixing and flow throughout a riser. Further, many chemical reactions occurring in fluidised beds are dependent upon a minimum residence time, therefore an understanding of this concept with regards to a specific reactor is important. Throughout the literature, a number of different techniques have been applied to determine PRTD's in cold models of CFB risers, including the use of phosphorescent, radioactive, ferromagnetic, chemically-different, coloured, and different –size, and different-temperature tracers, as well as the use of single particle tracking [170].

NaCl as a tracer measurement has been widely used, whereby a pulse of NaCl was injected into solids flow and bed material samples were taken at the downcomer of the fuel reactor particle overflow at given time intervals. Concentration of solid sample is determined by a conductivity method and RTD is derived by standard methods [182] [203]. Smolders and Bayens (2000) [204] calculated RTD of the total system from the experimentally measured salt concentration (Equation 4-10):

$$E(t) = \frac{C(t)}{\int_0^\sigma C(t)dt} \approx \frac{C(t_i)}{\sum_{i=0}^\sigma C(t_i)\Delta t_i} \quad \text{Equation 4-10}$$

Harris *et al.*, 2002 [205] developed the ‘fast response particle RTD technique’ using phosphorescent particles to trace solids movement, and in turn RTD. A small proportion of the bed becomes tracers when activated by a high intensity light pulse. Concentration time curves are measured, from which RTD is calculated. They found the RTD curves were indicative of core annulus flow within the riser, characterised by a short breakthrough time, sharp peak, and long tail. An increase in superficial gas velocity increased the mean RTD, also observed by Kuo and Cheng (2006) [206], although opposite to what was found by Mahmoudi *et al.*, 2011 [207] (Figure 4-3). An increase in solids flux however led to a decrease in mean RTD [205] [207], which Kehlenbeck *et al.*, 2002 [192] observed to decrease exponentially and from which developed Equation 4-11 to show the dependency of RTD on solids circulation rate.

$$t_{res} = 2 + \frac{1}{4 \times 10^{-3} \exp(4 \times 10^5 M)} \quad \text{Equation 4-11}$$

Where t_{res} is mean residence time of solids in entire system, M is dimensionless mass turnover.

M can be calculated from Equation 4-12 [192]:

$$M = \frac{m^* D_{riser}}{m u_t} \quad \text{Equation 4-12}$$

Where m^* is mass flow (kg/s), m is total mass load (kg), D_{riser} is riser diameter (m), u_t is the terminal settling velocity of particles (m/s).

The use of single particle radioactive particle tracking has been used to investigate effects of solids flux on RTD [208] [207]. Mahmoudo *et al.*, 2011 [207] confirmed from the results that solids mixing differs depending on the flow regime, with dilute and dense riser flows associated with dominant pug flow, whilst core-annulus regime

corresponds with solids backmixing. The RTD predictions were considered to be valid only for dilute and dense upflows.

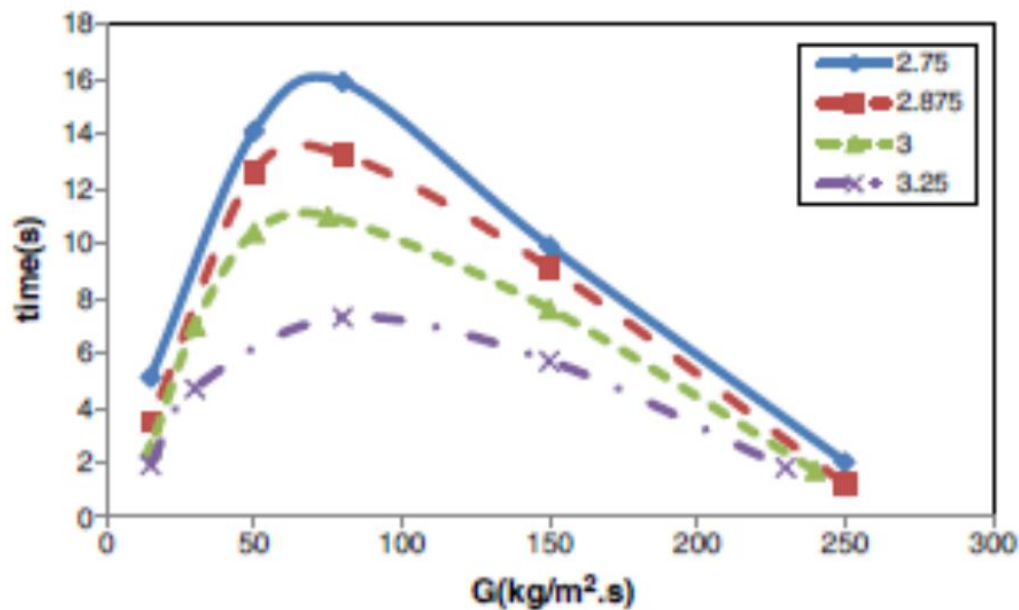


Figure 4-3 Residence time in the riser versus solids circulation flux, G , for superficial gas velocity, U , in the range 2.5 to 3.5 m/s [207].

Harris *et al.*, 2002 [170] suggest that in their investigation wall effects were pronounced, given the lower values for RTD when calculated by pressure drop, when compared with the tracer method.

With further regard to flow regime, Kronberger *et al.*, 2005 [182] suggest their PRT results show strong deviation from the assumption of ideal mixing of an ideal continuous stirred tank reactor as proposed by Geldart (1986) [209], due to less active regions in the bed existing at low fluidisation velocities.

Smolders and Baeyens (2000) [204] used a plug-flow with dispersion model to successfully predict RTD and average residence time.

4.5 Gas Bypassing

It is important to minimise gas bypassing within a CO₂ capture reactor in order to optimise the efficiency of the carbon capture process. Bypassing from fuel reactor to the air reactor will result in release of CO₂ to the atmosphere and reduce the efficiency of the process, whilst bypassing from the air reactor to the fuel reactor will

cause the CO₂ stream for storage to be diluted with N₂, further reducing process efficiency and introducing additional costs for N₂ removal.

Tracer gas techniques are widely used in cold model research to determine gas leakage and gas mixing [185] [179] [182] [191] [190]. The method uses an inert tracer gas which is added to, or replaces, the original fluidising medium, and concentrations are detected by a gas analyser from various ports located in the model. Solving mass balances depends on the amount of tracer gas detected which can then be used to determine the gas leakage from the reactor.

Johansson *et al.*, 2003 [190] studied gas leakage from a cold model of an interconnected fluidised bed for chemical looping combustion. They concluded pressure balance was important and that the pressure difference between the fuel reactor and the rest of the system should be as small as possible in order to avoid leakages. For the same reason, pressure in the fuel reactor should be higher in the cyclone but lower than in the air reactor and the particle pot seal. It was identified that leakage increased as the velocity in the fuel reactor increased, but decreased as the velocity in the air reactor increased, as a consequence of increased particle flow. Ryu *et al.*, 2007 [191] noted that gas mixing particularly occurred between the two cyclones and downcomers.

It was observed that for various designs of a CLC cold model, gas velocity in the fuel reactor riser did not significantly affect gas bypassing into the air reactor. Gas bypassing was however affected by the cross-sectional area of the slot opening, which allowed transfer of solids from the fuel reactor to the air reactor, and that gas bubble exchange through this opening was the prime cause of gas bypassing. Reducing the slot height appeared to improve this situation [182].

Ryu *et al.*, 2007 [191] also found that with higher gas velocities, solids flow through the solids injection nozzle was stable and resulted in minimal gas bypassing to the bubbling fluidised bed, when compared with low gas velocities through the solids injection nozzle when gas bypassing was observed. Similarly, gas bypassing through solid injection nozzles was also noted by Fang *et al.*, 2009 [124] (Figure 4-4), who proposed increasing the height of the hole on the solids injection nozzle to reduce gas bypassing.

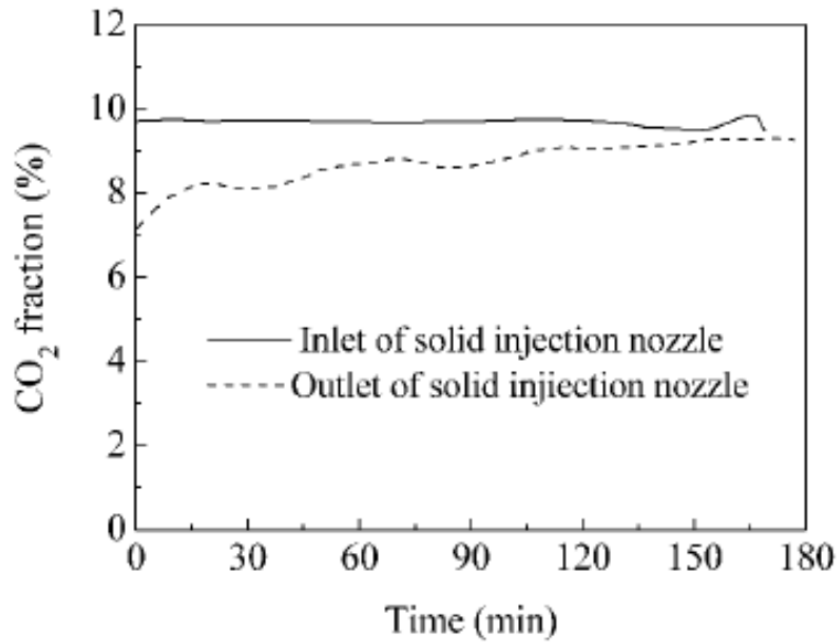


Figure 4-4 CO₂ tracer gas fraction at inlet and outlet of solid injection nozzle [124].

4.6 Solids Circulation Rate

Solids circulation fluxes depend on different operating conditions and characteristics of a FBR, such as gas velocity, particle size and density, diameter and height of the riser.

Solids circulation rate has been assessed using a number of methods described throughout the literature. These include the use of a sintered butterfly valve [179], solid sampling probes located inside the riser and calculation of the flux from Equation 4-13 [197], as well as from measurements of the pressure gradient in the riser.

$$G_{(r)} = \frac{W_s}{A_s T_s} \quad \text{Equation 4-13}$$

de Diego *et al.*, 1995 [197] identified that the measurement of solid fluxes using solid sampling probes depended on the suction velocity near to the wall. However, Rhodes *et al.*, 1991 [203] found in a CFB riser that the net flux was independent of the suction velocity when the suction velocity was high enough to prevent blockages of the sampling probe.

Huang *et al.*, 2009 [210] developed a model based on the Ergun equation which predicted solids flow rate and voidage in the dense phase of a standpipe. The model was then extended to successfully predict changes in the solids flow rate throughout a CFB. The method is considered beneficial due to the requirement for only a single pressure transducer, and because the model predictions include the profiles of pressure drop, voidage, solids and gas flow rates and hold-ups under transient conditions.

A number of papers describe the 'particle weight measurement technique' by which under steady state conditions, particles are diverted from the downcomer and captured, or the loop seals are not fluidised for a given interval, so that circulation rate can be calculated based on solids mass/bed height accumulation over a given time period [184] [191] [182] [87] [124]. This technique appears to be reproducible, providing the mass of particles accumulated in the measurement section is low compared to the total inventory in order to not disturb the system [184].

In a similar fashion, a cinematograph technique has been used whereby tracer particles are added to the particle bed and fluidisation is filmed, and the movie analysed frame by frame to determine solids circulation rate and pattern [198] [194] [201]. Phosphor material composed of SrAl_2O_4 has been used as a coating on particles, and in turn has been used as a method to observe and trace particle movement, whereby the solids are then activated with a UV source and emit visible light for several minutes. Part of the bed has the coating, allowing the mixing process to be tracked for later quantitative analysis. Tracer concentration is reportedly directly proportional to the luminescence in the images, given by Equation 4-7 [201].

For lower bed inventories, a low loop seal fluidisation limited the global particle circulation, but the lower loop seal was expected to be of less importance in the hot model because the ratio of wall surface to loop seal volume would be lower with the larger model [184]. This is in discrepancy with work undertaken by Kronberger *et al.*, 2005 [182] who identified that neither fluidisation velocity in the fuel reactor or particle loop seals affected solids circulation rate in a cold model. Total solids inventory and velocity in the riser strongly influenced the specific solids circulation

rate, with an increase in bed material increasing circulation rates, whilst reducing the riser length resulted in an increase in solids circulation rate [182] [193].

During experiments, air velocity in the riser was kept constant and solid circulation flux was increased progressively to the maximum, keeping the solid inventory constant. It has been reported that maximum solid circulation flux is dictated by the pressure balance in the CFB loop at a given superficial gas velocity in the riser and a given solid inventory. Solid circulation fluxes (dictated by pressure balance) increased exponentially when the gas velocity increased for both types of solids and their values were dependant on particle size used. Solid flux values obtained at each gas velocity decreased when the particle size increased [197]. Experimental results showed that although higher gas velocities did not improve circulation, solids circulation was greatest with high superficial gas velocities and thin walls (orifice length) [202].

Kuramoto *et al.*, 1986 [211] observed that the circulation rate of solids could be explained as a function of the pressure drop across an opening, shown by Equation 4-14.

$$W_d = C_{S0} \epsilon_u^{2.35} \frac{S_0}{S_d} \left[\frac{2\rho_d \Delta P_0}{1 - \frac{S_0}{S_d^2}} \right]^{0.5} \quad \text{Equation 4-14}$$

Where W_d is circulation rate of solids per unit area of a downcomer ($\text{kg/m}^2.\text{s}$), C_{S0} is particle discharge coefficient of an opening under outflow condition, ϵ_u is voidage at the bottom of an upflowing bed, S_0 is area of an opening (m^2), S_d is cross-sectional area of a downcomer (m^2), ρ_d is bed density of a downcomer (kg/m^3), ΔP_0 is pressure drop across an opening (Pa)

This work concludes that total solids inventory and velocity in the riser strongly influence the specific solids circulation rate.

4.7 Minimum Fluidisation Velocity

Minimum fluidisation velocity, U_{mf} , is the minimum gas velocity required for the particle bed to fluidise i.e. expand and formation of bubbles, whereby the upward drag of the gas is equal to the particle weight from gravity. An understanding of this

component for a fluidised bed is important from which to determine further hydrodynamic information. The force due to gravity is described by Equation 4-15, and the drag force represented by the Ergun equation (Equation 4-16), which provides the pressure drop along the length of a packed bed, taking into account factors such as sphericity, fluid density and particle packing.

$$W = (\rho_s - \rho_g) g (1 - \epsilon) h \quad \text{Equation 4-15}$$

$$\frac{\Delta P}{L} = \frac{\rho_g u_{mf}^2}{\Phi_s d_p \epsilon_{mf}^3} \left[\frac{150(1 - \epsilon_{mf})\mu}{\Phi_s d_p u_{mf} \rho_g} \right] + 175 \quad \text{Equation 4-16}$$

U_{mf} is therefore determined experimentally from bed pressure drop measurements. Pressure drop is approximately proportional to gas velocity, and the gas velocity value when the maximum pressure drop is reached is considered to be the minimum fluidisation velocity value (Figure 4-5) [191] [194]. Therefore, at minimum fluidisation velocity, the weight of the bed is equal to the pressure drop across the bed. When gas velocities exceed U_{mf} , the pressure drop remains largely unchanged. This is shown by Equation 4-17, based on the Ergun equation.

$$(\rho_s - \rho_g)g = \frac{\rho_g u_{mf}^2}{\Phi_s d_p \epsilon_{mf}^3} \left[\frac{150(1 - \epsilon_{mf})\mu}{\Phi_s d_p u_{mf} \rho_g} \right] + 175 \quad \text{Equation 4-17}$$

For particles of Reynolds number less than 10, typical of fluidisation systems, equation 11 can in turn be simplified to Equation 4-18 to calculate the minimum fluidisation velocity, U_{mf} .

$$U_{mf} = \frac{d_p^2 (\rho_s - \rho_g) g \epsilon_{mf}^2 \phi^2}{150\mu (1 - \epsilon_{mf})} \quad \text{Equation 4-18}$$

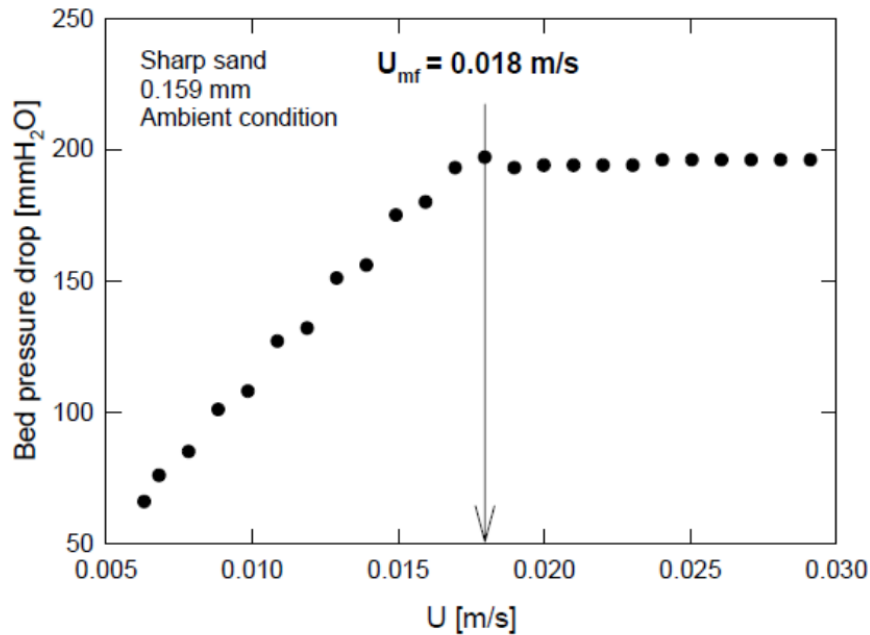


Fig. 3 Bed pressure drop versus gas velocity for sharp sand

Figure 4-5 Bed pressure drop versus superficial gas velocity, from which U_{mf} is determined [191].

Goo *et al.*, 2010 [212] investigated the effects of temperature on U_{mf} in a pilot scale dual fluidised bed gasifier. They found that increasing temperature from 25°C to 800°C decreased U_{mf} of silica sand particles, of density 255 kg m⁻³, from 0.065 m/s to 0.036 m/s. The same effect was also found by Zhiping *et al.*, 2007 [213] for U_{mf} experiments at high pressure (2.0 MPa), and with particles of 500 μm, for experiments in the temperature range 0 - 900 °C, whereby U_{mf} decreased from approximately 0.06 m/s at ~10°C to ~0.03 m/s at 900 °C. However, at the same pressure, the U_{mf} for slightly larger particles (750 μm) remained the same with increasing temperature, whilst the U_{mf} of large particles (2000 μm) increased with increasing temperature from ~0.25 m/s at ~10°C to ~0.45 m/s at 900 °C.

The inclusion of sphericity in Equation 4-17 and Equation 4-18 illustrates the importance of this factor in affecting U_{mf} values, and this too has been highlighted in the literature [214] [215]. Work carried out by de Vasconcelos and Mequita (2011) [216] looking at U_{mf} in a bench scale cold model bed of alumina fluoride of 0-250 μm particles, suggest that the correlation between experimental and predicted values of U_{mf} are sensitive to both sphericity and porosity. Similarly, Luckos and den Hoed (2004) [217] investigated fluidisation of ilmenite and titania slag particles and found

that measured U_{mf} values were higher for ilmenite particles due a higher density and sphericity. Further Kunni and Levenspiel (1991) [196] noted how the ratio of terminal to minimum fluidisation velocity is affected by particle size and sphericity, with the ratio increasing with increasing sphericity.

Seville *et al.*, 2000 [199] investigated effects of intermolecular forces on fluidisation. They looked at variation in U_{mf} with increasing temperature, for low-density polyethylene granules of 2 mm diameter, melting range 100–125 °C, and found that under non-sintering conditions, U_{mf} increased slightly in the temperature range 19-75 °C, and a U_{mf} value of 0.75 m/s was estimated at 100 °C, based on results extrapolation. However, above temperatures of approximately 100 °C, sintering forces came into effect, causing an increase in the U_{mf} value. The same authors note that adding a thin layer of liquid to fluidising powders, can cause powders to become more cohesive, resulting in an increase in U_{mf} due to an enhancement of the ‘liquid bridge effect’ between particles (Figure 4-6). This may account for variations in U_{mf} values between those estimated in cold models, and those in hot reactors, where in the latter steam effects will be more prevalent.

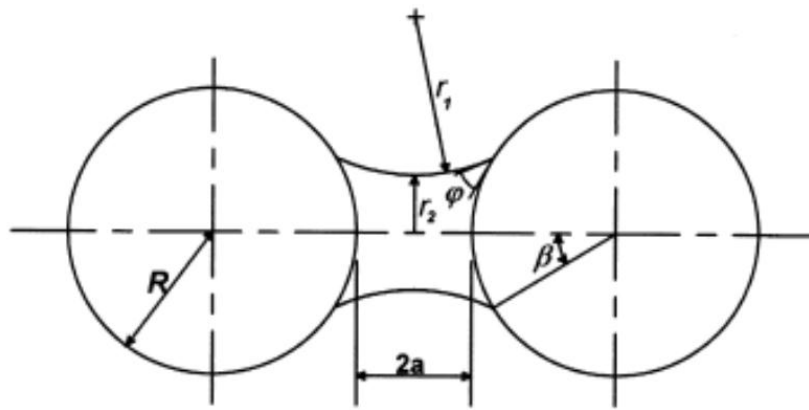


Figure 4-6 Liquid bridge effect between two equal spheres. a = half particle separation [199].

Foscolo *et al.*, 2007 [194] found agreement on U_{mf} values when increasing gas flux from zero to well above the U_{mf} value, and on reducing the bed from fluidised to fixed bed conditions.

Zhiping *et al.*, 2007 [213] investigated the effect of pressure and particle size on the U_{mf} of glass. They found that U_{mf} decreases with increasing pressure, and a greater increase in pressure is found as particle size increases (Figure 4-7).

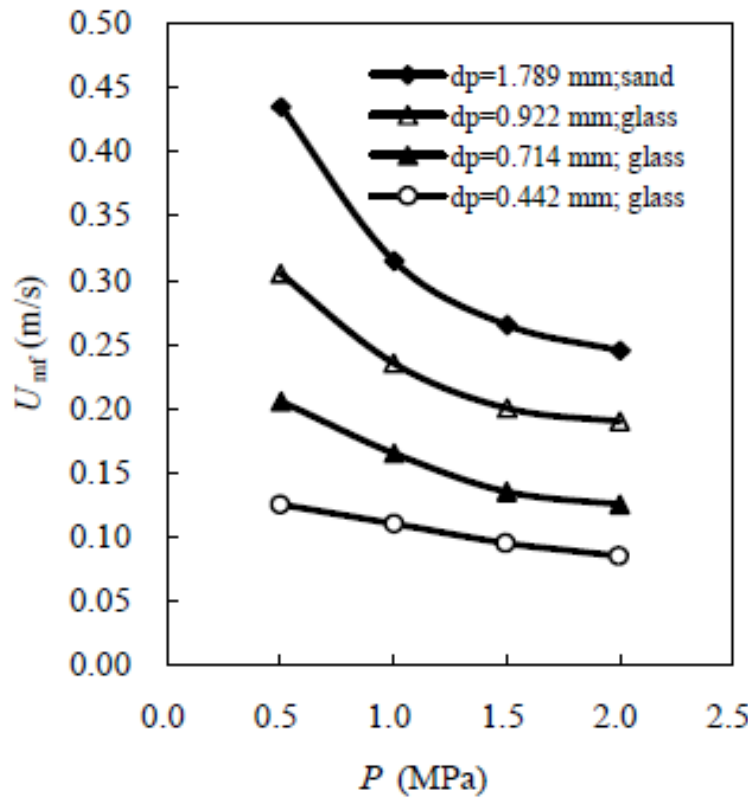


Figure 4-7 Effect of pressure and particle size on U_{mf} values for sand and glass particles [213].

Electrostatic Effects

Chang and Louge (1992) [179] observed electrostatic effects in a CFB facility. Effects were measured using capacitance probes, and were particularly pronounced with the use of plastic and glass powders. Visual effects could be seen from the adhesion of particles on the Plexiglass windows of the CFB. Electrostatic effects were less pronounced with the use of glass and steel powders. In addition, particle surface quality has found to affect flow: coating particles in a lubricant reduces surface friction, and therefore electrostatic effects, in the limit where the effective Coulomb friction coefficient is small. It is suggested in the literature that column wall effects come into force when column to packed particle ratios are smaller than approximately 30. Modifications to the Ergun equation are proposed to account for this wall effect [110].

5 ELEMENT PARTITIONING FROM LIMESTONE AND IN POWER GENERATION PROCESSES

5.1 Introduction

Extensive research on the calcium-looping cycle for carbon capture is available in the literature. However consideration of elemental emissions from this process appears to be minimal. Limestone is a naturally-occurring material, and thereby often contains other species in the form of trace, minor and major elements. The high temperature conditions under which carbonation and calcination occur present opportunities for elements to be released to the environment, thereby representing a potential source of environmental contamination, in addition to that produced from fossil fuel combustion.

With regards to elemental emissions from limestone use during the calcium looping cycle for CO₂ capture, Dean (2013) [218] carried out experiments at the bench scale to investigate the effect of coal use on limestone-derived sorbent trace element inventory. Experiments carried out without coal use showed no change in sorbent element inventory. Batch experiments carried out using La Jagua coal showed an observed increase in the concentration of Ba, Cr, K, Mn, Sr, and Ti, whilst concentrations of B, Na and K remain the same, whilst for Cu there was a small decrease. For continuous experiments comparing 2 different coals and refuse-derived fuel (RDF), an increase in Al content was observed suggesting some ash mixed in with the sorbent. The concentrations of Ba, K, Sr and Zn remained the same for all fuels. For Lea Hall coal, there was an increase in B over eight cycles from ~ 20 to 40 ppm, though not for La Jagua. For Cu, sorbent concentrations in the first cycle (~ 15 ppm) remained the same over eight cycles for the two coals, but increased over five cycles in the presence of RDF from ~ 20 ppm to ~ 180 ppm. Na remained the same for the sorbent cycled in the presence of La Jagua, but there was an increase in results for Lea Hall coal and RDF from ~ 250 to ~ 550 ppm and from ~ 200 to 400 ppm respectively, expected given that the Na content of the La Jagua coal is an order of magnitude lower than of the other two fuels. Ti remained the same for La Jagua over eight cycles, though saw an increase in the sorbent cycled in the presence of RDF over five cycles from ~ 50 ppm to ~ 150 ppm. There appear to be

no further studies available in the literature investigating elemental partitioning as a result of limestone use in the calcium looping cycle.

With regard to effects from other CCS technologies, there is information available in the literature on the potential environmental effects of post-combustion CO₂ capture using amines as a chemical sorbent [219] [220] [221] [222]. Work has also been carried out researching the environmental effects of CO₂ storage [223] [224] [225]. Work specifically directed towards the pollutant gaseous emissions from circulating fluidised bed combustors is also available in the literature [226] [227] [228], however it is apparent that no work to date has specifically investigated the potential emissions that may be produced by the calcium looping cycle at the pilot scale, as a result of limestone impurities.

5.1.1 Regulations

Elemental emissions in the UK have to comply with targets under the EU Ambient Air Quality Directive 2008 [229] and the UK Air Quality Standards Regulations 2010 [230]. In addition, specific industries are allocated permits by the UK Environment Agency which provides indicative best available techniques (BAT) emission levels for a variety of pollutants. The BAT emission levels for releases to air for particulate and element emissions from a lime works [231] / cement works [232] is provided as Table 5-1.

Table 5-1 Indicative best available technique (BAT) emission levels for releases to air for a lime works [231].

Pollutant	Kiln type (or other Source)	BAT Emission level (mg / Nm ³)	WID limit
Mercury and compounds	All kilns burning waste-derived fuels	<0.05*	0.05
Cadmium and thallium and compounds	All kilns burning waste-derived fuels	<0.05*	0.05
Group III metals (Sb, As, Cr, Co, Cu, Pb, Mn, Ni, V).	All kilns burning waste-derived fuels	<0.5*	Calculated using the mixing rule for co-incinerators

*Values shown are daily averages over the sampling period (spot measurements, for at least half an hour and not longer than eight hours).

5.1.2 Effect of elements on cement properties

Potential issues have been outlined that may arise in the cement industry from the use of calcium looping-derived CaO, decayed in CO₂ capture capacity, and that has been exposed to elements in flue gas from coal combustion. It is considered that less volatile elements, such as Be, are most likely to remain in the final cement product, and may impact on setting and strength properties of the cement [11]. Bhattu (1995) [233] suggests that although some elements have negative influences on cement properties, other major, minor and trace elements may act to conserve energy during clinker production, and enhance cement performance, for example Ni has been found to enhance cement strength properties. Elemental impurities present in cement production may arise from a variety of inputs to the cement production process, including primary raw materials, such as limestone and sand; regular fuels such as coal; secondary fuels such as used tyres, scrap wood, waste oil; secondary raw materials such as iron ore, coal fly ash; interground additives such as gypsum, fly ash, oil shale; and concrete additives such as basalt, blast furnace slag, coal fly ash, and sand [234].

Gypsum (CaSO₄) is used in cement manufacture at a concentration of 4-5 % [233] to improve the setting of cement, and the use of FGD-derived gypsum has been

reported [235], although it is considered generally more difficult to manage than natural gypsum due to higher moisture content [236]. Although it is chemically different from CaO, and is an additive to, rather than the main component of cement, it is a calcium-based compound that has also been exposed to flue gases from power generation. Few studies have looked at the elemental content of FGD-derived gypsum and those that have are mostly with regard to land applications rather than cement manufacturing, with Clark et al 2001 finding that FGD product application to crops could be feasible and beneficial to soil and plants. Achternbosch *et al.*, 2003 [234] found that gypsum in cement (based on 25 % FGD gypsum and 75 % natural gypsum) typically has Cr, Ni, Pb, V, and Zn in the highest concentrations at 8.8, 7, 5.5, 13.5 and 19 ppm respectively,

5.1.3 Elemental partitioning in energy processes

In energy process systems, solid-phase pollutants or particulate matter released from thermal treatment plants tend to be composed primarily of flyash, with small amounts of char. Elements that are found in the process fuel may concentrate in the ash, and those that are most problematic include alkali metals, heavy metals and radioactive elements [237].

Environmental and human health problems can arise from emissions of toxic heavy metals, with Pb, As, Hg, Cd, Cr and Zn of particular cause for concern. In addition, the presence of such elements may cause other effects, including corrosion of materials used in the CO₂ capture reactor itself [18] [17].

Alkali metals, including K and Na, can form oxides that melt at relatively low temperatures (just over 1000°C), causing slagging and fouling, resulting in deposit formation on reactor surfaces [237], thus reducing reactor lifetime. Heavy metals, including Hg and Pb, are also problematic due to their high toxicity and in turn environmental and human health issues. Hg emissions can be in both gaseous form and as fine particles, via nucleation and subsequent growth [238] cited in [237; 239]. During combustion processes, Hg in coal is volatilised into elemental mercury. As it cools elemental mercury may be converted to form ionic mercury, where it bonds with other compounds as monovalent or divalent mercury. Particulate mercury is the third form of mercury, whereby gaseous elemental mercury is adsorbed onto particle surfaces.

The volatility and vapour pressure of the elements and their compounds, as well as the energy process technologies in which they are found, can impact on the partitioning of heavy metal emissions between the solid and gaseous phases [240] cited in [237]. Potential metal impurities in the gases that are considered of particular interest are provided in Table 5-2.

Table 5-2 Potential metal impurities of interest from Ca-based CO₂ capture, and associated operability and durability issues, adapted from Finney *et al.*, 2010 [237].

Element	Reason for Interest	Reference	Process
Sodium, Na	Volatility, Operational issues including slagging and fouling	Armesto <i>et al.</i> , 2002 [241]	Rice husk combustion, bubbling fluidised bed
		Hodges and Richards (1989) [242]	Coal combustion, fluidised bed
Magnesium, Mg; Aluminium, Al; Calcium, Ca; Iron, Fe;	Common element	Xu <i>et al.</i> , 2004 [243][244]	Coal combustion
Potassium, K	Operational issues including slagging and fouling	Armesto <i>et al.</i> , 2002 [241]	Rice husk combustion, bubbling fluidised bed
Vanadium, V; Antimony, Sb	Toxicity	Finkelman (1994) [245]	Coal combustion
		IEACCC (2012) [246]	Coal combustion /gasification
Chromium, Cr	Toxicity - often in larger particles, less volatile	Miller <i>et al.</i> , 2002 [244]	Combustion of coal & biomass
		IEACCC (2012) [246]	Coal combustion/ gasification
Nickel, Ni; Thallium, Tl; Arsenic, As;	Volatility Toxicity	Miller <i>et al.</i> , 2002 [244]	Combustion of coal and biomass
		(IEACCC) 2012 [246]	Coal combustion / gasification
Copper, Cu	Volatility, Toxicity	Xu <i>et al.</i> 2004 [243]	Coal combustion

Element	Reason for Interest	Reference	Process
	Often in fine particles	(IEACCC) 2012 [246]	Coal combustion / gasification
Zinc, Zn	Volatility Often in fine particles	Pavageau <i>et al.</i> , 2002 [247]	Coal combustion
		Xu <i>et al.</i> , 2004 [243]	Coal combustion
Cadmium, Cd; Mercury, Hg	Toxicity Easily vaporized - more volatile, often in fine particles	Pavageau <i>et al.</i> , 2002 [247]	Coal combustion
		Chen <i>et al.</i> , 1999 [238]	Incineration
		IEACCC (2012) [246]	Coal combustion / gasification
Lead, Pb	Volatility Toxicity Can be vaporized Often in fine particles	Yoshiie <i>et al.</i> , 2013 [248]	Coal gasification
		IEACCC (2012) [246]	Coal combustion / gasification

5.2 Limestone Impurities

It is widely acknowledged in the literature that naturally-occurring limestone contains many metal oxides other than CaCO_3 . Koppatz, *et al.*, 2009 [249] investigating CO_2 capture from the steam gasification of biomass, identified the presence of aluminium, magnesium and iron oxides in the limestone sorbent, in addition to 94 % CaCO_3 , as well as SiO_2 and other elements. MgO , Al_2O_3 , Fe_2O_3 and SiO_2 have also been cited as common impurities (generally < 3.0%) in other limestone samples used for calcium looping cycle testing, with smaller amounts (< 0.5%) of TiO_2 and alkali metal oxides, such as K_2O and Na_2O [152] [88] [250] [251] cited in [237]. Barber (1974) [252] concluded that Ca, Mg, Mn and Sr are mainly restricted to the carbonate fraction of limestone, and that ‘mineralogical associations’ of trace elements in limestone are complex. X-Ray Fluorescence (XRF) elemental analysis of a Kelly Rock limestone confirmed the presence of a number of elemental impurities, as shown in Figure 5-1 [137]. These impurities present within the limestone sorbent

have the potential to impact the species and concentrations of solid- and gas-phase pollutants formed during the calcium looping CO₂ capture cycle.

With regards to emissions from integrated gasification and calcium-looping system, Koppatz *et al.*, 2009 [249] investigated hydrogen production via steam gasification of wood chips, in a dual fluidised-bed system, with continuous CO₂ removal using the calcium-looping cycle. Contaminants were identified in the biomass and in the limestone that may cause detrimental emissions: the biomass contained some N and very small amounts of S, which could lead to acid gas formation, whilst metal impurities in the limestone included Al, Fe and Mg, the latter being found as MgO. Other trace elements were also identified in the limestone. Product gas composition was provided, but other impurities in the gas were not determined, and no analysis was provided for the exhaust gas from the reactor [237].

Chen *et al.*, 2011 [253] investigated coal-based fluidised-bed steam gasification with the calcium-looping cycle to generate hydrogen for subsequent energy production [237]. Significant amounts of N and S were identified in the coal, and thus both N and S-based compounds were present in the gas from the gasifier and the riser, found in the forms of nitrogen and ammonia, and hydrogen sulphide and carbonyl/oxycarbon sulphide [237]. Other forms of these, such as oxides (acid gases) may also have formed if enough oxygen was present, and although not mentioned, it is anticipated that HCN formation may also have been likely. The temperature in the riser was found to impact the gas concentrations, in addition to the steam flowrate, with H₂ content in the flue gas being slightly higher for larger steam flow rates [253]. However, no analysis of flue gas elemental concentration was made.

component	content
SiO ₂ (wt %)	2.95
Al ₂ O ₃ (wt %)	0.74
Fe ₂ O ₃ (wt %)	0.32
TiO ₂ (wt %)	0.05
P ₂ O ₅ (wt %)	< 0.01
CaO (wt %)	52.43
MgO (wt %)	0.47
SO ₃ (wt %)	0.30
Na ₂ O (wt %)	< 0.096
K ₂ O (wt %)	0.21
Ba (ppm)	347
Sr (ppm)	286
V (ppm)	< 0.50
Ni (ppm)	< 0.50
Mn (ppm)	1023
Cr (ppm)	< 0.50
Cu (ppm)	42
Zn (ppm)	30
loss on fusion (wt %)	42.05
sum (wt %)	99.69

Figure 5-1 XRF Elemental Analysis of Kelly Rock Limestone [137].

Impurities present in the limestone-derived sorbent have the potential to influence species formation and concentrations of solid and gaseous pollutants formed during the calcium looping cycle process [237]. In addition, limestone impurities may also adversely affect both carbonation time and the decay in sorbent activity, and therefore the number of cycles for which it is able to maintain an acceptable level of capture, which in turn may affect process efficiency, % carbon capture and other operational requirements such as the need for additional fresh sorbent [254] [237].

Meij (1994) [12] analysed the concentrations and distributions of minor and trace elements within coal-fired power plants employing limestone-based flue gas desulphurisation (FGD) technology. It was found that the predominant source of trace elements within the FGD plants were from limestone, present in the FGD plant in the following decreasing order: Ca, Pb, Mn > Cd, Mg, Fe, Si, Sm > Ti, Al, W, As, Sb. It was observed that combustion flue gases contributed only a small proportion of the trace element content of the FGD plant, suggesting that the use of limestone-derived CO₂ sorbents may represent a further potential source of trace elements within power stations, and may in turn impact on downstream processes. With further regard to gaseous emissions, Meij (2013) [255] also suggests that gas phase elemental concentrations from a power station are dependent upon the particulate loading. In a coal-fired power station with low particulate loading, approximately 50

% of particulates may come from fly ash and the remaining 50 % from nucleated lime/limestone particles in the FGD scrubber liquid. However in a power station with higher particulate loading due to fly ash, the limestone-derived particulates will represent a lower percentage of the total particulate emissions. By contrast, in a situation as for instance where the UK government policy proposes increased use of natural gas-fired power stations over coal [39], employing calcium based CO₂ capture will mean that the limestone based sorbent will be the main source of both particulates and elemental emissions. Further, Sager (1999) [256] also suggests that lime used for gas scrubbing within a power plant may introduce trace elements to the system, including As, Pb, Cd and Zn [256].

In contrast to this however, Furimsky (2000) [257] concluded that limestone may have a diluting effect on trace element content in coal ash, whilst Cheng *et al.*, 2001 [258] suggested lime (CaO) may be beneficial in reducing trace element emissions from coal combustion. Further, Li *et al.*, 2006 [259] investigated the removal of selenium by CaO in the presence of SO₂, and concluded that when CaO conversion is relatively low and the reaction rate is controlled by chemical kinetics, the presence of SO₂ does not appear to affect selenium capture. However, when CaO conversion is very high and the reaction rate is controlled by product layer diffusion, the presence of SO₂ and associated product layer diffusion resistance work jointly to reduce selenium capture.

5.3 Trace Element Partitioning during Energy Processes

The US National Research Council (NRC) classified trace elements in coal according to levels of concern based on known adverse health effects and abundance in coal (Table 5-3) [246]:

Table 5-3 Trace element emissions from Coal [246].

Classification	Elements	Issue
Major Concern	Arsenic (As), Lead (Pb), Mercury (Hg), Cadmium (Cd) and Selenium (Se), Boron (B), Molybdenum (Mo)	All highly toxic above critical levels. B and Mo are phytotoxic, and Mo affects lactation in cows
Moderate Concern	Chromium (Cr), Vanadium (V), Copper (Cu), Zinc (Zn), Nickel (Ni), Fluorine (F).	All potentially toxic and present at elevated concentrations in coal residues. Bioaccumulation a concern. F has adverse effect on forage.
Minor Concern	Barium (Ba), Strontium (Sr), Sodium (Na), Manganese (Mn), Cobalt (Co), Antimony (Sb), Lithium (Li), Chlorine (Cl), Bromine (Br), Germanium (Ge).	All present in coal residues but of little environmental concern.
Of concern but negligible concentration	Beryllium (Be), Thallium (Tl), Silver (Ag), Tellurium (Te).	Adverse effects on health, but negligible concentrations in coal.
Radioactive	Uranium (U), Thorium (Th), Radium (Ra), Polonium (Po), Radon (Rn)	

Similarly, several studies have identified that trace elements released during coal gasification/combustion tend to partition either between gaseous emissions, or ash residues, dependant on their volatility. Those that are considered most volatile are generally considered as posing most risk, due to their tendency to release to the environment. Based on this partitioning tendency, it has been suggested that trace elements can be classed into three main groups [13] [12] [260] (Figure 5-2):

- Group I elements – least volatile, partition into ash residues e.g. Mn, Be, Co, Cr;
- Group II elements – moderate volatility, partition between ash residues and gaseous phase. As gases cool, vapour species condense onto particulate matter e.g. As, Cd, Pb, Sb; and
- Group III elements – High volatility and unlikely to condense from vapour phase e.g. Hg, Se.

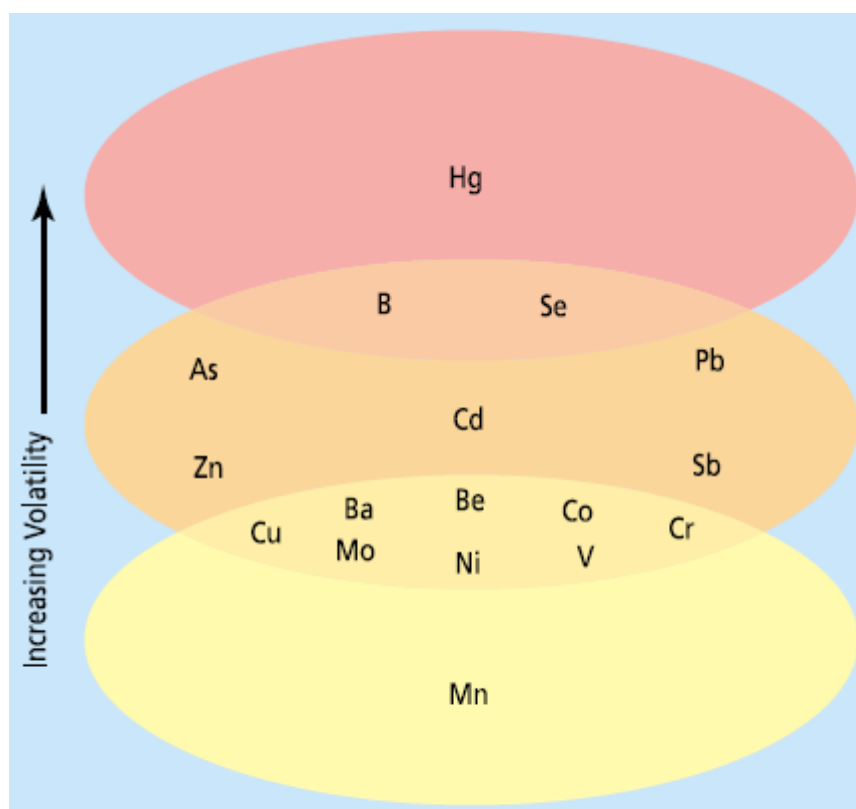


Figure 5-2 Trace element behaviour during combustion [261].

It should be noted that the Group names are independent of an element's location within the Periodic Table. Group III and Group II elements are considered to represent the greatest risk to the environment and human health due to their increased volatility compared to Group I elements.

The total mass of metallic trace element emissions from coal combustion can be calculated based on the amount of particulate matter emitted (Equation **5-1** and Equation **5-2**) [262]. Correction factors for enrichment (non-volatile elements) or retention in ash (volatile elements) are applied depending on the concentration of a particular element in the original coal sample, and subsequently in the ash. Typical enrichment and retention factors for UK coals are provided as Table 5-4 [262].

Non-volatile phase:

$$E_{nv} = PC_{coal} \cdot (100 / AA) \cdot F \cdot R \cdot PM \quad \text{Equation 5-1}$$

Volatile phase:

$$E_v = PC_{coal} \cdot (1 - F) \cdot CB \quad \text{Equation 5-2}$$

Where:

Env = Non-volatile pollutant emission (kg/yr), Ev = Volatile pollutant emission (kg/yr), PCcoal = Trace element weight fraction in the coal, AA = Average ash mass percentage in coal (%), F = Retention factor in ash (-), R = Enrichment factor (-), PM = Particulate matter emission (kg/yr), CB = Coal burned (kg/yr).

Table 5-4 Typical Retention and Enrichment Factors for Trace Elements in UK coals, for exhaust temperatures of approximately 130°C [262].

Element	Retention factor (F)	Enrichment factor (R)	FGD retention factor (vapour)
Arsenic	1	3.4	-
Selenium	0.8	9.0	0.65
Lead	1	2.9	-
Antimony	1	3.6	-
Boron	0.5	0.9	0.9
Nickel	1	1.9	-
Chromium	1	1.7	-
Copper	1	2.0	-
Manganese	1	1.7	-
Vanadium	1	1.4	-
Zinc	1	4	-
Beryllium	1	1.7	-
Cadmium	1	4.5	-
Mercury	0.5	4.0	0.5

It has been suggested that when considering coal, the partitioning of elemental species and therefore the release rate, may be determined by the ‘physical and chemical association of the elements with the decomposed mineral matter’, as well as by volatility [13]. This theory was also endorsed by a study looking at the release

of the trace elements As, Hg, Cd and Pb, during coal gasification, which suggested that the occurrence of elements within coal affected the release rate. Those metals generally associated with mineral matter, for example Pb, are volatilised most easily, whilst those that are organically bound to coal are generally in more stable forms and less likely to volatilise e.g. Cd (Figure 5-3) [13]. Those elements associated with organic matter and inorganic sulphides are oxidised during combustion, or react with Cl, F, Na or S, and thus volatilise more readily than the elements found in aluminosilicate materials [256] [263].

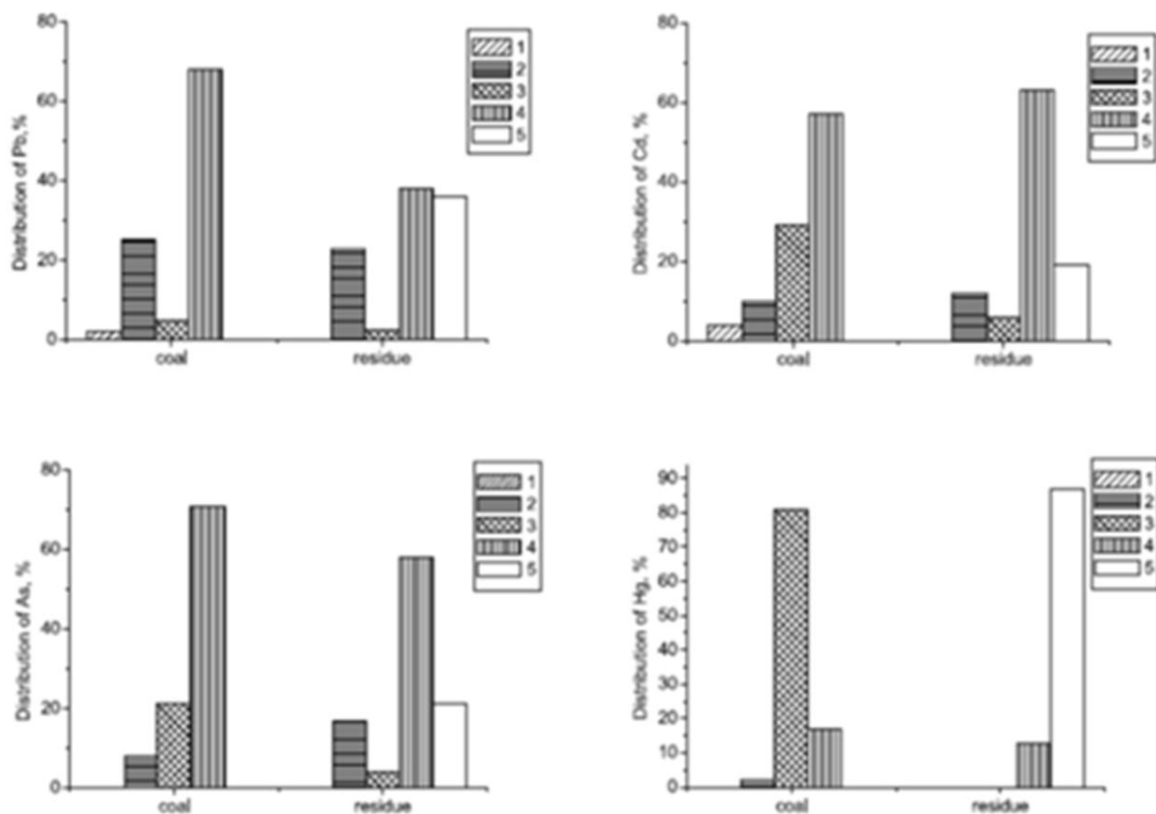


Figure 5-3 Distribution of Pb, Cd, As and Hg in YM coal and its residue after gasification. 1. Ion exchangeable; 2 . Bound to carbonates and Fe-Mn oxides; 3. Bound to organic matters; 4. Stable form; 5. Released into volatile phase [264].

The elements Cd, Cr, Co, Mn, Ni, U, Th are relatively non-volatile, and have been found more likely to condense out with particulate matter, resulting in an increase in trace element concentration with a decrease in sorbent size [265] [13], that could be removed during particulate removal. Research has found that during coal gasification

the elements As, Se, Sb, Pb and Hg tend to volatilise and remain in the vapour phase at temperatures typical of hot gas removal systems (500-600°C), suggesting that these would be removed during gas cleaning [265]. In contrast, Trembly *et al.*, 2007 [260] however observed that the above-named elements, as well as P and Cd remain present following gas clean-up. A trace metal mass balance analysis for a coal-fired IGCC plant confirmed that less than 5% of Pb emissions from coal were released to the atmosphere, with the majority removed in particulate and gas cleaning systems [266]. However, it was acknowledged that mercury has a low boiling point (375°C) and therefore is of key concern due to its likelihood to remain in the vapour phase. Therefore, there is some discrepancy regarding the fate of these elements perhaps associated with the efficiency of gas clean-up systems.

Investigations into trace element behaviour during coal combustion at the laboratory and pilot scale concluded that Zn, As, Sb and Se were generally concentrated in the smallest ash particles, perhaps due to nucleation. Combustion flame temperature has an effect on the trace element content in coal ash, particularly for As and Se suggesting element vaporisation during the combustion process [267] [268]. However, feed coal particle size had little effect on element concentration in the coal or ash [269] [268].

Further work on coal gasification experiments at the bench scale proved more reliable than those undertaken at the laboratory scale [13], implying that scale up of technology is important in order to gain further understanding of the potential issues facing industry.

Córdoba *et al.*, 2012 [270] investigated the partitioning of elements in a pulverised coal combustion power plant fitted with wet limestone flue gas desulphurisation (FGD). They found that 29 % of the original elemental Hg was emitted in the flue gas. The most volatile elements including S and F were retained by the FGD-derived gypsum, whilst moderately volatile elements including As and B were for the most part retained in the fly ash. Gaseous emissions were below European directive 2001/80/EC limits for large combustion plants and the pollutant release and transfer register (PRTR) threshold values, with the exception of Hg emissions and particulate Se, As, Zn, Cu, Ni, and Cr.

Trace element fate was investigated in a 90 kW oxy-combustion pilot plant fed with coal and limestone [271]. It was identified that 82 % of elemental Hg was emitted in the exhaust gas, as was 81 % of Cl. It was considered that the relatively low temperatures, and high Ca content in the system from limestone use promoted condensation and sorption of sulphate, fluoride and chloride species.

Oakey *et al.*, 2004 [17] investigated the potential for trace element release from biomass gasifiers and the effect on gas turbines, and concluded that control of trace alkali metals and other contaminants is required to minimise corrosion damage to gas turbine machinery. Further work on bio-fuel gasification using ICP-OES analysis confirmed the presence of Al, B, Cu, K, Na, P, S and Si in bio-fuel derived-syngas, although it was noted that tar residue caused some problems with the sampling system [272], which is why perhaps some other common elements associated with gasification, such as As, Se, were not identified during the experimental work. Compared to previous work on combustion gases, concentrations of some metals (Cu, K, Na, Zn) measured during gasification were extremely high, in some cases several orders of magnitude higher. Trace elements tend to have greater volatility during gasification compared to combustion [17] [273] and therefore those metals with high volatility generally, such as mercury, are likely to cause more concern in gasification systems due to their potential impacts on the environment and human health. However despite this, emissions measurements from large-scale gasification-based energy production systems, such as IGCC, have been found to be lower than from conventional coal-fired power plants with pollution-control technology installed [266].

In terms of the potential for the use of solid oxide fuel cells (SOFCs) with coal-derived syngas, trace elements present in syngas may be responsible for micro-scale changes in the morphology of SOFC anodes, with Sb, As and P emissions reacting with Ni in the anode noted to be of particular concern [211] [260].

5.4 Thermodynamic Equilibrium Modelling

Several studies within the literature cite the use of thermodynamic equilibrium modelling simulations in predicting elemental release during energy production. Thompson and Argent (2002) [15] [274] have used thermodynamic equilibrium modelling to investigate trace element mobilisation under both combustion and air-

blown gasification conditions. The Metallurgical and Thermodynamic Databank (MTDATA) software, produced by the National Physical Laboratory (NPL) (UK), is one of the most widely used thermodynamic equilibrium modelling software packages, and computes chemical equilibria based on Gibbs Energy minimisation, allowing the identification of the most prevalent species in a reaction, under specific conditions, including temperature and pressure.

MTDATA works by calculating the Gibbs Free Energy Minimisation of the formation of compounds (Equation 5-3 and Equation 5-4) [275]:

$$\text{Minimised } G = \sum_{j=1}^N n_j u_j \quad \text{Equation 5-3}$$

$$\sum_{j=1}^N a_{i,j} * n_j = r_i \quad \text{Equation 5-4}$$

$$n_i \geq 0, i = 1, 2, \dots, M \leq N$$

Where, G is the Gibbs energy which is to be minimised by varying the values of the n_j , $j = 1, 2, \dots, N$; n_j is the amount in moles of species j present in the system, each chemical substance with different phase designation being considered as a distinct chemical species; N = number of species in the system; u_j is the chemical potential of species j , which may be a function of some or all of the species amounts in the same phase and it also depends on temperature, pressure and model of the phase under consideration; $a_{i,j}$ is the number of units of component i per species j , M is the number of components in the system, and r_i is the number of moles of component i in the system.

MTDATA comprises a number of modules, the use of which depends on the type of calculation that is required for a process. For example, the module MULTIPHASE calculates equilibrium for multiple phases and components, whereas the TERNARY module calculates and plots isothermal ternary phase diagrams.

A number of databases are available for use within the software, including the SGTE Unary database, which comprises the assessed data for the stable and metastable phases of 78 elements from 298.15 K. Other databases are available for some specific elements, for example the MTAL database has been designed to allow

calculations of phase equilibria in Al-based alloys. The SGTE pure substance database, SGSUB, contains data for pure substances and gases, and allows the Gibbs Energy of substance to be calculated as a function of temperature, thereby phase equilibrium calculations to be carried out [275].

MTDATA has been used to investigate trace element release including during combustion of wood bark [276], combustion of sewage sludge with Polish coal [277], in investigating trace element release from biomass-fuelled gasification systems [278], and in investigating trace element, including mercury, emissions from gasification and combustion conditions [16]. Goni *et al.*, 2010 [279] utilised MTDATA to model fusibility during combustion of different coal blends, and confirmed that the equilibrium calculations were a valid tool in doing so. Khodier *et al.*, 2011 [18] used MTDATA to model the combustion and deposition process when co-firing miscanthus with coal, and concluded it a useful predictive tool to support experimental analytical techniques.

With regards to CCS in particular, MTDATA has been used to predict the impact of impurities on CO₂ transport in relation to the pipeline transport of dense phase CO₂ from a capture plant to a subsurface storage site [19], but otherwise, it can be concluded that there is limited data available in the literature with regards to using thermodynamic modelling to support experimentally-derived elemental emissions results from calcium-based CO₂ capture.

Therefore, in terms of the use of limestone as CO₂ sorbent, although studies have suggested its importance in sorbing heavy metals released during coal combustion [243] it will also be important to gain an understanding of the contribution that limestone may make to the elemental emissions produced calcium-based CO₂ capture.

5.5 Industrial Contaminant Removal Processes

A number of methods are employed by industry to remove and reduce particulate matter and associated trace metals from flue gas. These are outlined in further detail below. The key pollutants to be removed from coal-fired power plants in particular include SO_x, NO_x and particulate matter.

5.5.1 Flue Gas Desulphurisation

The principal aim of flue gas desulphurisation (FGD) is to remove SO_x from flue gas, but the process can also remove particulate matter as well. There are numerous FGD processes which use a wide range of reagents, but typically the process can use either a Ca or Na derived sorbent, and may take the form of either a wet or dry process. Srivastava *et al.*, 2001 [280] report that of all the FGD systems worldwide in 1998, 86.8 % employed wet FGD technology, 10.9 % dry technology, and the balance was made up of regenerable technology.

The wet process involves a slurry of water and CaCO₃ being sprayed into the flue gases, from which SO₂ is absorbed (Equation 5-5). The SO₂-containing slurry is then sent to an oxidation zone where gypsum is produced as a by-product (Equation 5-6), and sold to the construction industry [281]. The efficiency of SO₂ removal may be up to 98 %, although typically most are designed for around 90 % efficiency [280].



The dry FGD process can again make use of a number of sorbents, but typically for low to medium sulphur coal, the process involves injection of powdered calcium oxide into the flue gas, from which SO₂ is absorbed. Bag filters are used to collect the solid gypsum from the exhaust. Efficiencies of up to 90% can be achieved [280], and the method is considered one of the cheapest for SO₂ removal from industry.

5.5.2 Mechanical (Cyclone) Filters

Cyclone filters comprise conical vessels into which flue gas is passed. Due to the shape of the filter, the gas moves in a circular path around the filter, and due to centrifugal forces, particulate matter 'drops out' of the gas stream, and is collected at the bottom of the filter. The flue gas then passes out of the cyclone and continues to the exhaust. Mechanical filters have a removal efficiency of 75-99 % for particle size distribution of 0.01-100 µm [281].

5.5.3 Fabric Filters

Fabric filters use filtration in order to separate particulate matter from flue gases. Flue gases pass through the fabric filter, leaving the particulate matter behind in the filter bag. They are considered a cost-effective and efficient method of particulate removal from industry. Cleaning of fabric filters may be by mechanical movement of the filter, reverse flow of air, or pulse jet of air [281].

5.5.4 Electrostatic Precipitators

Electrostatic precipitators use electrical forces to collect particulate matter from flue gas streams. Firstly the flue gas passes over a charged grid, ionising the particulate matter contained within, whilst leaving the gases as they are. The particulate matter is then attracted to, and collected on, collecting plates of the opposite charge. Particulate matter is then removed from the collecting plates by mechanical movement (rapping) at lower temperature (130-180 °C), or by scrubbing at high temperatures (300-450 °C) in which a liquid film of water is sprayed onto the plates. Due to the high cost, this technology is generally only used in industrial-scale processes, but removal efficiency can be up to 99 % for a particle size range of 0.01-100 µm [282].

Fly ash contains trace metals due to the process of nucleation (described above) and therefore elements contained within particles of particle size at which ESP remove particulates, will also be removed from the flue gas. For highly volatile elements, such as arsenic and selenium, the metal capture efficiency is lower than the particulate capture efficiency. However, for elements with lower volatility, such as beryllium and manganese, metal capture efficiency is comparable to particulate capture efficiency [283] (Table 5-5).

Table 5-5 Trace element capture efficiencies: field data (facilities utilizing ESP alone for particulate control) [283].

Element	Average particulate capture efficiency	Average element capture efficiency	Ratio
Hg	99.1	28.9	0.291
Se	99.0	49.1	0.496
As	99.2	96.1	0.969
Cd	99.1	96.1	0.970
Pb	99.2	96.8	0.976
Ni	99.1	97.6	0.985
Cr	99.2	98.0	0.989
Co	98.9	98.2	0.992
Be	99.0	98.3	0.993
Mn	99.2	98.5	0.993
Sb	98.9	98.5	0.996

5.6 Summary

The literature review has identified a number of gaps in the knowledge base with regards to pilot scale calcium looping for CO₂ capture. Firstly, the pilot scale reactor at Cranfield had not previously been operated before as a continuous looping system, and therefore an understanding of the hydrodynamics of the system is required to determine the optimum operating conditions for the system. A cold model facility is considered the most appropriate method of doing so. Although there are a number of cold models in operation at research institutions, none are specific to the 25kW_{th} reactor at Cranfield.

It is widely accepted that scale-up of the calcium looping cycle is required for industry implementation. A number of pilot scale reactors are in operation globally, and some have suggested that there are data discrepancies between work carried out at pilot and smaller scale [10]. However, there appears to be minimal work looking specifically at engineering challenges that arise on scale up of the technology. Further, as the reactor at Cranfield has not yet been operated in continuous mode, optimisation of the CO₂ capture efficiency of the reactor is required.

The literature suggests that limestone may be a source of elemental impurities which have the potential to be emitted to the environment under high temperature, fluidised bed conditions required for the calcium looping cycle. This has to date not been investigated in the literature with specific regard to the calcium looping cycle. The use of spent sorbent in the cement industry could reduce the energy penalty and CO₂ emissions of the capture and cement manufacturing processes, but impurity elements present in cement can affect its properties [11]. There appears to be no research to date that has investigated the potential elemental partitioning from the pilot scale calcium looping process as a result of limestone use. Furthermore, the use of thermodynamic equilibrium modelling software is gaining in popularity due to its relative low cost and use in supporting experimental work. Again, the use of such software does not appear to have been applied to elemental partitioning from limestone use within the calcium looping cycle.

6 EXPERIMENTAL METHODOLOGY

This chapter outlines the methodology used in designing a cold model of Cranfield's pilot scale reactor, in order to investigate the hydrodynamic processes taking place within the reactor, from which to determine the optimum process conditions in the hot reactor. The equipment used and the methodology undertaken in order to carry out the cold model hydrodynamic investigations, pilot scale calcium-looping cycle experiments, and elemental sampling is provided below.

6.1 Cold Model Design

A cold model (Figure 6-1) of the 25kW_{th} pilot-scale CO₂ capture rig was designed and built based on Glicksman's Simplified Scaling Laws [174], and has been designed at full scale in order to allow the optimum representation of the hot reactor and in a bid to reduce wall effects [284], and therefore achieve the most accurate results. Table 6-1 provides a comparison of the component values used for the cold model, and the hot reactor, and compares the values with those of other cold work available in the literature. Table 6-2 provides a comparison of the dimensionless parameter values for the cold model and the CO₂ capture reactor, compared with those of a cold model designed by Pröll *et al.*, 2009 [184]. Figure 6-2 identifies that both reactors are designed correctly to fit within the required fluidisation regimes, with the hot reactor and cold model carbonator both in the transport fluidisation regime, and the hot reactor and cold model calciner both in the bubbling regime [285] [286].

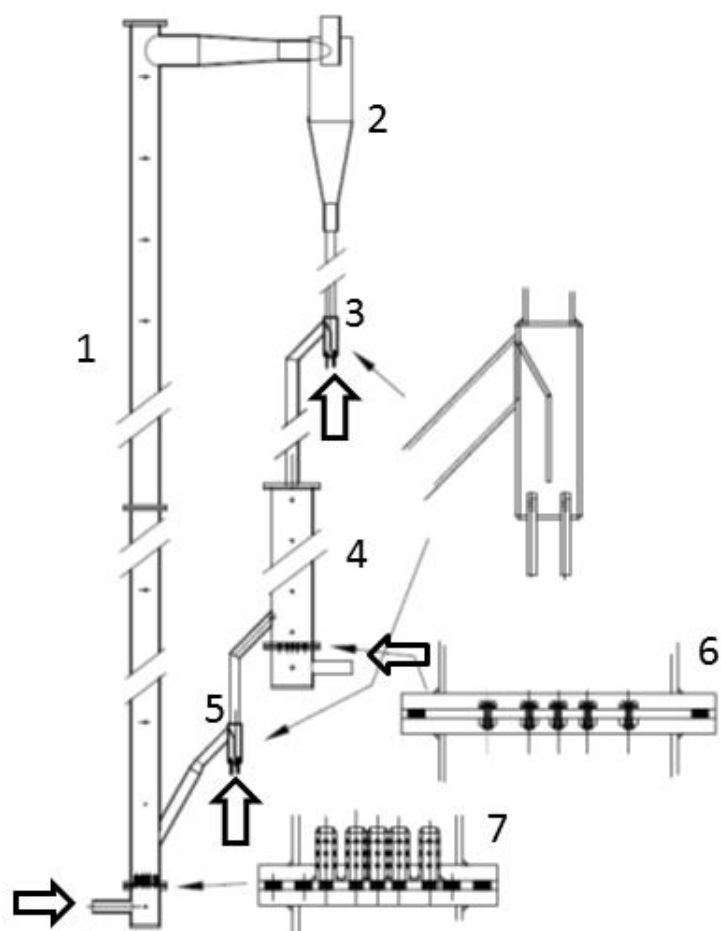


Figure 6-1 Cold model diagram of a 25kW pilot-scale CO₂ capture rig, comprising an entrained flow carbonator (1), cyclone (2), upper loop seal (3), bubbling fluidised bed calciner (4), lower loop seal (5), calciner gas distributor (6), and carbonator gas distributor (7). Hollow arrows denote gas (Air/N₂) input locations. Not drawn to scale.

Table 6-1 Component values for the hot reactor and cold model, compared with literature data.

Comp- onent	Unit	Current study				Pröll <i>et al.</i> , 2009. [184]				Johannson <i>et al.</i> , 2003 [190]		Kronberger <i>et al.</i> , 2005 [182]	
		1:1 scale Cold Model		25 kW Reactor		1:3 scale Cold Model		120 kW Reactor		1:10 scale Cold Model	30 MW Reactor	Cold Model (no scale given)	10 kW Reactor
		Carb	Calc	Carb	Calc	Air Reactor	Fuel Reactor	Air Reactor	Fuel Reactor	Average	Average	Average	Average
d_p	μm	125-250	125-250	125-250	125-250	54	54	161	161	150	300	67.5	120
ρ_s	Kg m^{-3}	2650	2650	2650	2650	8730	8730	3200	3200	2600	5240	2550	2550
ρ_g	Kg m^{-3}	1.2	1.2	0.57	0.43	1.22	1.22	0.316	0.288	1.19	2.46	~ 1.2*	~0.5*
η	Pa.s	1.8e-5	1.8e-5	3.9e-5	3.9e-5	1.79e-5	1.79e-5	4.7e-5	4.1e-5	1.81e-6	48.8e-6	~1.8e-5*	~3.9e-5*
u_0	m s^{-1}	1.9	1.9	2.74	2.74	4.25	1.21	7.32	2.08	0.32 u_0	u_0	n/a	n/a
D	m	0.1	0.165	0.1	0.165	0.050	0.054	0.150	0.159	L/10	1.9m/0.5m air/fuel	0.55L	2.2m overall
Φ	-	0.99	0.99	0.99	0.99	1.0	1.0	0.99	0.99	n/a	n/a	~1	~1

*Approximate assumed values for gas density and viscosity, derived from information on the gases used, and temperatures at which experiments were carried out, as provided in reference.

Table 6-2 Comparison of Glicksman's full set of scaling law dimensionless parameter values (from which the Simplified Scaling Laws are derived, and as used in this study), with those achieved by Pröll *et al.*, 2009 [184].

Dimension-less Parameter	Expression	Current study						Pröll <i>et al.</i> 2009 [184]					
		Cold Model		Hot Reactor		$H_{carb}:C_{carb}$	$H_{cal}:C_{cal}$	Cold Model		Hot Reactor		$H_{air}:C_{air}$	$H_{fuel}:C_{fuel}$
		Carb	Calc	Carb	Calc			Air	Fuel	Air	Fuel		
Reynolds Number	$\frac{d_p u \rho_g}{\eta}$	23.8	4.4	7.3	1.01	0.31	0.23	15.9	4.5	7.9	2.4	0.5	0.52
Archimedes Number	$\frac{\rho_g(\rho_s-\rho_g)d_p^3 g}{\eta^2}$	639	639	64	44	0.1	0.07	53	53	19	23	0.36	0.43
Froude Number	$\frac{u^2}{g \cdot d_p}$	1.96e3	6.6e1	4.07e3	1.82e2	2.0	2.7	3.4e4	2.7e3	3.4e4	2.7e3	1	1
Density ratio	$\frac{\rho_s}{\rho_g}$	2.21e3	2.21e3	4.65e3	7.84e3	2.1	3.5	7.27e3	7.27e3	10.1e3	11.1e3	1.39	1.53
Reactor to particle diameter	$\frac{D}{d_p}$	531	878	531	878	1	1	1250	1350	1260	1340	1.01	0.99

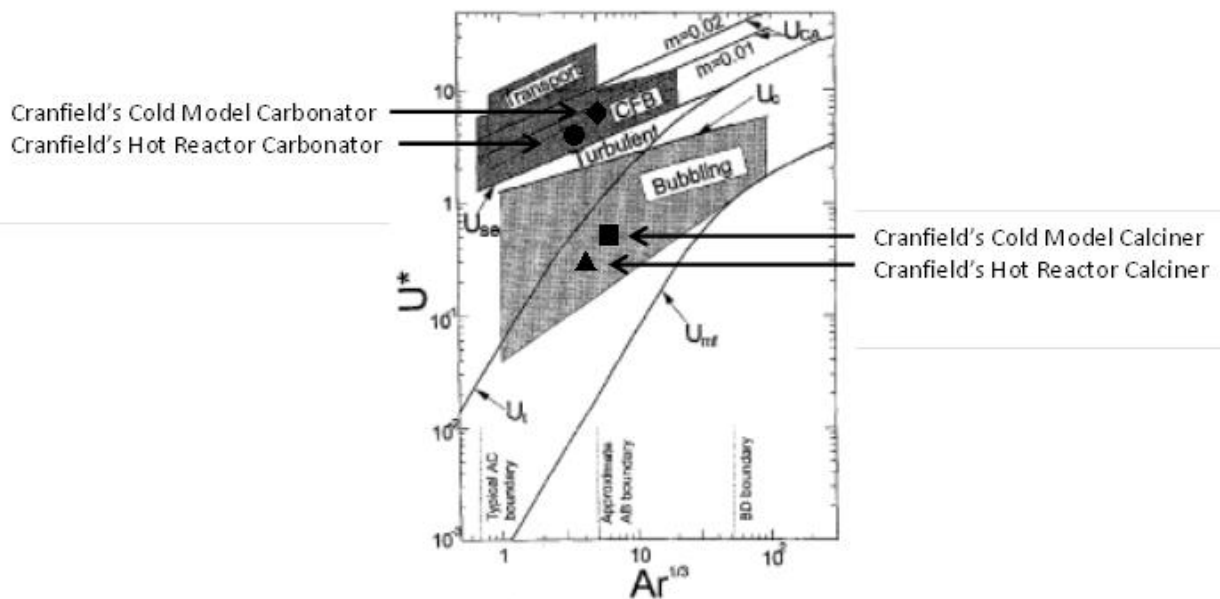


Figure 6-2 Comparison of the fluidisation regimes for the hot reactor carbonator (●) and cold model carbonator (◆), and for the hot reactor calciner (▲) and cold model calciner (■), adapted from Bischi *et al.*, 2011 [285], Lim *et al.*, 1995 [286], where $U^* = Re \cdot Ar^{-1/3}$.

6.2 Cold Model Hydrodynamics Experiments

6.2.1 Pressure Profile

Pressure measurements using electronic pressure meters were taken across the length of the carbonator, calciner and also loop seals, in order to provide indications of solids and gas flows. This provided information on solids transfer and inventories, and in turn enabled judgement to be made on whether modifications to the cold model had a beneficial effect on the system hydrodynamics.

6.2.2 Minimum Fluidisation Velocity

With a bed inventory of 4.5 kg of Longcliffe SP52 limestone of particle size 125-250 μm , the superficial gas velocity in the carbonator was increased from 0 in 0.002 m/s increments using the rotameter, and the pressure change recorded once it had stabilised, with each 0.002 m/s increase. Increasing the superficial gas velocity in increments of 0.002 m/s continued, until it was apparent that the pressure plateaued

which corresponded with small vibrational movements in the bed. The superficial gas velocity at which both of these events occurred is considered the minimum fluidisation velocity. An average was taken from three repeats of each test.

6.2.3 Solids Flux

Solids flux was measured by stopping fluidisation of either the upper (carbonator) or lower (calciner) loop seal for a set period of time of one minute, and measuring the solids accumulation in the entry standpipe of the relevant loop seal. After the set time period, fluidisation of the loop seal was continued until visual observations confirmed that the system had stabilised, and the process was repeated.

6.2.4 Gas Bypassing

The cold model can be considered to have four main components requiring fluidisation and from which gas bypassing could occur, comprising the carbonator, calciner, lower loop seal (LLS), and upper loop seal (ULS). A tracer method was used to investigate bypassing from each component, whereby N₂ gas was used as the fluidising medium for the component from which gas bypassing was being investigated. Air was used as the fluidising medium for the three remaining components of the reactor. The % O₂ was measured in the outgoing gas flow from the cyclone or the calciner exhaust, and from that value the % gas bypassing was calculated. A bed inventory of 4.5 kg limestone, particle size 125-250 µm, was used in each test.

6.3 Pilot Scale Hot Reactor

Experiments were undertaken in a 25kW_{th} pilot-scale CO₂ capture rig (Figure 6-3) comprising an entrained flow bed carbonator reactor, and a bubbling fluidised bed calciner reactor. The carbonator is of 0.1 m diameter, and 4.3 m length, and the fluidizing gases are provided by a natural gas-fuelled air burner, the fuel gas in which provides the fluidised bed. The calciner is of 0.165m diameter, and of 1.2m length, and is a natural gas oxy-fuel combustor. Both reactors and associated fittings are made of 310 stainless steel.

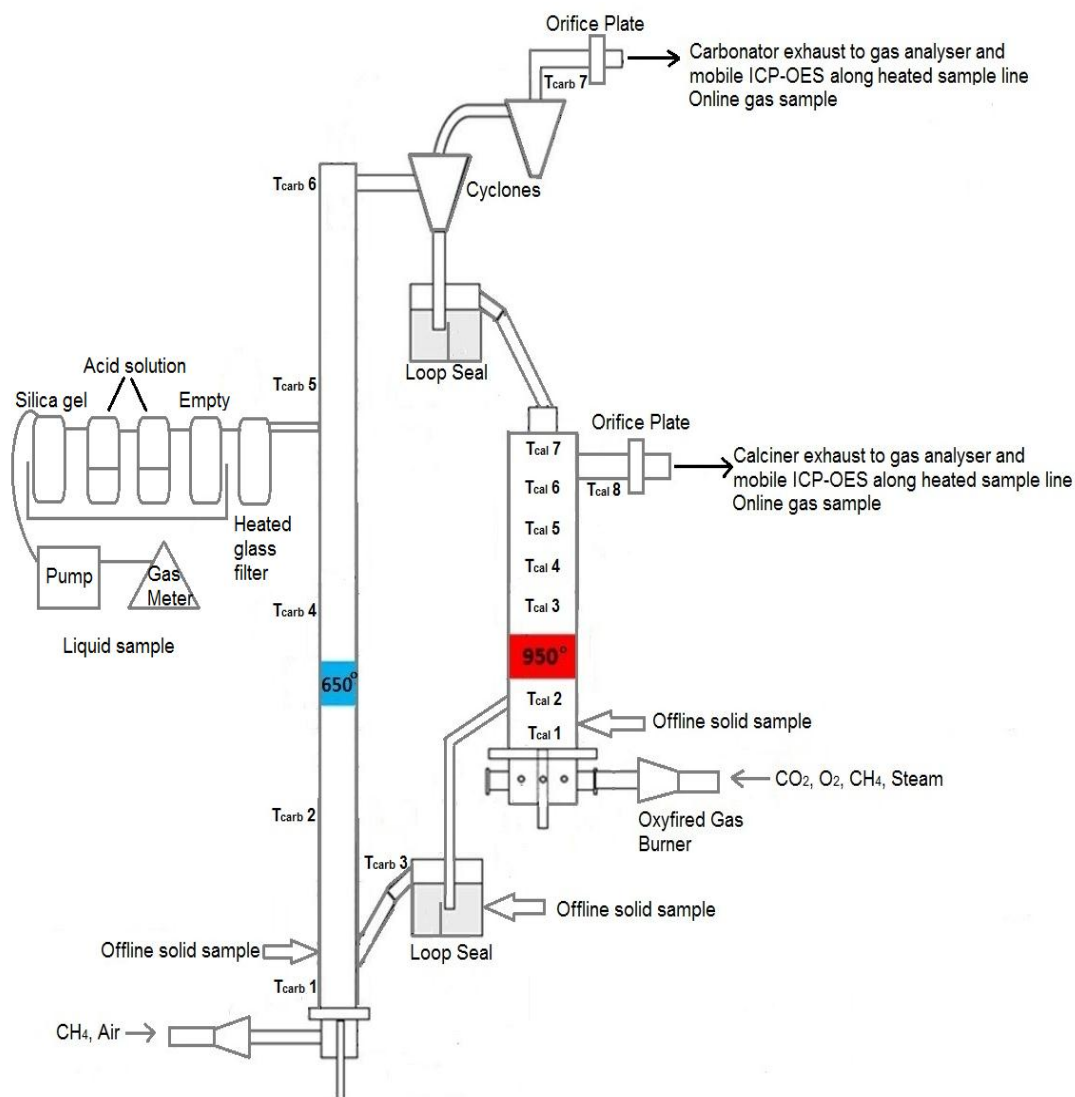


Figure 6-3 25kW_{th} pilot scale, calcium-looping cycle reactor for CO₂ capture, comprising air-fired carbonator, oxy-fired calciner, loop seals and cyclones.

The carbonator gas distributor (Figure 6-4a) has a total of 8 nozzles, each drilled with twenty 2mm holes. The calciner gas distributor (Figure 6-4b) has a total of 20 nozzles, each with six 1mm holes.



Figure 6-4 a) Carbonator gas distributor comprising eight nozzles; b) Calciner gas distributor comprising twenty nozzles.

A view port is located at the top of the calciner from where the reactor is filled with solids prior to testing, and the calciner also has a drain to allow sampling of solids during and after testing. Furthermore, a screw-feeder and feed port allow additional solids input to the calciner during testing, as required. The screw feeder has been calibrated to provide a maximum feed input of 1.6kg/hour.

Two cyclones are present in series at the carbonator exhaust to ensure efficient particulate removal from the flue gases, and therefore prevent particulate emissions to the environment.

The carbonator and calciner are connected by two loop seals, comprising an ULS and a LLS, allowing controlled solids transfer, and thus regulating the solids flux from the calciner to the carbonator, and vice versa. Following entrainment of solids in the carbonator, solids are separated from the gas stream by the first cyclone, allowing exhaust gases to exit the system, and solids to continue in a looping mode. The ULS is present downstream of the cyclone exit standpipe, to allow controlled transfer of solids to the calciner. The LLS is located towards the bottom of the calciner, allowing controlled transfer of solids from the calciner to the carbonator. Both loop seals must be fluidised in order for the solids to be transferred. Therefore, each loop seal has two gas distributor nozzles in the 'entry' half of the loop seal, and two distributor nozzles in the 'exit' side of the loop seal (Figure 6-3).

Trace heating is present the length of the carbonator and calciner and is required to ensure the desired temperature for the initial start-up of the system, to maintain the required operating temperatures, and also to reduce condensation effects. The carbonator has a total of eight trace heating elements due to its increased size compared to the calciner, which has a total of four heating elements along its length.

Each heating element can be controlled independently of the next, allowing different temperatures to be set in order to meet the required thermal conditions and to maintain a constant temperature along each reactor length. Typically, each carbonator heating element was set to approximately 600°C, whilst each calciner heated element was set to approximately 900°C. Figure 6-5 shows typical temperatures in the carbonator and calciner during testing.

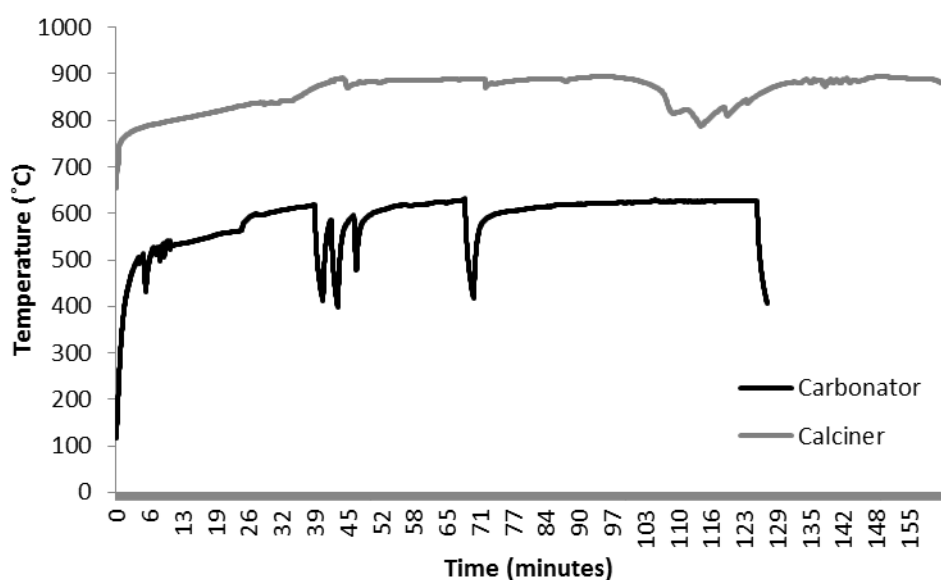


Figure 6-5 Typical temperatures in carbonator and calciner during testing, showing carbonator at approximately 600°C and calciner at approximately 900°C.

Online data loggers allow for continuous data acquisition, for temperature, pressure, flow, and flue gas analysis. K-type thermocouples (~ 90 % Ni, 10 % Cr) are present in 8 locations across the length of the carbonator including one at the lower loop seal and one at the exhaust, and in 7 locations across the length of the calciner including one at the exhaust. Pressure meters are also located across the length of both the carbonator and calciner, and also at the lower loop seal, providing important information on the fluidisation and entrainment of the solids.

In order to produce a representative syngas, the required gases were provided by feeding the relevant cylinder gases, and their input to each reactor was controlled by rotameters. In the carbonator, the simulated flue gas had a CO₂ concentration of approximately 8 %, based on that expected by a typical of a power plant [104], and chosen due to limitations with the CO₂ analyser. When investigating effects of SO₂, concentrations of 1000 ppm and 2000 ppm were used to represent a low and high

sulphur coal respectively. Loop seals were also fluidised by cylinder gases, with the LLS fluidised using air, and the ULS fluidised using CO₂.

Both the carbonator and calciner exhausts had an orifice plate fitted in accordance with British Standard BS EN ISO 5167-1:2003 [287], to allow measurement of exhaust gas flow. Two pressure meters either side of the orifice plate allow calculation of the gas flow through the orifice plate, as shown in Equation 6-1.

$$Q = C_f A_0 \sqrt{\frac{2 \Delta p}{\rho}} \quad \text{Equation 6-1}$$

Where Q = volumetric flow rate (m³ s⁻¹); C_f = flow coefficient; A₀ = orifice area (m²); Δp = pressure difference across orifice (Pa); and ρ = gas density (kg m⁻³)

6.4 Flue Gas Analysis

Flue gas samples were analysed for concentrations of CO₂ and O₂, sampled from a sampling port from the exhaust of the carbonator and calciner. For the calciner, samples were analysed using an ADC 7000 Gas Analyser to measure CO₂ concentrations, whilst for the carbonator, an ADC 4 channel Gas Analyser was used to measure flue gas concentrations of CO₂ and O₂. Both reactors have an accuracy of 1 %. In order to maintain the integrity of the analysers, flue gas samples were passed through a series of bubblers containing glass wool and located within a water bath in order to remove any liquid through condensation, or any particulate matter, before the sample was analysed. As a result, the flue gas sample was measured dry. Results were continuously recorded by an online data acquisition system. CO₂ capture % achieved in the reactor was calculated from Equation 6-2:

$$\%C = \frac{V_{\text{CO}_2 \text{ in}} - V_{\text{CO}_2 \text{ out}}}{V_{\text{CO}_2 \text{ in}}} * 100 \quad \text{Equation 6-2}$$

Where % C is % CO₂ capture, V_{CO₂in} is total known volume of CO₂ introduced into carbonator, and V_{CO₂out} is total volume of CO₂ exiting carbonator, measured at carbonator orifice plate and analyser.

An example calculation is provided as Appendix B.

6.5 Sorbent Properties

Longcliffe SP52 limestone was used as the CO₂ sorbent in each test. The limestone is carboniferous and comprises a minimum of 98.25% calcium as CaCO₃, and minimum 55 % calcium as CaO. It has a specific gravity of 2.65 g/cm³. The limestone was mechanically sieved to the required particle size, which for the majority of tests was either 106-125 µm or 125-250µm. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Perkin Elmer 400) analysis of the limestone was carried out to determine its element composition prior to testing (Figure 6-6).

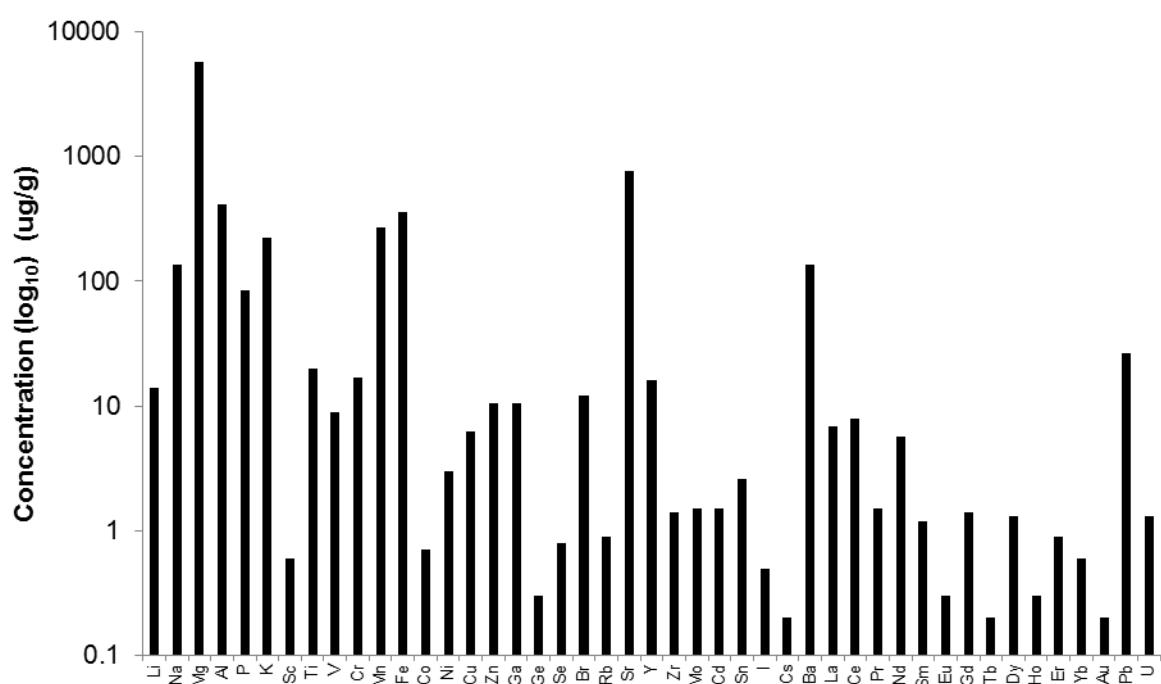


Figure 6-6 Elemental analysis of Longcliffe SP52 limestone by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Perkin Elmer 400).

6.6 Sorbent Sampling

Sorbent samples were taken prior to testing, and also after testing from both the carbonator and the calciner, and also the lower loop seal when required. When possible, samples were also taken from the calciner drain mid-test. This was in order to compare any change in sorbent morphology during and after testing.

6.7 Sorbent Analysis

In order to observe any morphological changes which may have occurred to the limestone sorbent as a result of the calcium-looping process, a number of chemical analytical techniques have been used. An Environmental Scanning Electron Microscopy (ESEM) was used to observe the sorbent under magnification of up to 3000x, and Energy Dispersive X-Ray Spectroscopy (EDS) was used to confirm the elemental composition of each sample. This instrument is considered to have an accuracy of 1 % and a variability of 0.1 %. X-Ray Diffraction (XRD) (Siemens D500) analysis of samples was undertaken to identify compounds present in the samples, and has an accuracy of 3 %. Particle size distribution analysis was carried out prior to and after testing using a Malvern Mastersizer 2000. Brunauer-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) (Tristar 3000) pore size and volume analysis were also carried out to determine any changes in sorbent morphology as a result of testing. Appendix C and Appendix D provide example PSD and BJH analysis results respectively.

6.8 CO₂ Capture Experimental Procedure

Prior to the start of each test, the required quantity of sorbent was added to the calciner, and the upper loop seal was filled to ensure it was sealed, after which the trace heating for the carbonator and calciner was switched on. Once the calciner had reached approximately 500°C, the calciner burner was lit to further increase the temperature in the reactor, and also to fluidise the bed in order to fill the lower loop seal. Once the calciner had reached the optimum temperature (850-900°C) and calcination had occurred (i.e. CO₂ % at calciner analyser stopped increasing), the carbonator burner was lit. The loop seals were then fluidised to facilitate the calcium-looping cycle to run as a continuous system, until burner switch-off at the end of the test.

6.9 Elemental Sampling

6.9.1 General flue gas sampling

Elemental sampling was undertaken based on United States (US) Environmental Protection Agency (EPA) Method 29: Determination of Metal Emissions from Stationary Sources [288].

Trace metal sampling from the reactor took place from the carbonator, because although the carbonator operates at lower temperatures (600-650°C) than the calciner (800-950°C) and therefore elemental release may be slightly lower due to lower volatility, at a power plant the carbonator would receive the full flue gas stream and therefore would be exposed to the widest range of impurities. In addition, the carbonator may produce a wider sample range because of the increased particle fluidisation (entrained flow bed compared to bubbling fluidised bed in calciner).

The experimental set up, as outlined in Figure 6-7, comprised a 'sampling train' based on that of EPA Method 29 [281] (Appendix E) consisting of several bubblers through which a stack sample of the flue gas was passed. Several bubblers, located within a water bath, contained aqueous acidic dilution to allow collection of condensed elements in the flue gas which passed through. A vacuum pump allowed the gas to be sampled through the bubblers, and a dry gas meter recorded the volume of gas which was sampled. A glass filter prevented particulate matter from passing through the bubblers. Prior to, and between each experiment, the glassware was acid washed in 1.8 M nitric (HNO_3) acid in order to prevent contamination.

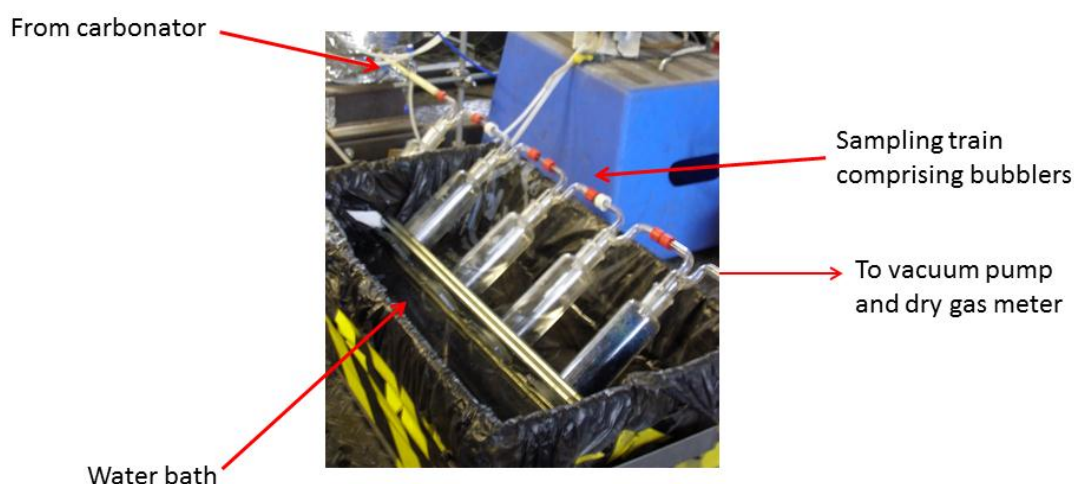


Figure 6-7 Sampling train comprising series of bubblers through which carbonator flue gas is passed, to sample elemental composition of flue gas.

The sampling system was started as the reactor was heating up, at approximately thirty minutes prior to the beginning of the experiment. This allowed the sampling of gases for a longer time period, and to take into account any emissions produced prior to the start of the actual experiment, which may occur as both the reactor material and Ca-based CO_2 sorbent were being heated. Although the majority of

element release is likely to occur at the start of each test, with emissions likely to decrease to a steady level as looping cycles continue, the sampling of the initial release is important to identify total emissions. Sampling was stopped when the burner was turned off at the end of experiment. Results are therefore shown for average test duration of approximately two hours. Trace metal analysis of the acidic solution was carried out using Inductively Coupled Plasma - Mass Spectrometry, which uses high temperature argon plasma to generate positively-charged ions from the sample, allowing concentrations of such ions to then be measured and quantified. Sampling was carried out on flue gas whilst no solids were in the reactor to provide a blank from which to compare results with solids in the reactor.

6.9.1.1 Mass Balance Analysis

A mass balance analysis was undertaken for effects of bed inventory and effects of SO₂ concentration for looping cycle tests, whereby incoming elements were considered to be those identified from analysis of solid samples taken post-test from the carbonator, calciner and lower loop seal, and outgoing elements were considered to be those identified from bubbler liquid analysis from both the carbonator and calciner flue gas streams. The mass balance was calculated from Equation 6-3 [289].

$$Q_{ab} = c_{ab} q_b$$

Equation 6-3

Where Q_{ab} is the flow rate of element a in the incoming or outgoing material stream b from the reactor (ug/min); $c_{a,b}$ is the content of the element a analysed in the representative sample of the material stream b from the reactor (ug/kg for solid samples, ug/l for liquid samples), and q_b is the flow rate of the material stream b from the reactor (kg/min for solid streams, l/min for liquid streams).

The closure of the mass balance was determined from the ratio of outgoing to incoming element flows. When the ratio is equal to one, the outgoing stream is equal to the incoming stream; similarly a value of less than one shows that the outgoing stream in the flue gas is lower than the incoming stream from the solids.

6.9.2 Inductively-Coupled Plasma – Optical Emission Spectroscopy

Analysis of gaseous elemental emissions from the CO₂ capture reactor was carried out online for a single CO₂ capture test, using Inductive-Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

The ICP-OES used for these tests was a mobile laboratory, designed and built by Spectro AI, in Kleve, Germany [290]. The ICP-OES performs simultaneous detection of multiple elements within entrained metal aerosols and vapours, by the direct injection of sample gas into the spectrometer via a heated primary sample line at 180 °C, and a secondary sampling line (Figure 6-8) [237].

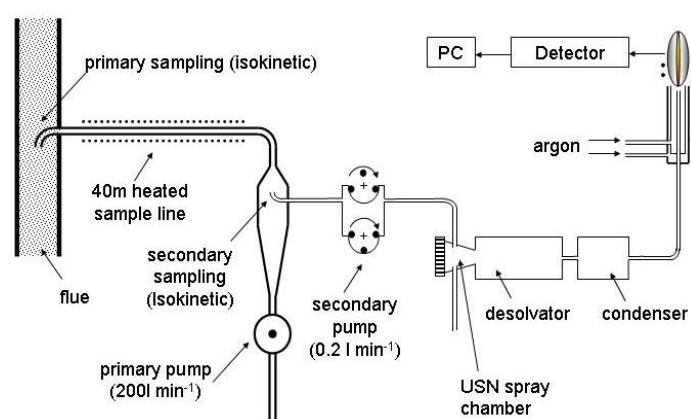


Figure 6-8 ICP-OES components and configuration [237].

Figure 6-8 provides the configuration of the main components of the ICP-OES and Table 6-3 outlines the operating parameters [237]. The primary sampling probe is positioned within the flue gas exhaust from the reactor, and withdraws a continuous gaseous sample from the exhaust, using a membrane pump. The gaseous sample then passes through a heated line, to minimise condensation of the gas. A secondary sampling stage is then used to reduce the sample volume to that required for analysis. The sample stream is then passed through a condenser to remove excess water before it is atomised in the ultrasonic nebulizer (USN), which provides an aerosol of metals to the ICP-OES, and also normalises the water content of the gas samples introduced to the system. The sample is then injected into the centre of the plasma torch, allowing the elemental spectra to be detected in the spectrometer, and results recorded electronically [237].

The inductively coupled argon plasma unit operates at over 6000 K, and can identify approximately 30 different metallic elements in the emissions spectrum, including sodium, lead and zinc, aluminium, barium, calcium, chromium, iron, cobalt, copper, magnesium, nickel, silver, thallium, vanadium, antimony, cadmium, mercury and tin.

Table 6-3 ICP-OES operating parameters, including temperatures and gas flow rates [237].

Parameter	Value
Generator Frequency (MHz)	27.15
Power RF (kW)	1.65s
Plasma Gas Flow Rate (l/min)	20.0
Auxiliary Gas Flow Rate (l/min)	0.8
Aerosol Carrier Gas Flow Rate (l/min)	0.5
Sample Gas Flow Rate (l/min)	0.125
Injector Tube Diameter (mm)	1.8
Read Time (s)	44
Desolvator Temperature	170°C
Condenser Temperature	0°C

The ICP-OES was firstly connected to the carbonator exhaust and sampled the flue gas for 75 minutes, before it was disconnected, and the process repeated for the calciner. Before being connected to the calciner, the ICP-OES was purged with nitrogen for five minutes to avoid cross- contamination [237].

6.10 Test programme

In order to achieve the PhD aims and objectives, a cold model test programme and a CO₂ capture and elemental sampling programme have been followed, provided as Table 6-4 and Table 6-5 respectively. In addition, Table 6-6 provides details of each of the % CO₂ capture tests carried out in addition to those outlined in Table 6-5, and details of amendments made in each test to the reactor and/or process are also provided. These tests form the basis of this PhD work, which are described in further detail in Chapters 8, 9 and 10 where relevant.

Table 6-4 Cold Model Test Programme.

Parameter investigated	Variant		
Minimum Fluidisation Velocity	125-250 μm CaCO_3	<125 μm CaCO_3	100-120 μm Cu
Solids flux	4.5 kg bed inventory	6 kg bed inventory	
Gas Leakage	Effect of loop seal, carbonator and calciner superficial velocity		
Pressure Balance	Effect of increasing carbonator superficial velocity		
	Effect of increasing calciner superficial velocity		
	Effect of particle size (125-250 μm and <125 μm)		
	Effect of cold model modifications		

Table 6-5 CO₂ Capture and Elemental Sampling Programme.

Parameter	Variant		
<i>Process Optimisation (see also Table 6-6)</i>			
Effect of particle size	<125 μm	125-250 μm	>250 μm
Effect of carbonation temperature	650-700 °C		600-650 °C
Effect of bed inventory *	4.5 kg	6 kg	13 kg
<i>Steam</i>			
Effect of steam (batch) *	5 % additional steam	10 % additional steam	20 % additional steam
<i>SO₂</i>			
Effect of SO ₂ (batch) *	0 ppm	1000 ppm	2000 ppm
Effect of SO ₂ (looping) *	0 ppm	1000 ppm	2000 ppm

*Tests for which elemental sampling was undertaken.

Table 6-6 CO₂ Capture Tests encompassing process and reactor modifications.

Test	Operating Conditions	Value
All	Carbonator gas flow rate	350l/min
	Experiment type	Looping Cycle
1	Carbonation temperature	550-600°C
	Bed inventory	4.5 kg
	Sorbent PSD	125-250 µm
2	Carbonation temperature	550-600°C
	Sorbent mass in reactor	4.5 kg
	Sorbent PSD	125-250 µm
	Other amendment	Increased trace heating temperature
3	Carbonation temperature	650-700°C
	Sorbent mass	4.5 kg
	Sorbent PSD	125-250 µm
	Other amendment	Increased trace heating and CH ₄ flow rate to increase temperature
4	Carbonation temperature	650-700 °C
	Sorbent mass	4.5 kg
	Sorbent PSD	125-250 µm
	Other amendment	Pre-calcination of limestone for looping test
5	Carbonation temperature	650-700 °C
	Sorbent mass	6.5 kg
	Sorbent PSD	125-250 µm
	Other amendment	Air shakers added to loop seals to encourage solids transfer
6	Carbonation temperature	650-700 °C
	Sorbent mass	13 kg
	Sorbent PSD	125-250 µm

	Other amendment	Limestone mass increased to improve space time
7	Carbonation temperature	650-700 °C
	Sorbent mass	13 kg
	Sorbent PSD	125-250 µm
	Other amendment	Limestone mass increased to improve space time
8	Carbonation temperature	600-650°C
	Sorbent mass	13 kg
	Sorbent PSD	125-250 µm
	Other amendment	LLS heated elements introduced
9	Carbonation temperature	600-650°C
	Sorbent mass	13 kg
	Sorbent PSD	106-125 µm
	Other amendment	Heated elements added to lower loop seal to increase temperature

7 RESULTS AND ANALYSIS: COLD MODEL

This section describes the results obtained from operation of the cold model, in order to enhance understanding of the hydrodynamics of the hot reactor, and to allow the determination of the optimum conditions to run the hot reactor to achieve maximum CO₂ capture efficiency. This is in accordance with Aim 1 and Objective 1a as provided in Chapter 1.

The first part outlines results from pressure balance, minimum fluidisation velocity, solids flux and gas bypassing tests, whilst the second part describes and analyses results obtained prior to and after modifications made to the reactor.

Results from this work have been published in the following journal paper:

Cotton, A., Patchigolla, K., Oakey, J.E. (2013) 'Hydrodynamic characteristics of a pilot-scale cold model of a CO₂ capture fluidised bed reactor' *Powder Technology* 235; 1060-1069.

7.1.1 Pressure Balance

The pressure balance of a system can provide important information with regards to solids entrainment and the flow of gas and solids throughout a system. Figure 7-1 and Figure 7-2 below outline the results of increasing carbonator flow and calciner flow respectively, on pressure balance of each reactor. The results confirm that increasing flow causes an increase in pressure, implying improved solids entrainment across the length of the reactor. This is in agreement with work available in the literature, including that by Pröll *et al.*, 2009 [184] who too identified increased pressure across both the fuel (calciner equivalent) and air (carbonator equivalent) reactor with increasing fluidisation. Pröll *et al.*, 2009 [184] observed exponential decay of pressure in the fuel reactor, and linear decay of pressure in the air reactor. Exponential decay in pressure across the calciner is however not so apparent in Figure 7-2, but rather both reactors appear to show linear decay in pressure with increasing height above the dense zone, implying constant solids movement (entrainment up carbonator, and transfer from upper loop seal (ULS) down to calciner) across each reactor. For lower carbonator flows, slugging of solids was

visually observed in the dense phase section of the carbonator. This however became less apparent with increasing carbonator gas velocity, implying improved solids entrainment.

Figure 7-3 shows the effect of particle size on pressure drop, and therefore solids distribution along the carbonator. The test with no solids provides the pressure effects due to friction, primarily due to the reactor walls. For the smallest particle size of $<125\ \mu\text{m}$, the highest pressures are achieved, when compared to the larger PSD of $125 - 250\ \mu\text{m}$, implying that the smaller particle size fraction is entrained to a greater extent than the large particle size, thus providing higher pressures along the reactor length.

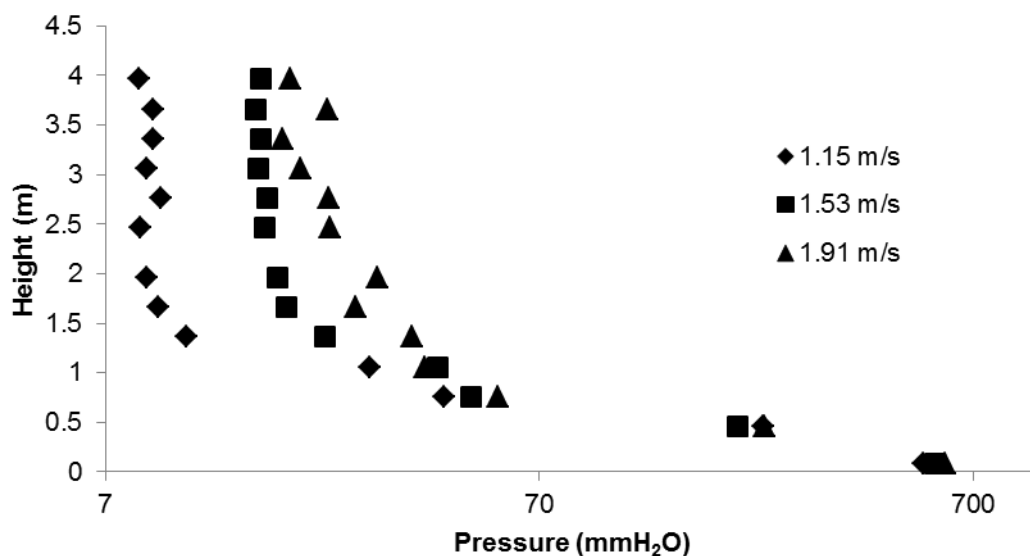


Figure 7-1 Effect of increasing carbonator flow on carbonator pressure balance, for 4.5 kg CaCO₃. 95 % confidence limit is $\pm 2.75\ \text{mmH}_2\text{O}$.

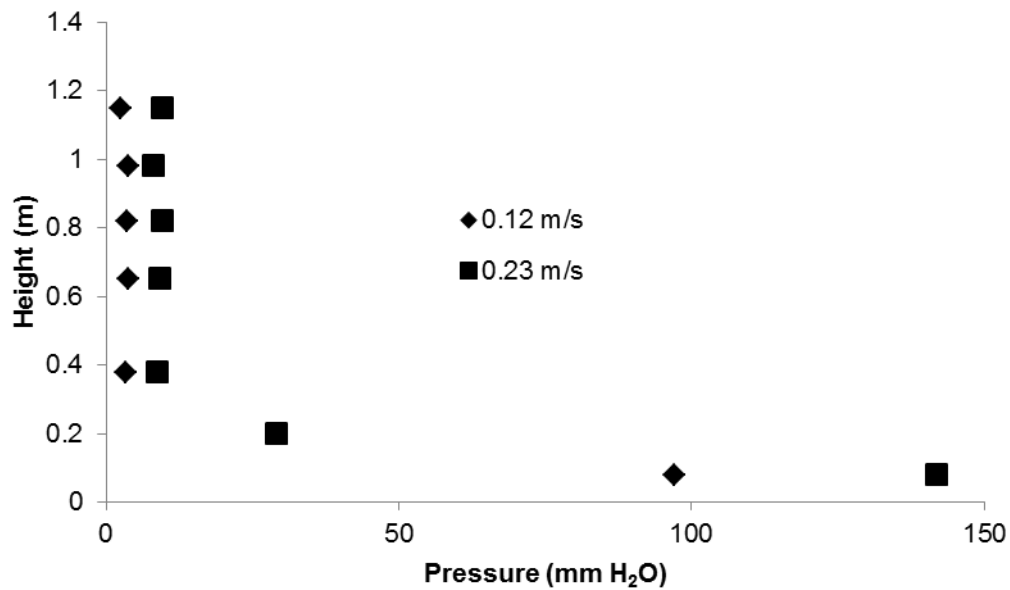


Figure 7-2 Effect of increasing calciner flow on calciner pressure balance, for 4.5 kg CaCO₃. 95 % confidence limit is ± 1.04 mmH₂O.

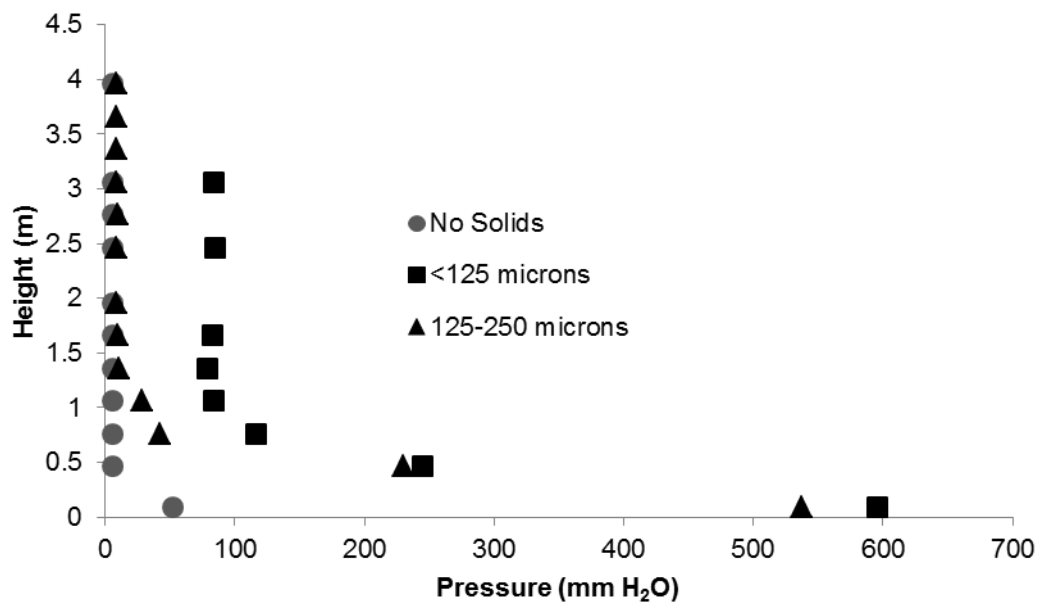


Figure 7-3 Effect of particle size on pressure drop along carbonator for 4.5kg CaCO₃. 95 % confidence limit is ± 2.30 mmH₂O.

7.1.1.1 Pressure Balance Model

A one-dimensional (1D) model of pressure balance along the carbonator length has been developed based on representative equations (Equation 7-1 and Equation 7-2) available in the literature [291]:

$$\Delta P_{\text{dilute}} = \frac{M_{\text{dil}} \cdot g}{A} \quad \text{Equation 7-1}$$

$$\Delta P_{\text{dense}} = \frac{M_{\text{den}} \cdot g}{A} \quad \text{Equation 7-2}$$

Where ΔP_{dilute} is pressure loss across dilute phase region of riser (N/m^2), ΔP_{dense} is pressure loss across dense phase region of riser (N/m^2), M_{dil} is mass of solids in dilute phase of carbonator (kg), M_{den} is mass of solids in dense phase region of riser (kg), g is the acceleration due to gravity (9.81 ms^{-2}), and A is cross-sectional area of carbonator (m^2).

A comparison of excel 1D model predictions, with cold model experimental data is provided in Figure 7-4. A correction factor has been applied to the excel 1-D results, after which shows that the model does successfully predict the general trend in pressure change across the carbonator. The over-prediction by the excel model in the dilute phase of the bed may be a result of errors in estimating bed voidage, which is based on the bubble fraction of solids. This is endorsed by the fact that the model under-estimates the pressure in the dense phase of the bed, below approximately 1m. The slight variation in pressure experienced by the cold model is not accounted for in the 1-D model, shown by the linear results, and can be considered a limitation of the model when compared to realistic data, again accounted for due to slight discrepancies in calculating bed voidage. However, it is apparent that the 1-D model is useful in predicting general trends in pressure across the riser length.

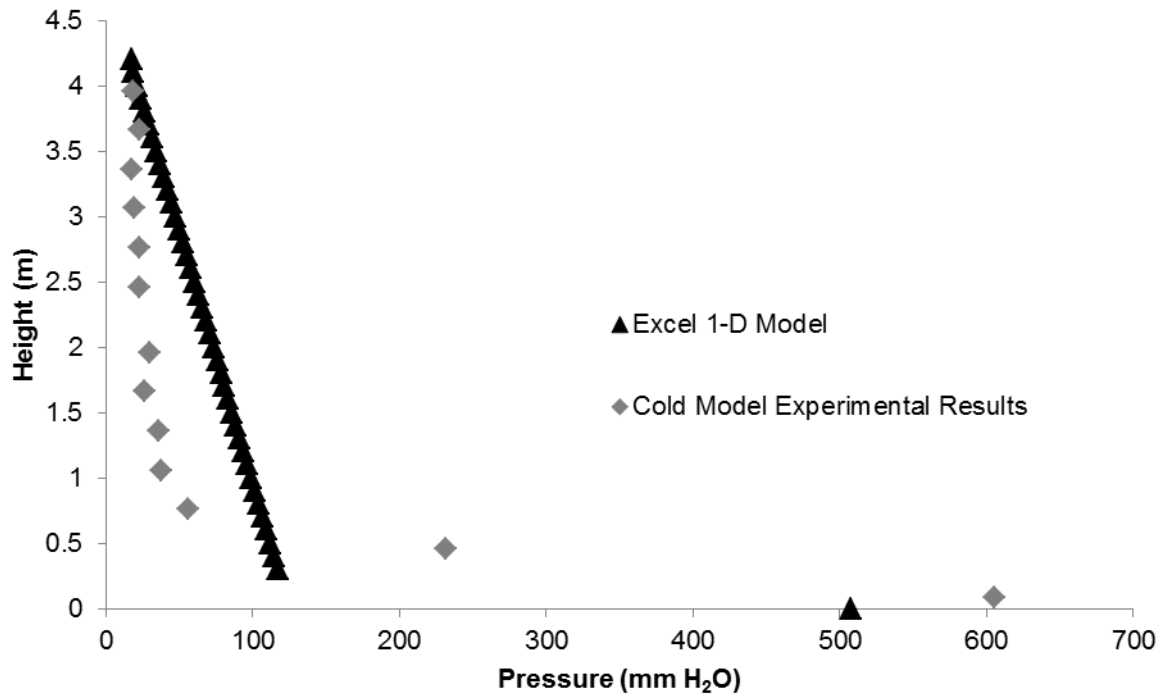


Figure 7-4 Comparison of predicted and experimental change in pressure across carbonator length.

7.1.2 Minimum Fluidisation Velocity

Minimum fluidisation velocity was investigated for varying PSD, the equation for which is provided as Equation 7-3.

$$U_{mf} = \frac{d_p^2 (\rho_s - \rho_g) g \epsilon_{mf}^3 \phi^2}{150 \mu (1 - \epsilon_{mf})} \quad \text{Equation 7-3}$$

Figure 7-5 shows minimum fluidisation results for limestone of particle size 125-250 μm , for which a U_{mf} of ~ 0.06 m/s was achieved, which corresponds well with that achieved by Goo *et al.* 2010 [212] of 0.065 m/s for 270 μm silica sand particles at 25 $^{\circ}\text{C}$. Similarly, at 26 $^{\circ}\text{C}$, Subramani *et al.* 2007 [292] achieved U_{mf} of approximately 0.045 m/s for sand particles of 200 μm . Wu *et al.* 1991 [293] achieved U_{mf} of 0.031 and 0.049 m/s also for sand of d_p 134 μm and 253 μm , respectively, at 20 $^{\circ}\text{C}$. For a limestone of particle size <125 μm , a U_{mf} of 0.016 m/s was obtained in this study, which closely corresponds with work by Ryu *et al.*, 2007 [191] who determined a U_{mf} of 0.018 m/s for 106-212 μm sand. In this study, the minimum fluidisation velocity for

spherical copper particles of size 100-120 μm was established to be 0.042 m/s, a value higher than that achieved for limestone, which can be attributed to the higher density of copper over limestone (8000 kg m^{-3} over 2650 kg m^{-3} respectively). Similarly, Foscolo *et al.*, 2007 [194] for copper particles of 122 μm and density 8822 kg/m^3 state a U_{mf} value of 4.4 cm/s (0.044 m/s), although the units on the x-axis of the relevant graph state otherwise at 4 m/s, considered to be a discrepancy.

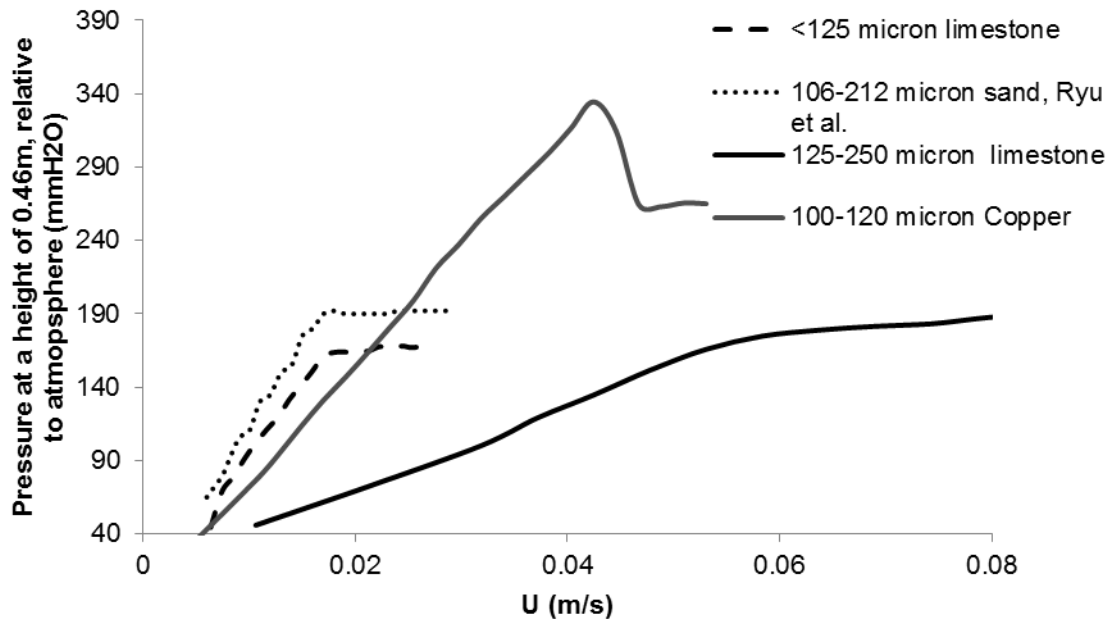


Figure 7-5 Effect of particle size on minimum fluidisation velocity, U_{mf} , measured at a height of 0.46m up the reactor length, and compared with results from Ryu *et al.*, 2007 [191].

The experimental results achieved correspond well with those determined theoretically, as shown in Table 7-1. The theoretical value for copper is slightly overestimated compared to the experimental value, in comparison to the limestone results for which the theoretical value is slightly underestimated compared to the experimental results. The reason for this may be due to the increased density of the copper (8800 kg/m^3) compared to the limestone (2650 kg/m^3) causing a slight discrepancy in the results. The theoretical U_{mf} for CaO has been calculated at a value of 0.05 m/s. The density of CaO is also greater than CaCO_3 , thus accounting for the increased U_{mf} value over CaCO_3 . The attrition rate of Longcliffe SP52 limestone of original PSD 125-250 μm , after 40 cycles has been assumed to be between that of a fragile limestone (Cadomin) and an attrition-resistant limestone

(Havelock), with a reduction in particle size of 11%. Based on this, the U_{mf} after 40 cycles has been calculated based on the revised particle size, providing a value of 0.031 m/s. This decreased value from the original 125-250 μm is attributed to the decreased particle size, outlining the effect that particle size and density has on U_{mf} values.

Table 7-1 Comparison of experimentally and theoretically derived U_{mf} values for cold model.

Particle Type	Particle Size	Experimental U_{mf}	Theoretical U_{mf} $U_{mf} = \frac{d_p^2 (\rho_s - \rho_g) g}{150 \mu} \frac{\epsilon_{mf}^3 \phi^2}{1 - \epsilon_{mf}}$
Limestone (CaCO_3)	<125 μm	0.018 m/s	0.012 m/s
Limestone (CaCO_3)	125-250 μm (average 188 μm)	0.058 m/s	0.040 m/s
Copper (Cu)	100-120 μm (average 110 μm)	0.042 m/s	0.045 m/s
Lime (CaO)	125-250 μm (average 188 μm)	n/a	0.050 m/s
Limestone having undergone attrition after 40 cycles	167.2 μm (11% loss from 188 μm)	n/a	0.031 m/s

This has been investigated further, with Figure 7-6 providing the theoretical U_{mf} calculations for Longcliffe limestone of average particle size 188 μm , as used in this study. The same figure also shows the theoretical U_{mf} for a median particle size based only on particles >75 μm , as determined by PSD analysis (Appendix C). Jia *et al.*, 2007 [132] suggest that based on work by Fuertes *et al.*, 1991 [133] particles <75 μm tend to partition to the overhead ashstream in a circulating FBC, and therefore attrition effects are generally only considered for particles >75 μm [132]. Theoretical U_{mf} has been calculated at the chosen % reduction in particle size values of 5, 10, 15, 30 and 40 %, because Jia *et al.*, 2007 [132] found that when testing five different limestones, attrition extents varied between 1.29 and 39.47 %. The results show that a reduction in average particle size due to attrition effects causes a reduction in U_{mf} ,

with a smaller change in theoretical U_{mf} as attrition effects increase for the limestone of the smaller average particle size, 120 μm . For an average particle size of 188 μm , U_{mf} is reduced from 0.043 m/s to 0.016 m/s for a reduction in particle size of 0 and 40 % respectively, whereas for the sorbent bed of average size 120 μm , U_{mf} decreases from 0.018 to 0.006 m/s for a reduction in particle size of 0 and 40 %. This is to be expected as a smaller initial average particle size would be likely to have a lower U_{mf} value.

Table 7-2 shows the % change in U_{mf} with increasing reduction in particle size. Similar values for change in U_{mf} are shown for the two different initial average particle sizes, with an approximate decrease in U_{mf} of 0.09 m/s for every 5 % reduction in particle size. This confirms that decrease in U_{mf} is fairly constant for a given decrease in particle size, with initial particle size not seeming to be a factor.

These calculations show that attrition effects may have an impact on the superficial gas velocity required to fluidise a bed. With regards to running the pilot scale reactor, this implies that if necessary a reduced gas velocity over time may be possible as attrition of sorbent takes place, due to the 'sorting' nature of a fluidised bed.

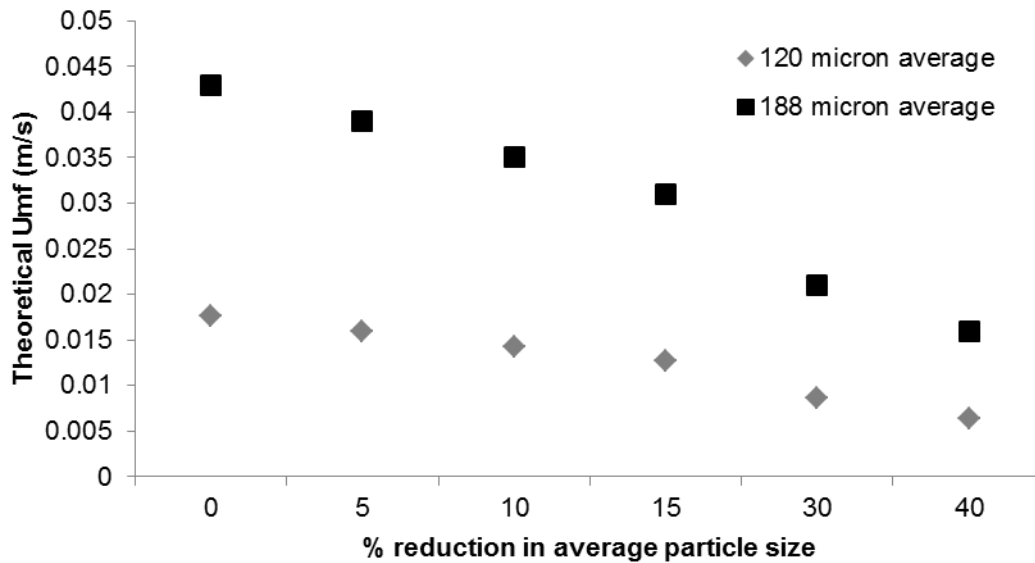


Figure 7-6 Effect of attrition on theoretical U_{mf} values for initial average particle size of 120 μ m and 188 μ m.

Table 7-2 Percentage change in U_{mf} as a result of attrition-induced reduction in particle size.

% Reduction in particle size from attrition effects	% Reduction in U_{mf}	
	120 μ m average initial particle size	188 μ m average initial particle size
0	0.097	0.093
5	0.190	0.186
10	0.278	0.279
15	0.510	0.512
30	0.640	0.628
40	0.097	0.093

7.1.3 Solids Flux

Figure 7-7 below shows that for a given gas velocity, the solids flux is higher for an increased bed inventory of 6 kg compared to 4.5 kg limestone of 125-250 μ m. This is due to increased hydrostatic pressure transferring particles through from the carbonator to the calciner, thereby increasing particle concentration in the circulatory system [184]. This is also apparent when observing the running of the cold model, that increases in bed inventory up to an optimum point also increase solids

entrainment. This is important for optimising the hot reactor, in that increasing bed inventory should increase mass of particles circulating throughout the reactor, and thus act to optimise sorbent conversion and CO₂ capture efficiency. Bischi *et al.*, 2011 [284] compared the effect of 35 kg and 45 kg solids inventory on solids circulation rate, and concluded that increasing inventory increased solids flux (Figure 7-7). The lower solid flux values achieved by Bischi *et al.*, 2011 [284] for approximately 7.5 times the mass of solids used in this study can be accounted for by the increased diameter of the reactor used by Bischi *et al.*, 2011 [284]. Pröll *et al.*, 2009 [184] compared solids flux for 4.0, 4.5 and 5.0 kg of 55 µm bronze powder, and too confirmed that increasing bed inventory increased solids flux. The values increased from approximately 60 kg m⁻² s⁻¹ for 4.0 kg, to 90 kg m⁻² s⁻¹ for 4.5 kg, to 105 kg m⁻² s⁻¹ for 5.0 kg, for a superficial velocity of 4.2 m/s. The values are similar to those achieved for the limestone in this study, but the increased superficial velocity required is a result of the increased density of the bronze powder (8730 kg m⁻³) compared to limestone.

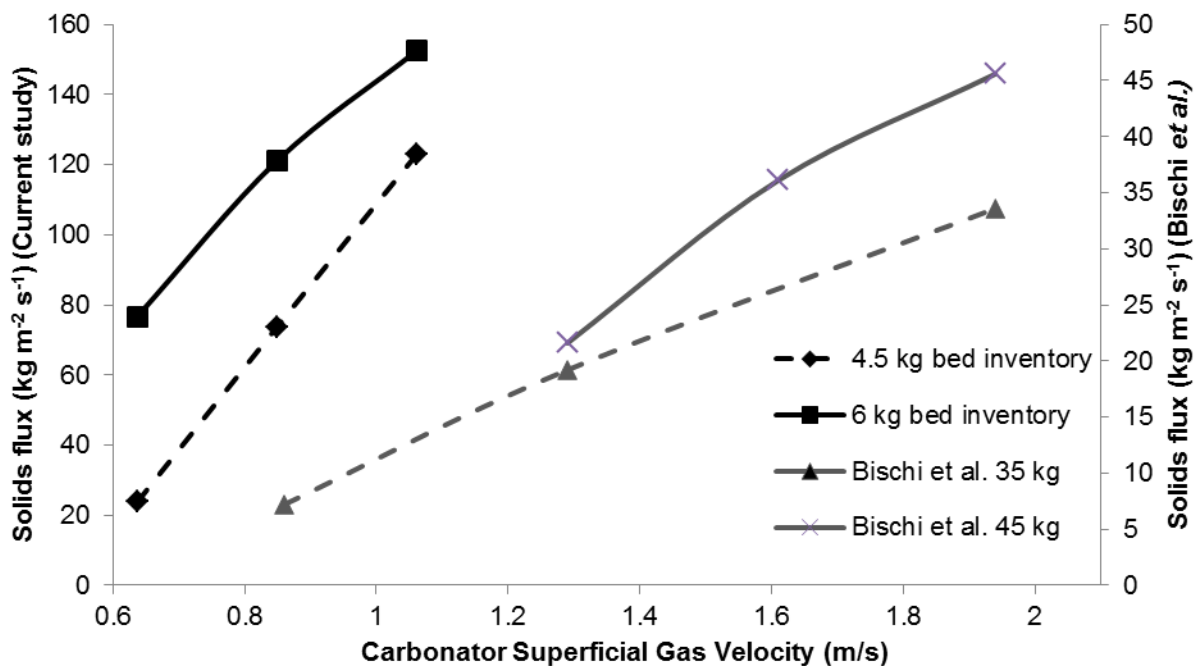


Figure 7-7 Effect of bed inventory on solids flux, for a sorbent bed of 4.5 kg and 6 kg, from carbonator to calciner reactor, compared with work by Bischi *et al.*, 2011 [284].

Figure 7-8 shows the solids flux through the lower loop seal (LLS), and outlines the effect of calciner superficial gas velocity and operation of the ULS on solids flux from

the calciner to the carbonator, for 4.5 kg of limestone of particle size 125-250 μm . Operation of the ULS and increasing calciner gas velocity had a positive effect on solids flux from the calciner to the reactor, in that additional gas flow was inherent in achieving greater solids flux due to greater pressure. The operation of the ULS has a positive influence on solids flux through the LLS, reaching a maximum of $290 \text{ kg m}^{-2} \text{ s}^{-1}$ at a calciner superficial gas velocity of 0.23 m/s and carbonator superficial gas velocity of 1.06 m/s, compared to a value of $244 \text{ kg m}^{-2} \text{ s}^{-1}$ for the same bed inventory and gas velocity when the ULS was not operated. This is again due to greater pressure from increased gas velocities, enhancing solids transport through the calciner reactor.

The curves of the graphs for the experiments carried out at a calciner superficial velocity of 0.23 m/s, appear to initially differ in shape and provide lower initial solids flux values for carbonator superficial gas velocities between 0.64 and 0.85 m/s, compared to those carried out at a calciner gas velocity of 0.12 m/s. This may be because high calciner and low carbonator gas velocities cause an increase in the pressure experienced at the top of the calciner and upper loop seal, therefore impeding solids flux from the carbonator. When the carbonator flow is increased, this overcomes the increase in pressure at the top of the calciner and upper loop seal, thus increasing solids flux. The curve for a calciner superficial gas velocity of 0.12 m/s with the ULS on appears to follow the same trend as the two curves when the calciner gas velocity is 0.23 m/s. This is perhaps due to the influence of the ULS, even at lower calciner superficial gas velocities.

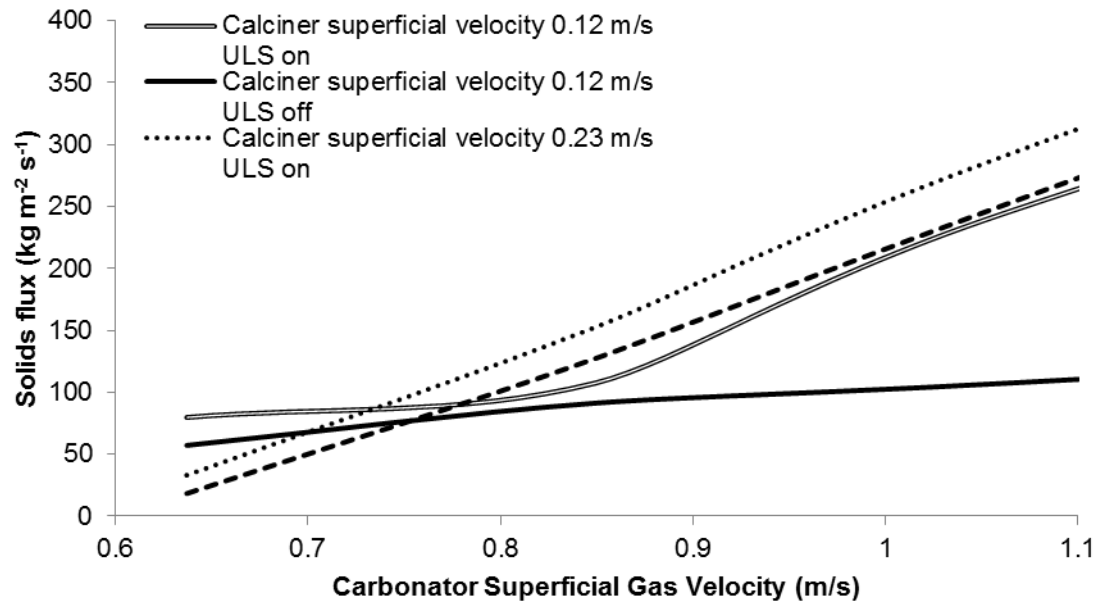


Figure 7-8 Effect of calciner and carbonator gas velocity, and upper loop seal operation (gas velocity of 0.66 m/s when operated), on solids flux, for a lower loop seal fluidisation velocity of 0.66 m/s.

Figure 7-9 shows the solids flux through the ULS, and the effect of increasing calciner flow and the influence of operating the lower loop seal, on the solids flux from the carbonator and through the ULS. It is again apparent that increasing calciner superficial gas velocity increases the solids flux, due to a greater pressure enabling solids transport, although the effects are most pronounced at higher carbonator gas velocities. At the higher calciner superficial gas velocity of 0.23 m/s and the LLS not in operation, the solids flux is initially the lowest value for a low carbonator superficial gas velocity of 0.64 m/s, but then appears to increase steadily as carbonator gas velocity increases. This may be due to the pressure balance experienced at the top of the calciner and upper loop seal, as previously discussed. Operation of lower loop seal again has a positive effect on solids flux, and this is in agreement with work by Pröll *et al.*, 2009 [187].

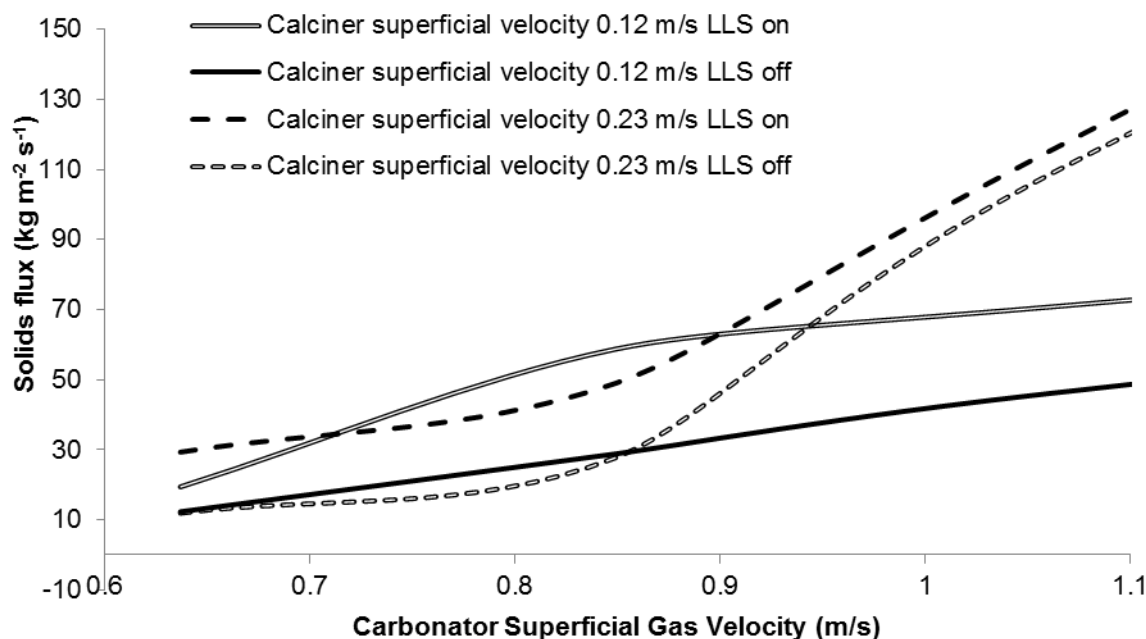


Figure 7-9 Effect of increasing carbonator and calciner gas velocity, and influence of lower loop seal operation (gas velocity of 0.66 m/s when operated) on solids flux, for an upper loop seal gas velocity of 0.66 m/s.

7.1.4 Gas Bypassing

The cold model can be considered to have four main components requiring fluidisation and from which gas bypassing could occur, comprising the carbonator, calciner, LLS, and ULS. A tracer method was used to investigate bypassing from each component, whereby either N₂ or air was used as the fluidising medium for the component from which gas bypassing was being investigated. The % O₂ was measured in the outgoing gas flow from the cyclone or the calciner exhaust, and from that value the % gas bypassing was calculated. A bed inventory of 4.5 kg limestone, particle size 125-250 μm, was used in each test.

7.1.4.1 Bypassing from lower loop seal to calciner

The LLS was fluidised with N₂ and the % O₂ measured at the cyclone exit. Figure 7-10 shows the effects of increasing the LLS gas velocity on gas bypassing to the calciner. It identifies that the gas bypassing increases with increasing gas velocity in the LLS, from approximately 4% at LLS superficial velocity 0.66 m/s, to approximately 14 % at a gas velocity of 1.98 m/s.

The effect of increasing calciner gas velocity is shown in Figure 7-11, which identified that increasing gas velocity into the calciner, acted in reducing bypassing from the LLS. This is because increasing pressure from the calciner acts to encourage gas in the LLS to flow towards the carbonator, thus improving the pressure balance of the system. In addition, fluidisation of solids occurred to a greater extent with increased gas flow, thus enhancing the pressure balance effect. This too was confirmed by work available in the literature [190]. The difference between the minimum gas bypassing at the highest calciner superficial velocity, and the highest bypassing at the lowest calciner gas velocity also increased for a given LLS gas velocity. For example, at a LLS gas velocity of 0.66 m/s, there is a difference of approximately 4 % between the gas bypassing at a calciner gas velocity of 0.12 m/s and 0.23 m/s, whereas this figure increases to 11 % when the LLS gas velocity is increased to 1.98 m/s. This identifies the strong influence that both LLS and calciner superficial gas velocities have, on gas bypassing from the LLS to the calciner. This work highlights the ideal operating conditions to reduce gas bypassing: calciner gas velocity 0.23 m/s, and both loop seals at 0.66 m/s. This produced a low gas bypassing of approximately 2 %, suggesting that the system is efficient in terms of gas bypassing.

Figure 7-12 outlines the effect of increasing carbonator and LS gas velocity, showing that the highest carbonator gas velocity of 1.91 m/s and lowest LS gas velocity of 0.66 m/s for both the ULS and LLS provides the lowest % leakage at 4.4 %. This trend is apparent, although for a carbonator gas velocity of 1.53 m/s and LS gas velocity of 0.66 m/s, the % leakage appears to increase to 10.6%, and conversely for the same carbonator gas velocity, and LS gas velocity of 1.98 m/s, the leakage decreases to 28.8%. This implies that the LS gas velocity has an effect on gas leakage for medium carbonator flows, and is important in maintaining the correct pressure balance and in turn direction of flow of solids and gas. From this information, it is apparent that a high carbonator and low LS gas velocity are required to minimise gas bypassing.

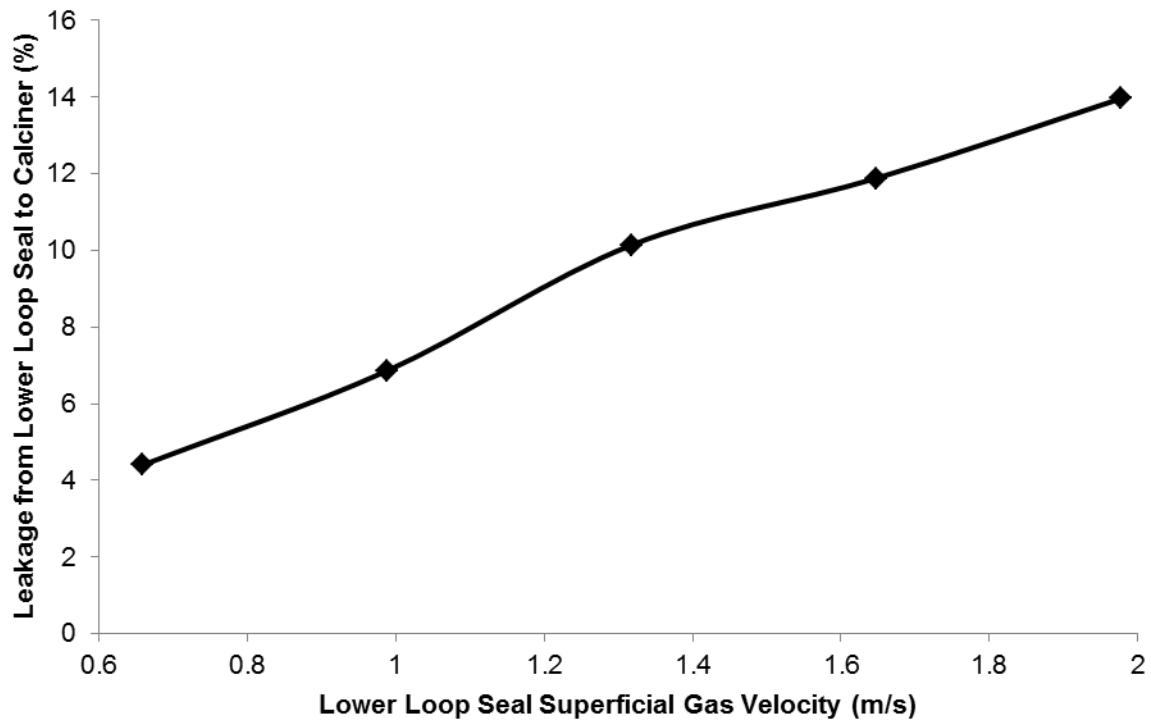


Figure 7-10 Effect of lower loop seal gas velocity on gas bypassing from lower loop seal to calciner, for a carbonator gas velocity of 1.91 m/s, calciner gas velocity of 0.23 m/s and upper loop seal gas velocity of 0.66m/s.

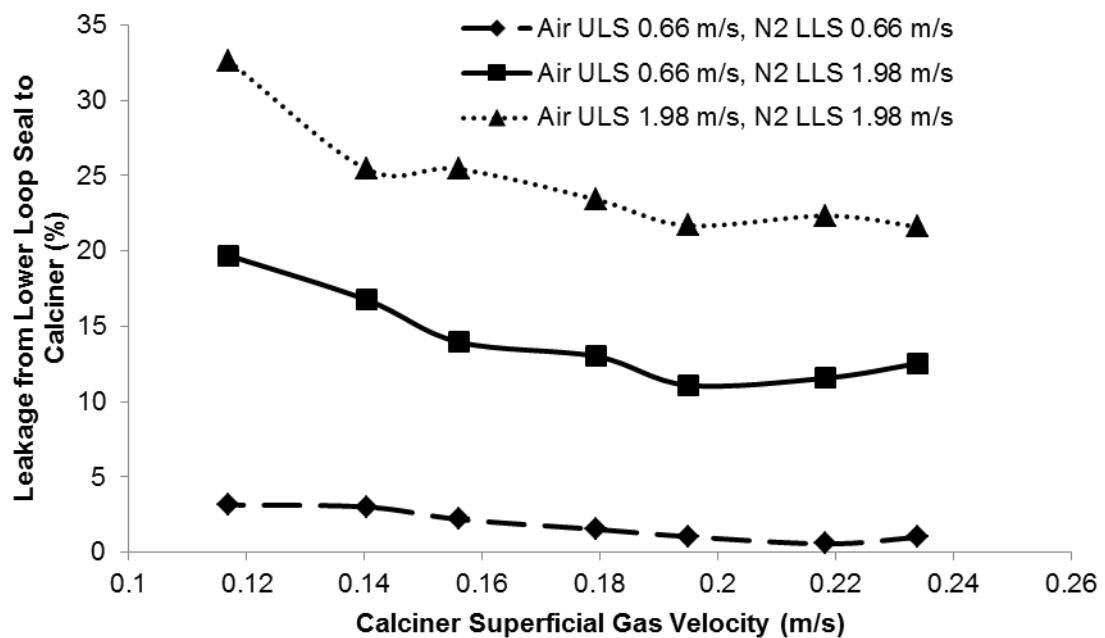


Figure 7-11 Effect of calciner gas velocity and loop seal gas velocity on gas bypassing from lower loop seal to calciner, for a carbonator gas velocity of 1.91 m/s.

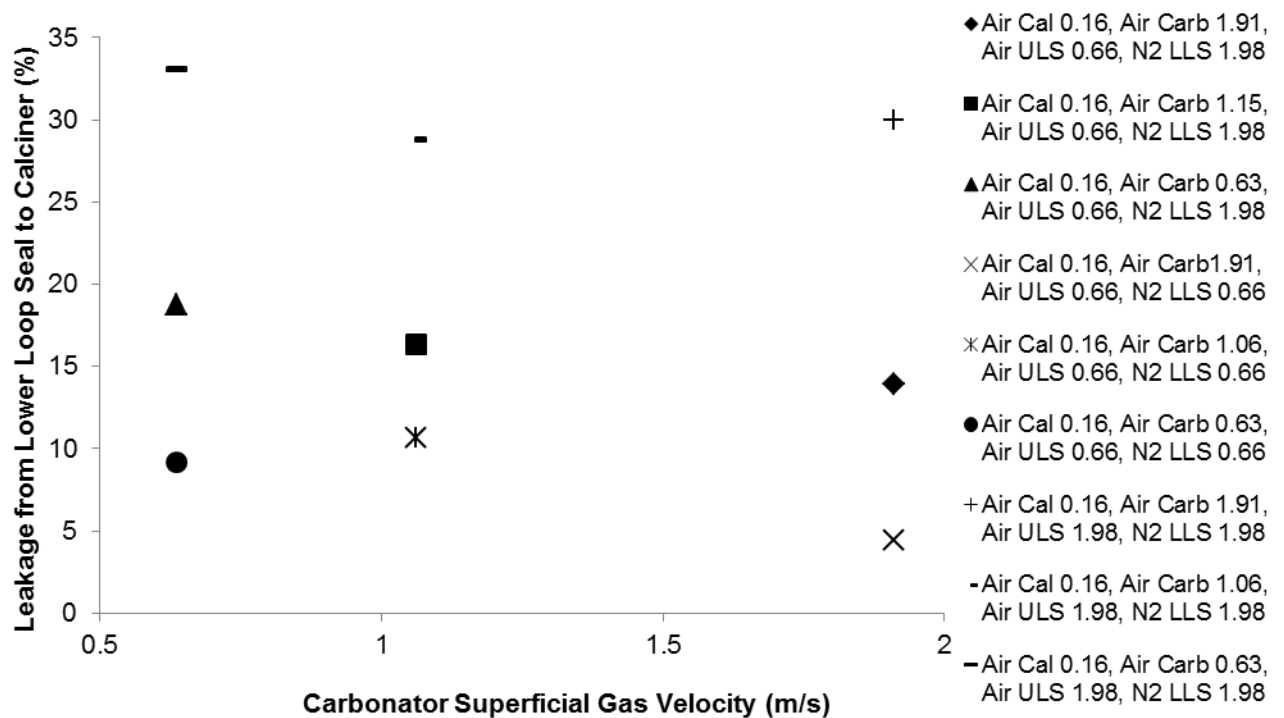


Figure 7-12 Effect of carbonator gas velocity for a calciner gas velocity of 0.16 m/s.

7.1.4.2 Bypassing from upper loop seal to calciner

N₂ was added to the upper loop seal, and the % O₂ measured at the calciner. Figure 7-13 confirms that increasing ULS gas velocity increases gas bypassing to the calciner, but in addition, increasing calciner gas velocity appears to decrease bypassing. This again can be explained by the increase in pressure that occurs due to the increased flow from the calciner, discouraging the movement of gases in the downward direction from the ULS. Furthermore, increasing calciner gas velocity would act to dilute N₂ gas from the ULS, therefore reducing the apparent gas bypassing. One anomaly however is for an ULS gas velocity of 1.32 m/s and a LLS gas velocity of 0.66 m/s which shows that as calciner gas velocity increases, gas bypassing increases at a calciner flow of around 0.15 m/s before then decreasing again. This however appears to be the only data point in the figure which shows this, and therefore it can be assumed that increasing calciner flow decreases gas bypassing. Further the gas bypassing values for an ULS gas velocity of 1.65 m/s and a LLS gas velocity of 0.66 m/s, and also for an ULS gas velocity of 1.98 m/s and a

LLS gas velocity of 1.98 m/s, are lower than for other data points at lower ULS and LLS gas velocities. It may be that these combinations of the specific ULS, LLS and calciner gas velocities act to reduce gas bypassing by optimising the pressure balance of the system. A calciner gas velocity of 0.16 m/s and LS gas velocity of 0.66 m/s providing the lowest leakage of 0.1 %. In comparison, low calciner gas velocity and high LS gas velocity provided the highest leakage at almost 20 %.

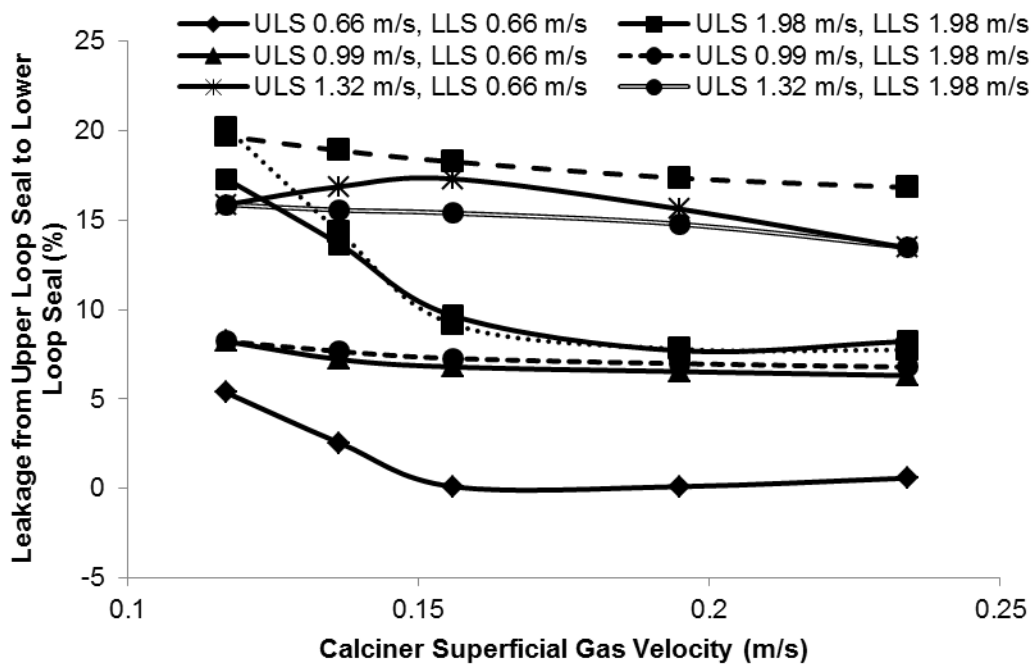


Figure 7-13 Effect of calciner and loop seal superficial gas velocities on leakage from upper loop seal to calciner, for a carbonator superficial velocity of 1.91 m/s.

7.1.4.3 Bypassing from carbonator to calciner

Air was added to the carbonator, whilst the calciner and loop seals were fluidised with N_2 . This experimental set-up differed from the other gas bypassing tests, in order to achieve a high enough superficial gas velocity required for the carbonator. Figure 7-14 shows that bypassing from the carbonator to the calciner was low at around 1.43 %, and did not vary extensively with carbonator gas velocities. This suggests that a 'base' bypassing exists from the carbonator to the calciner, and may be caused by the 'backflow' of gas occurring through the lower loop seal to the calciner. Johansson *et al.*, 2003 [190] did not identify any bypassing from the air reactor (carbonator equivalent) to the fuel reactor (calciner equivalent), suggesting that for most systems gas bypassing between the two reactors is generally minimal. This may be because of the high gas velocities required in the carbonator compared

to the rest of the system, for which the 'easiest' exit for the gas, assuming the loop seals are sealed, is through the carbonator reactor, thus creating the preferred pressure balance and reducing bypassing to the calciner. A bypassing of 1.43 % is the equivalent of 1.43 % dilution of CO₂ in the calciner in the hot system, which is a small percentage of the total amount.

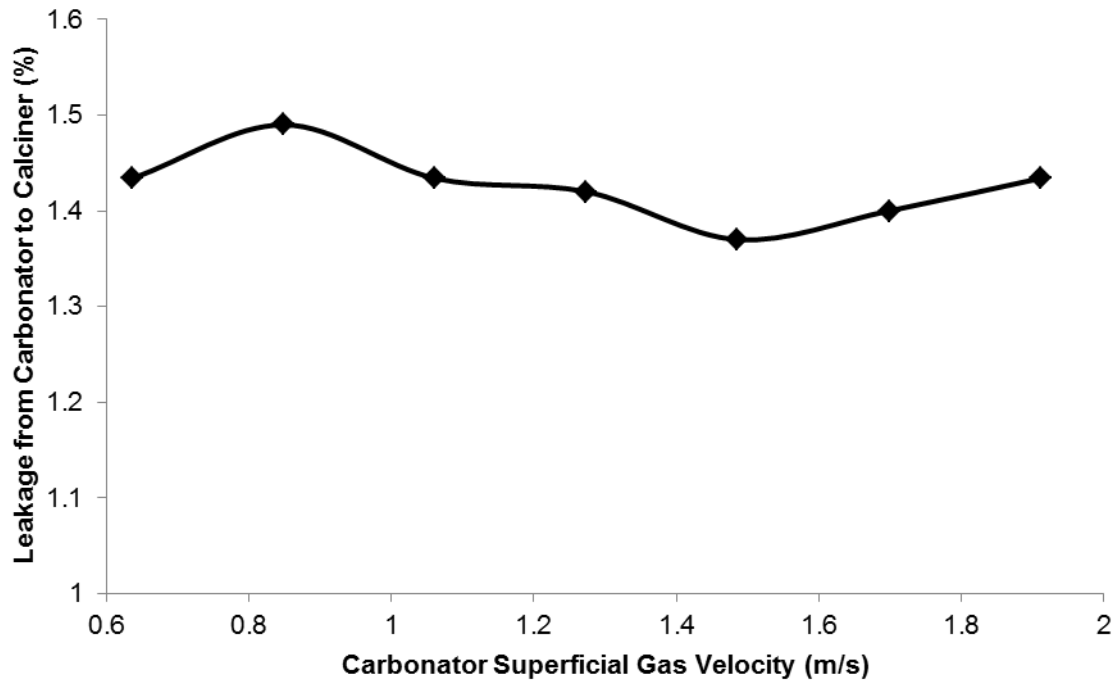


Figure 7-14 Effect of carbonator gas velocity on bypassing from carbonator to calciner, for a calciner gas velocity of 0.23 m/s, and upper and lower loop seal gas velocities of 0.66 m/s.

7.1.4.4 Bypassing from calciner to cyclone

N₂ was used as the fluidising gas for the calciner, and % O₂ at the cyclone exit was measured. Figure 7-15 shows bypassing from the calciner to the cyclone as a function of calciner loop seal gas velocities. The bypassing does not increase above 1.6 % which is a relatively low value, and the graph shows that increasing loop seal superficial velocity acts to increase bypassing to the cyclone when the calciner gas velocity is at 0.16 m/s. It is interesting, however, that for a calciner gas velocity of 0.12 m/s, the bypassing does not change when the loop seal gas velocities are increased from 0.66 m/s to 1.98 m/s, suggesting that at this calciner gas velocity, loop seals have little effect on gas bypassing. The lowest bypassing rate of 0.6 % occurred for a calciner gas velocity of 0.16 m/s and loop seal gas velocities of 0.66

m/s. This result is encouraging in that the process can be run at high efficiencies in terms of reduced gas bypassing.

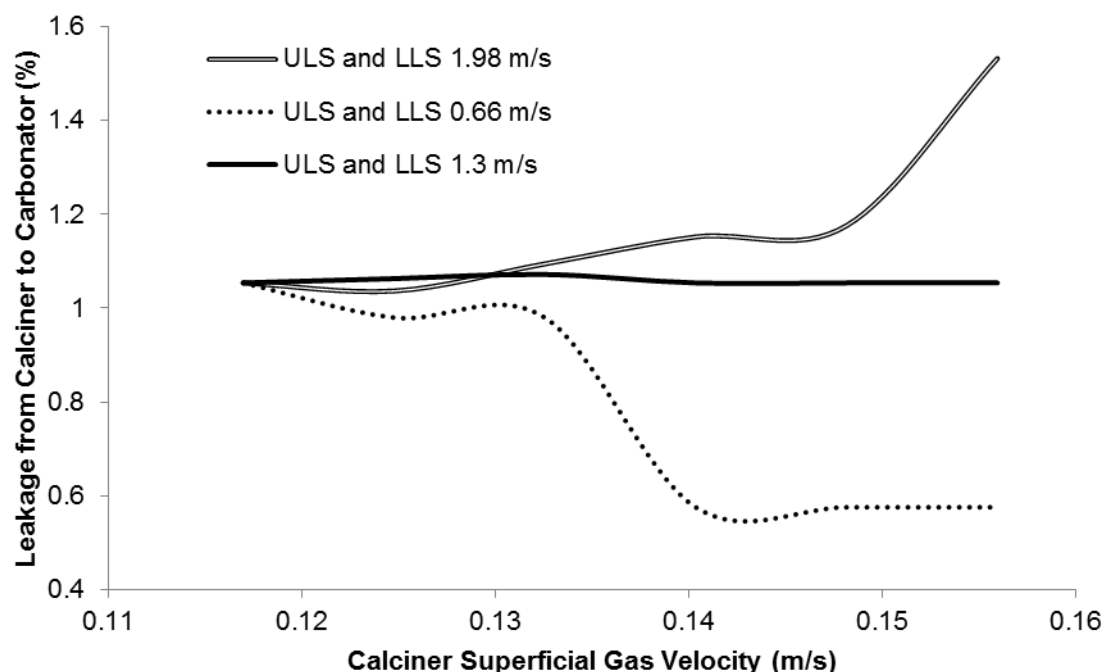


Figure 7-15 Effect of calciner gas velocity and loop seal gas velocity of gas bypassing from calciner to cyclone, for a carbonator gas velocity of 1.91 m/s.

7.1.5 Cold Model Modifications

Following analysis of the results outlined above, a number of modifications were made to the cold model to improve particularly the pressure balance across the system and to further minimise gas bypassing.

7.1.5.1 Loop Seals

Experimental results (pressure balance and gas leakage) and visual observations confirmed that back flow of gas and solids was occurring up through the lower loop seal and towards the calciner i.e. in the incorrect direction, reducing process efficiency. In initial tests, the entry side of each loop seal was filled with approximately 0.13 kg solids, but it was observed that during testing the loop seal would often have emptied within the first minutes. To attempt to remedy this, prior to testing the loop seal was filled with approximately 0.6 kg solids up to the top of the entry standpipe [294], a length of approximately 200 mm. The increased mass of sorbents in the loop seal appeared both visually and experimentally to reduce

'backflow' of gas and solids up the lower loop seal and into the calciner, by creating a sorbent seal, which has the added effect of improving the pressure balance (Figure 7-16) of this region of the system. Figure 7-17 shows that prior to increased filling, the pressure at the exit of the lower loop seal was slightly higher (30.6 mmH₂O) than for the entry side (25.9 mmH₂O) implying flow in the 'incorrect' direction from the exit to the entry. Also, the low values suggest absence of solids. After modification, there is a much greater change in pressure, with the entry side having a value of 508 mmH₂O, and the exit 327 mmH₂O, implying presence of solids acting as a seal, and 'correct' direction of flow.

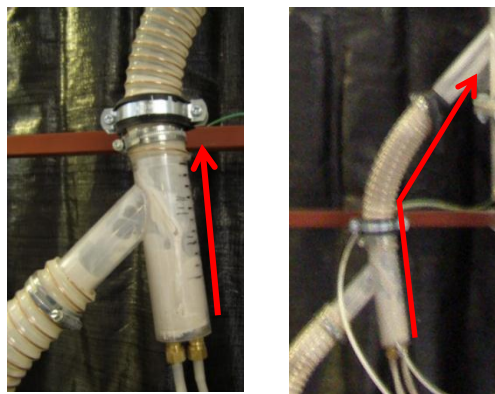


Figure 7-16 Extent of loop seal sealing before modification with approximately 0.13 kg solids, and after with approximately 0.6 kg solids.

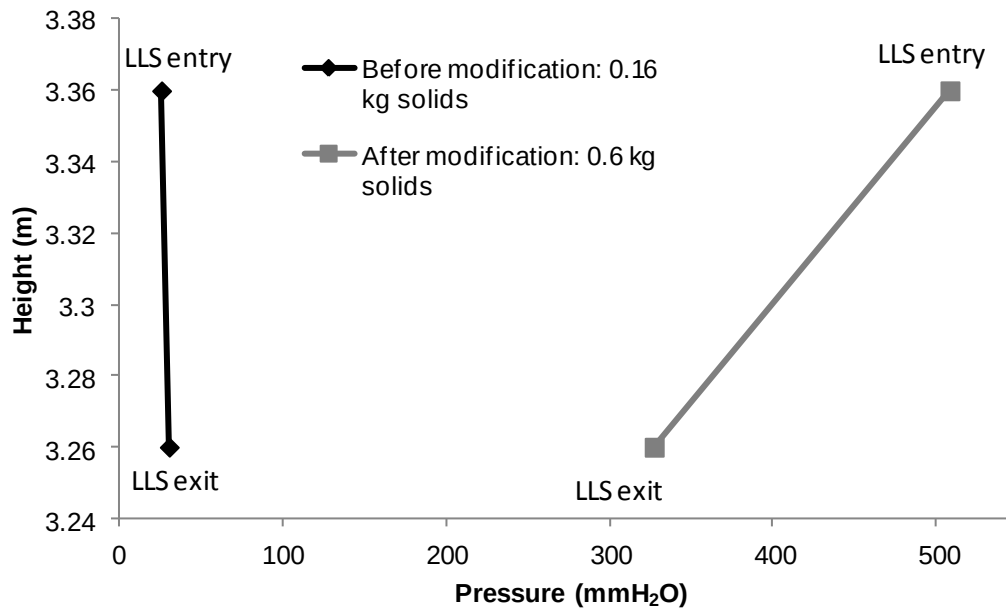


Figure 7-17 Effect of increase mass of solids in lower loop seal on pressure balance.

7.1.6 Calciner Exhaust Position

The cold model was designed with a calciner exhaust at a 45° angle to the standpipe joining the calciner. Visual observations confirmed that solids entering the calciner from the upper loop seal standpipe were being swept up the calciner exhaust with exit gases, and an average solids loss of 0.46 kg/hour was realised. Therefore, some solids were not being transferred to the calciner for reaction, instead were being removed from the circulatory system, thus reducing process efficiency. It was considered that if the exhaust was moved so that it was located off the calciner reactor itself rather than from the standpipe, a situation more representative of the hot reactor, then the solids would have an improved chance of being deposited because they would have a larger diameter to fall through, and therefore be at a lower velocity than previously, reducing the chance of entrainment with the exhaust gas. Further, an increased exhaust angle would also reduce the likelihood of solids transfer with the exhaust gases. Therefore, modification was made to the calciner so that the exhaust was fitted at a 90° angle to the standpipe (Figure 7-18). The modification reduced quantitative solids losses from an average of 0.46 kg per hour to 0.18 kg per hour, and there was also a visible reduction in solids movement from standpipe to exhaust. This can be explained by Bernoulli's principle (Equation 7-4), whereby an increase in fluid speed occurs simultaneously with a

decrease in pressure, experienced by the fluid on the outside corner. Although this may be balanced by a reduction in fluid speed on the inside corner, the angular acceleration experienced by the fluid causes an overall increase in speed, and thus solids loss around the smaller angle.

$$p_1 + 0.5\rho V_1^2 + \rho gh_1 = p_2 + 0.5\rho V_2^2 + \rho gh_2$$

Equation 7-4

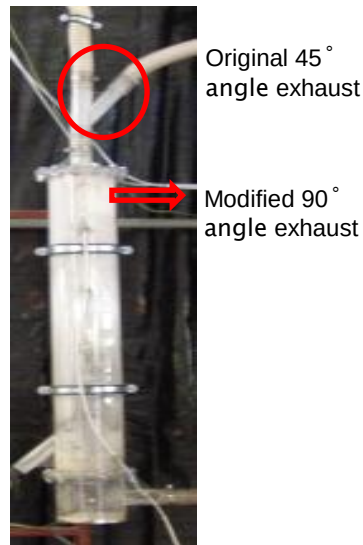


Figure 7-18 Calciner exhaust modification from original 45° angle off standpipe, to 90° angle off reactor.

7.1.7 Exhaust Diameter

The cold model was originally constructed with carbonator and calciner exhausts of 49 mm diameter. However, backflow of gas and solids was occurring from the carbonator and up the lower loop seal, implying an incorrect pressure balance. It was considered that a reduction in exhaust pipe diameter would produce a pressure restriction, thus encouraging solids to flow through the loop seal towards the carbonator, rather than in reverse. Therefore a pipe of 27 mm diameter pipe was introduced onto the original carbonator and calciner exhausts.

7.1.8 Gas Distributors

In an attempt to improve solids entrainment up the length of the carbonator, the nozzle gas distributors were changed for a gauze plate, which is though would improve entrainment due to the greater surface area over which fluidisation can

occur. Figure 7-19 compares the pressure balance up the carbonator length for nozzle and gauze distributors. Overall, there is very little change in pressure between the two distributor types, and the change that there is can be attributed to variations in air compressor flow, as shown by orifice plate differential pressures for when the pressure recordings were taken. Figure 7-20 compares gas bypassing throughout the reactor for the two distributor types. The use of the gauze distributor in the carbonator appeared to reduce gas bypassing throughout the whole cold model. This may be due to a more even distribution of gas across the carbonator, and given that the carbonator has the greatest flow, this influences the whole model. The nozzles may result in preferential flow, particularly if blocking occurs. Despite this, the gas bypassing was considered low even with the nozzles, and given that the investigation was to improve solids entrainment and there was little difference in pressure balance between the two distributors, the nozzle distributors were used for the remainder of the work.

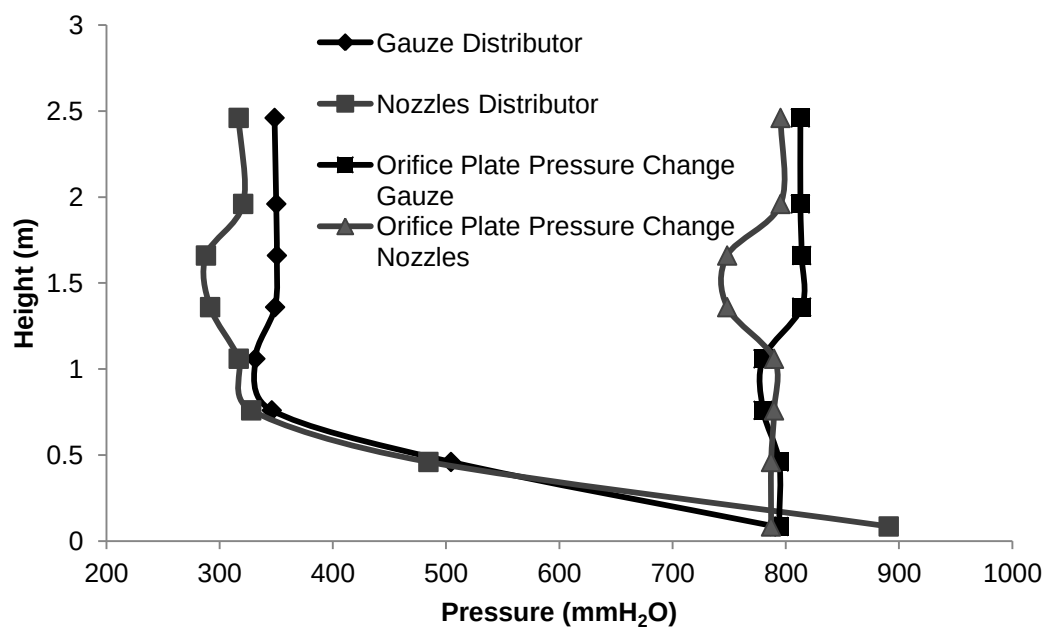


Figure 7-19 Effect of nozzle and gas distributor on carbonator pressure.

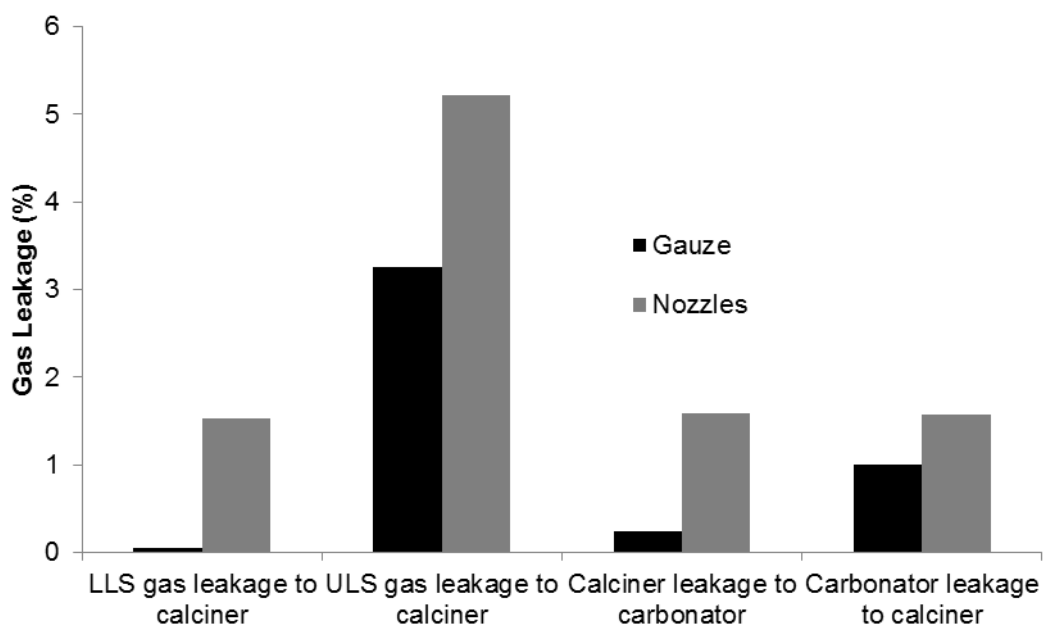


Figure 7-20 Effect of gas distributor type on gas by passing throughout the cold model.

7.1.9 Combination of Modifications

Figure 7-21 shows the effect of the combined modifications on gas bypassing throughout the cold model. Gas bypassing from the calciner to the cyclone, and also from the carbonator to the calciner appeared to increase following the modifications, albeit by a small percentage. The calciner bypassing to the cyclone may have increased as a result of minimising the exhaust pipe diameter, thereby creating a higher pressure gradient between the calciner and the cyclone. Although this situation improved the pressure profile between the calciner and the LLS, it may have had the opposite effect in terms of the calciner and the ULS, and cyclone, despite the increased sealing of the ULS, implying that the system is in a very fine state of balance with regard to pressure gradients. The increase in bypassing between the carbonator and calciner is surprising given the significant decrease in bypassing from the LLS to the calciner, considered to have the same flow path; however, the increase was only by 0.1 % and, therefore, is not considered to be of concern. This information is important for the operation of the 25 kW reactor to ensure optimum process efficiency.

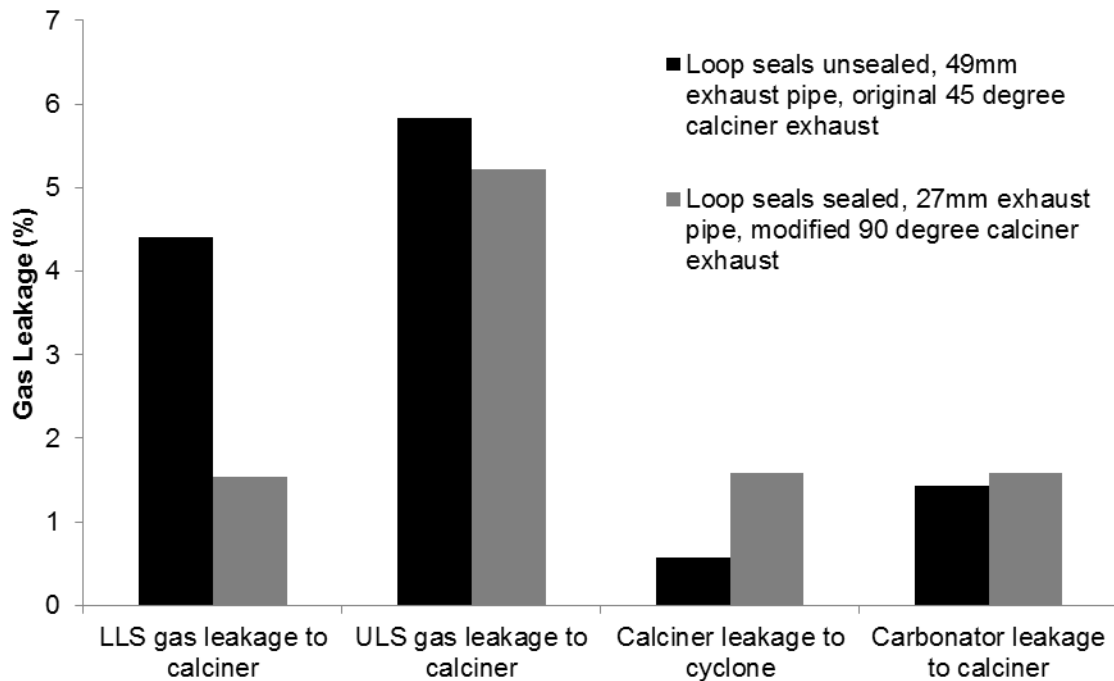


Figure 7-21 Effect of improved sealing of loop seals, on gas bypassing throughout the cold model, for gas velocities of 1.91 m/s in carbonator, calciner gas velocity of 0.23 m/s and 0.66 m/s in loop seals.

7.1.10 Pressure Profile

Figure 7-22 shows the pressure profiles of the system, before and after modifications were made to the cold model. Prior to modifications being made, it was apparent from pressure measurements taken along the length of the carbonator that solids were not reaching the top of the carbonator and hence were not being conveyed round the loop system. Pressure measurements showed higher pressures for the first metre of the reactor where slugging was visible, above which pressures decreased to an almost constant level.

Figure 7-22 demonstrates that the modifications made an improvement to the pressure profile of the reactor, and, therefore, the solids entrainment. Overall pressure throughout the system was increased as a result of the modifications, implying greater solids transfer. Further, the pressure profile for the new situation was more linear, particularly up the length of the carbonator, suggesting a more even distribution of solids. In the modified situation, the pressure measurements taken from 0.085 m and 3.36 m up the length of the carbonator were 978 mmH₂O and 532 mmH₂O respectively, compared to pressure values of 605 mmH₂O and 18 mmH₂O

for the original situation. In addition, the loop seal pressure profiles have been improved. Prior to the modifications, the pressure at the exit of both loop seals was higher than the entry pressure (30.6 and 25.9 mmH₂O for LLS exit and entry respectively, and 80.4 and 33.9 mmH₂O for ULS exit and entry respectively). Solids move from areas of high pressure to low pressure, and therefore the original situation was having a negative effect in terms of solids transfer through the loop seals, in that some solids were moving from the carbonator to the calciner in the LLS, and from the calciner to the cyclone in ULS, which is the opposite direction to which they should transfer. The modifications appear to have improved the situation, in that the pressure at the entry to both loop seals was greater than that at the exit (327.2 and 508.1 mmH₂O for LLS exit and entry respectively, and 254.6 and 317.9 mmH₂O for ULS exit and entry respectively), thus encouraging solids transfer in the appropriate direction, and also reducing gas bypassing. In addition, visual observations from the cold model confirm the improvements made as a result of the modifications, in particular the elimination of both slugging and the back flow of solids and gas from the carbonator to the calciner, as well as improved solids entrainment along the carbonator.

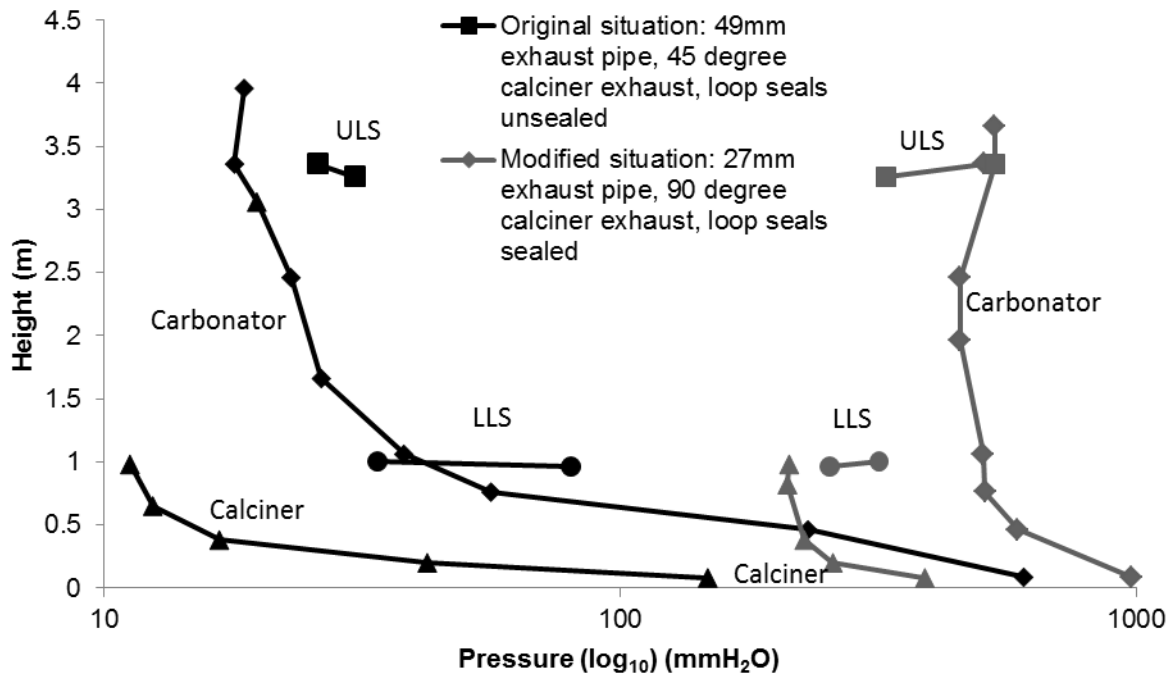


Figure 7-22 Effect of modifications to the cold model on the pressure profile of the system, where ● is lower loop seal, ◆ is carbonator, ■ is upper loop seal, and ▲ is calciner.

7.2 4. Conclusions

The cold model investigations have provided useful information on the hydrodynamics of the pilot-scale calcium-looping CO₂ capture reactor in order to identify the optimum operation conditions for the pilot scale reactor which previously remained un-operated in continuous mode. I have advanced the available literature by providing pilot scale cold model experimental results for a previously unknown system, and where possible have compared this with known data. Experimental and theoretical minimum fluidisation results have been compared for two different particle sizes of limestone, the experimental values of which compare well with literature data. The effect of attrition on U_{mf} has also been investigated by calculating U_{mf} for given reductions in particle size likely to occur as a result of attrition. Results found that an initial larger average particle size would experience a greater decrease in U_{mf} for a given reduction in particle size, and that for the two initial particle sizes calculated for, a decrease in U_{mf} of approximately 0.09 % occurs for every 5 % decrease in particle size, regardless of the original size of the particle. It is apparent that solids flux throughout the system is positively affected by increases in both

calciners and carbonators superficial gas velocities, as well as by operation of both the upper and lower loop seals. This is due to an increase in pressure created, thus improving solids transport throughout the system. Gas bypassing tests confirmed that the greatest amount of gas bypassing has the potential to occur from the lower loop seal to the calciner, particularly when loop seals are operated at high gas velocities. This work has helped determine the optimum gas velocities for the system to reduce gas bypassing: 1.91 m/s carbonator superficial gas velocity, 0.23 m/s calciner superficial gas velocity and 0.66 m/s superficial gas velocity in the loop seals, in order to achieve minimal gas bypassing in the region of 1 %. Pressure profiles have been identified and have proved useful in evaluating modifications that have been made to the cold model, and confirming that the modifications are appropriate in improving the running of the process. The implications of this work include identification of modifications that could be made to improve the general running of fluidised beds, particularly those employing loop seals to control solids transfer. Further, the work has made a contribution to knowledge with regards to understanding the operating conditions required in order to optimise the operation of the pilot scale reactor at Cranfield University. This work therefore meets the requirements of Objective 1a and 1b.

8 RESULTS AND ANALYSIS: CO₂ CAPTURE OPTIMISATION

This chapter describes the results obtained from operation, development and optimisation of the pilot scale, calcium-looping, CO₂ capture reactor at Cranfield University.

Results are presented and operational issues are highlighted. A comparison is made where possible with bench-scale work [121] [146], and other pilot scale reactors [105] [7] [295] [169], to highlight where possible engineering scale-up challenges of the calcium-looping process. In addition, results from pilot scale, continuous mode tests investigating the effects of bed inventory and SO₂ concentration on the calcium looping cycle are presented and discussed, as are results from batch tests investigating effects of additional steam and also SO₂ concentration.

The work outlined in this chapter has been presented in part at the following international conferences and summer school:

- Cotton, K. Patchigolla, J.E. Oakey, 'Effect of steam and SO₂ on pilot scale, post combustion CO₂ capture' IEAGHG 4th Network Meeting on High Temperature Solid Looping Cycles, August 2012, Beijing, China (oral presentation);
- Cotton, M. Kavosh, K. Patchigolla, J.E. Oakey, 'Calcium Looping Cycle Technology Developments at Cranfield University', IEAGHG 3rd Network Meeting on High Temperature Solid Looping Cycles, August 2011, Vienna University of Technology, Austria (oral presentation);
- Cotton, M. Kavosh, K. Patchigolla, J.E. Oakey, 'Technology Scale-Up Effects of the Calcium Looping Cycle', UKCCSC and Nottingham University EngD Summer School, July 2011, Guwahati, India (oral presentation); and
- Cotton, K. Patchigolla, J.E. Oakey, 'Engineering Issues for Carbon Capture via Calcium Looping Cycle in a 25kW Reactor', 5th International Conference

on Clean Coal Technologies, CCT2011, May 2011, Zaragoza, Spain (oral presentation and conference proceedings).

The following journal paper on sequential capture of CO₂ and SO₂ has been published during the PhD, and is peripheral to the work carried out for this thesis:

- Chen, H., Zhao, Z., Huang, X., Patchigolla, K., Cotton, A., Oakey, J.E. (2012) 'Novel optimized process for utilization of CaO-based sorbent for capturing CO₂ and SO₂ sequentially' *Energy Fuels*, 2012, 26: (9) 5596 – 5603.

8.1 Process Optimisation

In this study, optimisation of the pilot scale reactor has been an important factor to consider, in order to enhance the capture efficiency and identify scale-up issues. A number of different factors have been explored throughout the work in order to optimise the % capture efficiency of the rig, including particle size distribution (PSD) and temperature. Figure 8-1a shows typical CO₂ flow rates into and out of the carbonator reactor, with Figure 8-1b providing the % CO₂ capture achieved towards the end of the testing regime, following extensive rig modifications. CO₂ capture % was calculated using Equation 6-2.

Figure 8-2 shows the results from another CO₂ capture test, with annotations defining reasons for changes in the CO₂ capture % for the test duration. It can be seen that burner failure occurred numerous times throughout the test, and in doing so affected the CO₂ capture efficiency. The % capture was however restored to the original value once the burner had been relit. The effect of the enhanced loop seal operation is also apparent, in that increasing the flow rate and therefore solids transfer between the reactors acted to increase the % capture. This is likely due to an increased calcium looping ratio, providing a greater amount of solids per unit time, allowing a greater % of CO₂ to be captured.

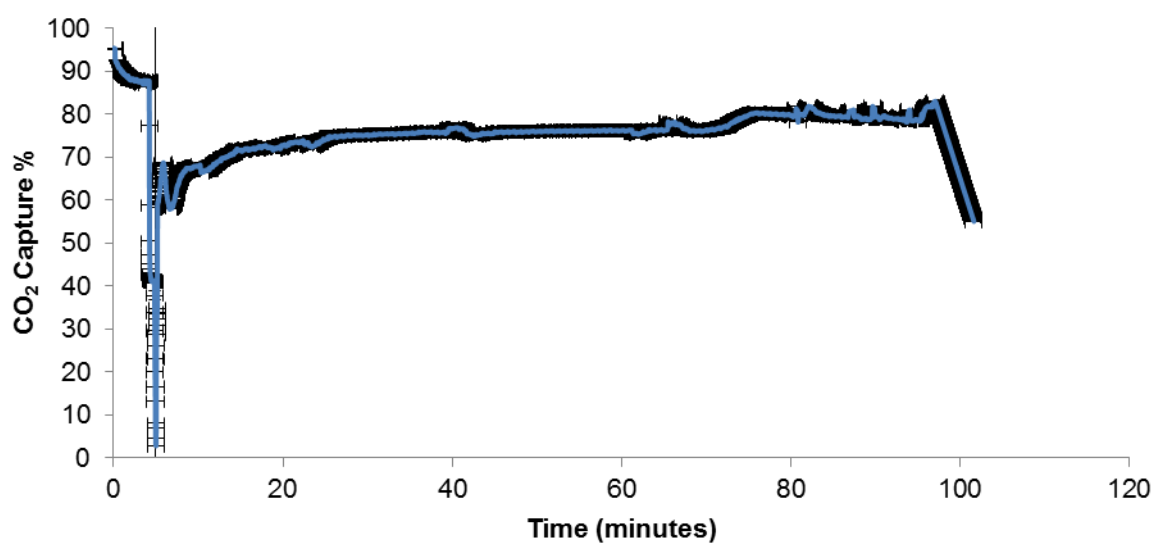
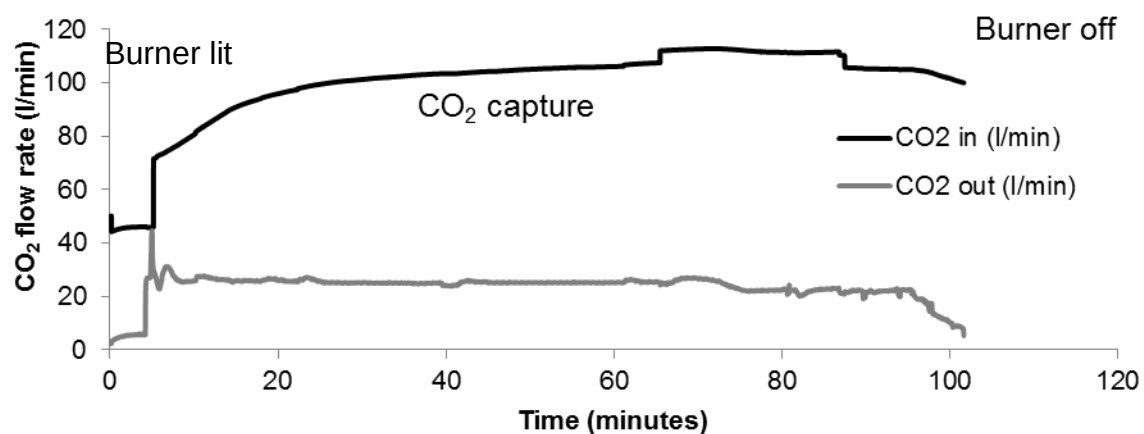


Figure 8-1 a) Typical CO₂ flow rates into and out of the carbonator reactor, and b) associated CO₂ capture % based on known CO₂ input and measured output. Error bars are shown based on variance of results. Standard error bars are provided on graph.

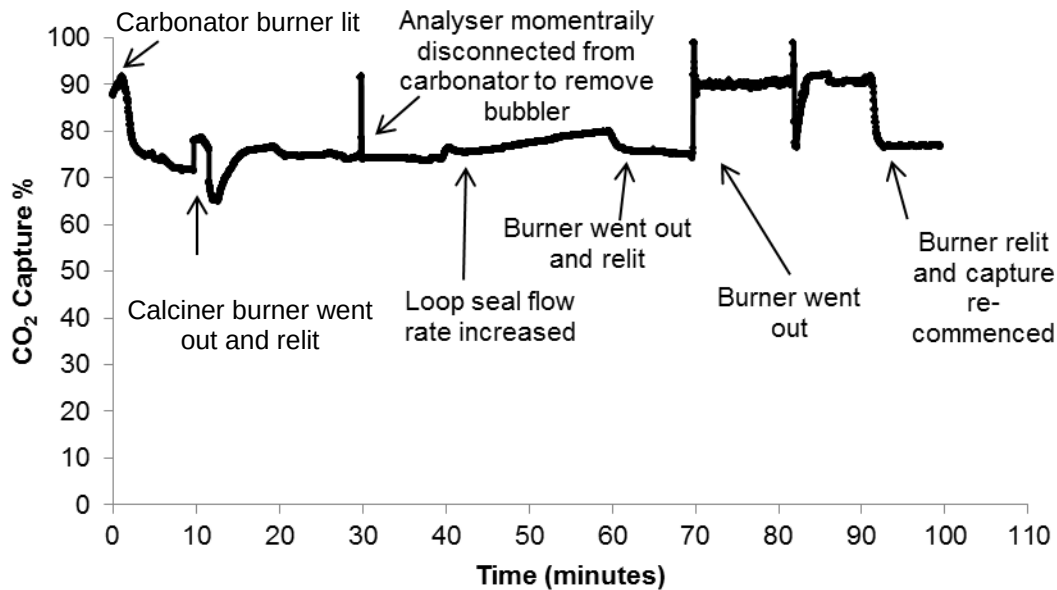


Figure 8-2 CO₂ capture test with burner and loop seal effects.

8.1.1 Carbonator Pressure

The carbonator hydrostatic pressure was measured during batch and continuous looping cycle experiments to confirm that solids were being entrained. Figure 8-3 shows that the carbonator pressure for the batch experiment was very similar to that of the cold model for the same bed inventory of 4.5 kg. This implies that the use of the cold model in predicting the hydrodynamics of hot reactor fluidised bed systems is appropriate. Data is also shown for a continuous looping cycle test with a bed inventory of 13 kg, showing a higher pressure across the carbonator length compared to the batch test. This is to be expected due to the higher bed inventory and thus greater mass of particles being entrained. Also, although in theory there is no gaseous exchange between the reactors, gas input from the lower loop seal into the carbonator during continuous testing may have contributed to some extent to the higher pressures observed.

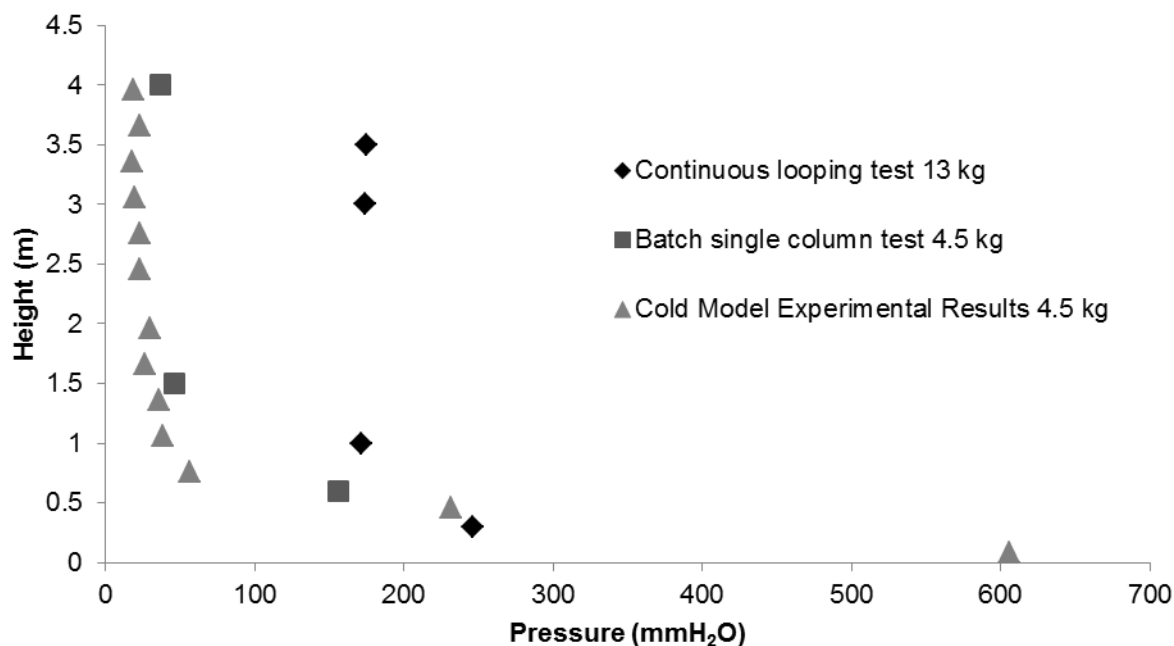


Figure 8-3 Measured carbonator pressure for a continuous and batch test, compared with cold model data.

8.1.2 Effect of particle size

Single column batch experiments were run in the reactor to investigate the effect of particle size (and thus surface area) on % CO₂ capture. Particle size distributions (PSD) of <125 μ m, 125-250 μ m, and >250 μ m were investigated. Figure 8-4 shows that the particles of 125-250 μ m had the greatest CO₂ capture. It was expected that the smallest PSD would have the greatest % capture because of the increased surface area, but it was apparent from inspection of the reactor viewport during the tests that a significant fraction of the sorbent of PSD <125 μ m had agglomerated and stuck to the reactor walls, and therefore the bed was not fluidising correctly. Hence it is clear that a compromise between high surface to volume ratios, and the risk of potential agglomeration effects is required. This work is also in agreement with bench-scale batch experimental work carried out by Kavosh (2012) [121] who tested the effect of PSD on CO₂ capture with Longcliffe SP52 limestone, with PSD's of < 125 μ m, 125-250 μ m and >800 μ m, and concluded that a PSD of 125-250 μ m provided the optimum CaCO₃ and CaO conversion results. As a result, a PSD of 125-250 μ m limestone was used for the first calcium looping tests.

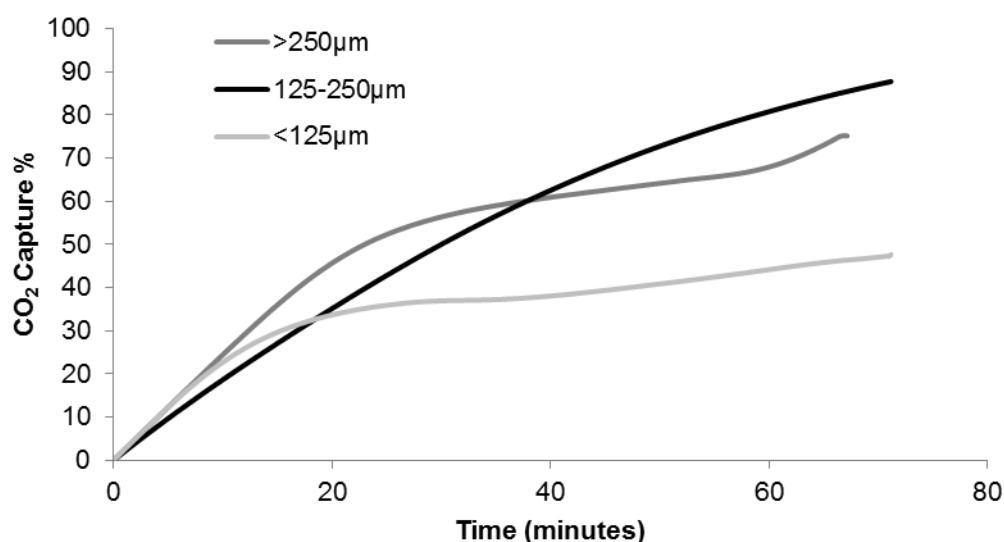


Figure 8-4 Effect of particle size distribution on CO₂ capture % carried out in pilot scale, batch single column, carbonation experiments carried out as part of this study.

In order to further improve CO₂ capture efficiency in the reactor, a smaller PSD of 90-125 µm was also later tested, results for which are provided as Figure 8-5, and show a marginally improved % capture when compared to a PSD of 125-250 µm. The % CO₂ capture was improved with the smaller PSD compared to the larger PSD of 125-250 µm. This implies that the increased surface to volume ratio made an improvement, but the particle size was large enough to prevent agglomeration of the whole bed. For the PSD initially tested of <125 µm, this included particles of very small diameter, some of which were therefore likely to have been be of Geldart's Group C, i.e. cohesive and difficult to fluidise [296]. Limestone of PSD 125-250 µm however falls within Geldart's Group A, and very close to the boundary of Group B, of which Group A is known to fluidise well, with smooth fluidisation at low gas velocities, and controlled bubbling with small bubbles at higher gas velocities [296]. Therefore, although the particles of 90-250 µm had a slightly larger surface area compared to particles <125 µm, the powder properties are preferential for fluidisation, and therefore reaction with CO₂.

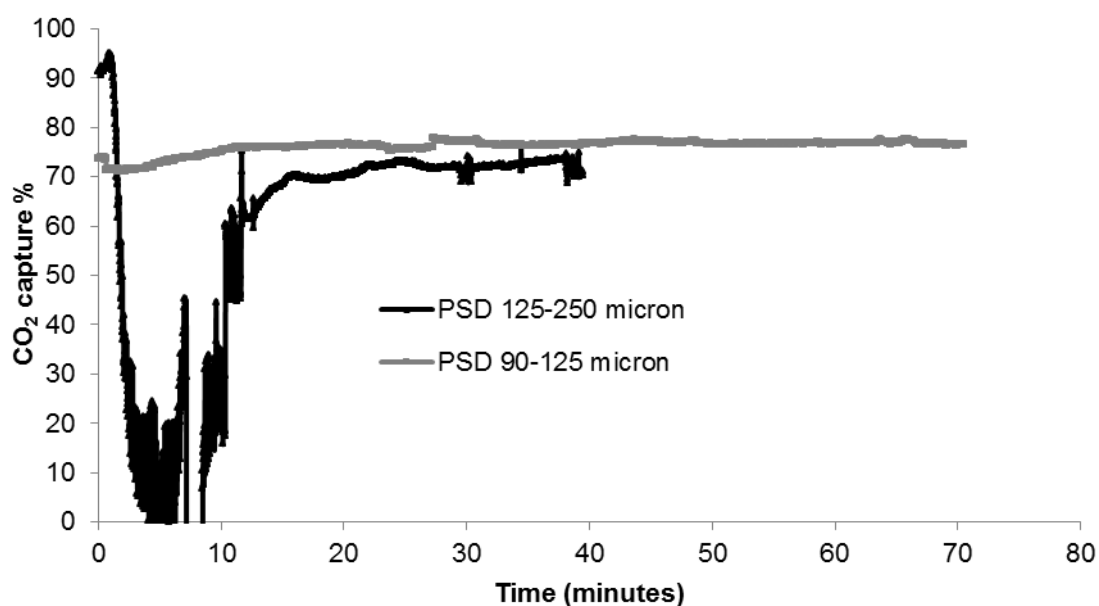


Figure 8-5 Comparison of CO₂ capture capacity of 125-250 μ m and 90-125 μ m PSD limestone.

8.1.3 Effect of temperature

Initial tests were based on identifying optimum reactor conditions to achieve maximum CO₂ capture results. First tests were aimed at achieving steady state operation at the desired carbonation temperature of approximately 650°C, through varying the use of trace electric heating and also the air-fired natural-gas burner. Figure 8-6 shows CO₂ capture results from these initial tests, identifying that a carbonator temperature of 650-700°C was preferential over temperatures of 550-600°C.

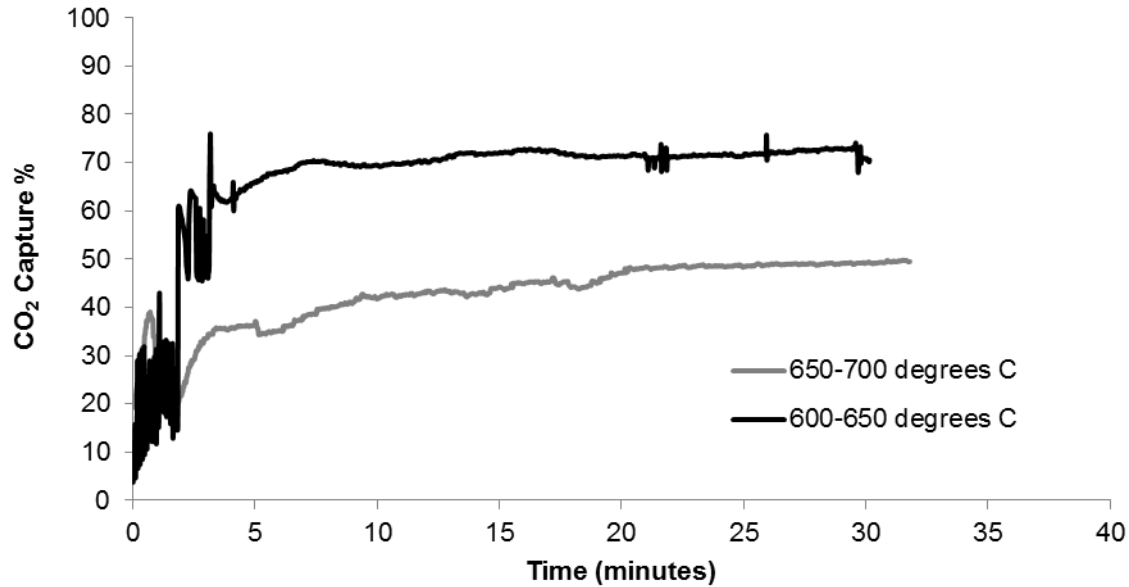


Figure 8-6 Initial tests aimed at achieving appropriate carbonator temperatures, showing effect on CO₂ capture capacity.

The effect of carbonation temperature was later investigated at approximately 650°C and 600°C. The majority of work in the literature states the optimum temperature for carbonation at 650°C but on calculating partial pressures of CO₂ for varying the experimental conditions, it was decided that a lower temperature be investigated. Figure 8-6 shows that decreasing carbonation temperature by approximately 50°C had a positive effect on increasing % capture in the reactor, from an optimum capture of approximately 60 % for a carbonator temperature of 650-700°C, to approximately 70 % capture for a carbonator temperature of 600-650°C. This is primarily due to the effect of partial pressure of CO₂ on the carbonation reaction. Carbonation is an exothermic reaction, and is determined by temperature, which in turn affects the partial pressure of the system. By reducing the temperature in the carbonator, the partial pressure required for carbonation was also reduced, thereby driving forward the formation of CaCO₃ from CaO and CO₂. Similar findings were made by Lu *et al.*, 2008 [8] who identified that decreasing carbonator bed temperature below 650°C increased % capture, with 580 - 600°C being the optimum temperature with a CO₂ % capture of 98 %. This was explained by an improvement in thermodynamics caused by the temperature difference across the length of the bed, whereby a higher temperature was present at the bottom of the bed than at the top of the bed. This too is apparent in the reactor in question, where a higher

temperature is present in the lower 0.5 m of the bed, due to the proximity of the natural-gas fired burner. Despite the presence of trace heating, the small difference in temperature along the carbonator length remains. A similar result was found by Charitos *et al.*, 2010 [7] in a pilot scale 10kW reactor. They identified an optimum capture efficiency of 93 % for a carbonator temperature of 625 °C, which decreased to approximately 90 % and 77 % capture at temperatures of approximately 655 and 705 °C respectively. This again is explained in terms of equilibrium, in that increasing carbonator temperature increases equilibrium CO₂ concentration, causing equilibrium capture efficiency to decrease. This is described by Equation 3-6 [109].

Bench scale work on carbonation was carried out at 650 °C and 700°C (Figure 8-7) for sorbents that had undergone calcination at 850 and 950°C respectively [121]. It is apparent that a lower carbonation temperature resulted in higher CaO conversion over a shorter period of time, implying that the lower carbonation temperature of 650°C is preferential in this case. However, no further results or discussion with regard to this are provided, including at temperatures below 650 °C, and the effect of a lower calcination temperature on the improved carbonation result may be an influencing factor in the improved result. Further bench scale TGA work carried out by Hughes *et al.*, 2009 [297] found that carbonation temperatures below 650°C resulted in reaction rates that were too low, and instead carbonation temperatures of between 700 - 740°C were deemed preferential. This difference in optimum temperature highlights a key difference between bench scale and pilot scale work in terms of optimising the CO₂ capture process.

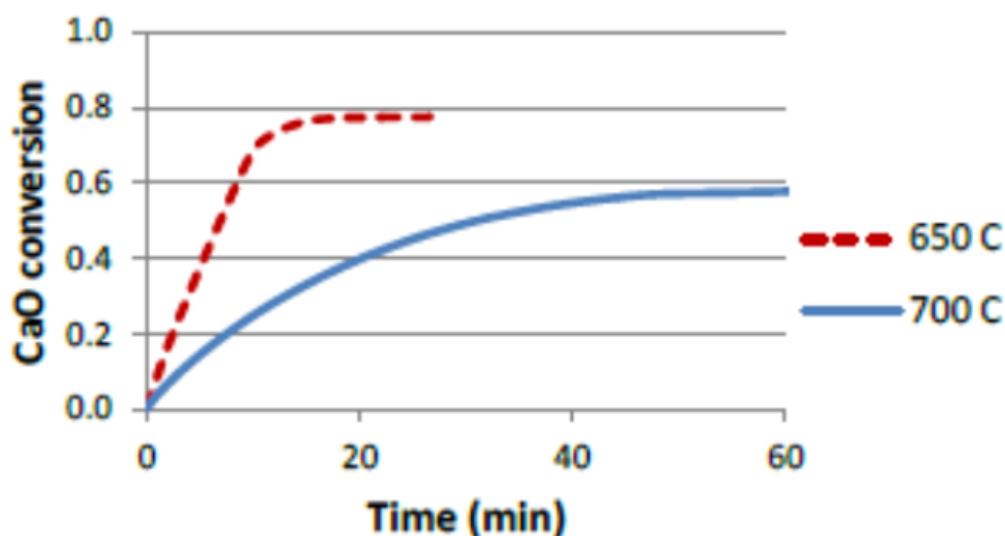


Figure 8-7 Effect of carbonation temperature on CaO conversion in a bench scale reactor [121].

8.1.4 Effect of bed inventory

The effect of bed inventory on CO₂ capture efficiency is shown in Figure 8-8. Initially, lower quantities of sorbent were used for testing in the reactor, but over time, this was gradually increased to improve the space time (CaO inventory per molar flow of CO₂ in the carbonation reaction) [6], and in turn the % capture efficiency.

It is apparent that increasing bed inventory had a strong influence in increasing the capture efficiency of the reactor, as particularly seen for 13 kg bed inventory, with a larger bed inventory resulting in a higher CO₂ capture %. There appears to be little difference between the % capture for bed inventories of 4.5 and 6 kg, probably because the ratio of moles of CaO to moles of CO₂ in the carbonator was very similar for the two bed inventories. In other pilot scale work, it has been noted that insufficient total inventory of solids in the riser can lead to lower CO₂ capture efficiencies and in turn low solids circulation rates, a situation to be avoided to obtain optimum CO₂ capture levels [295] [298].

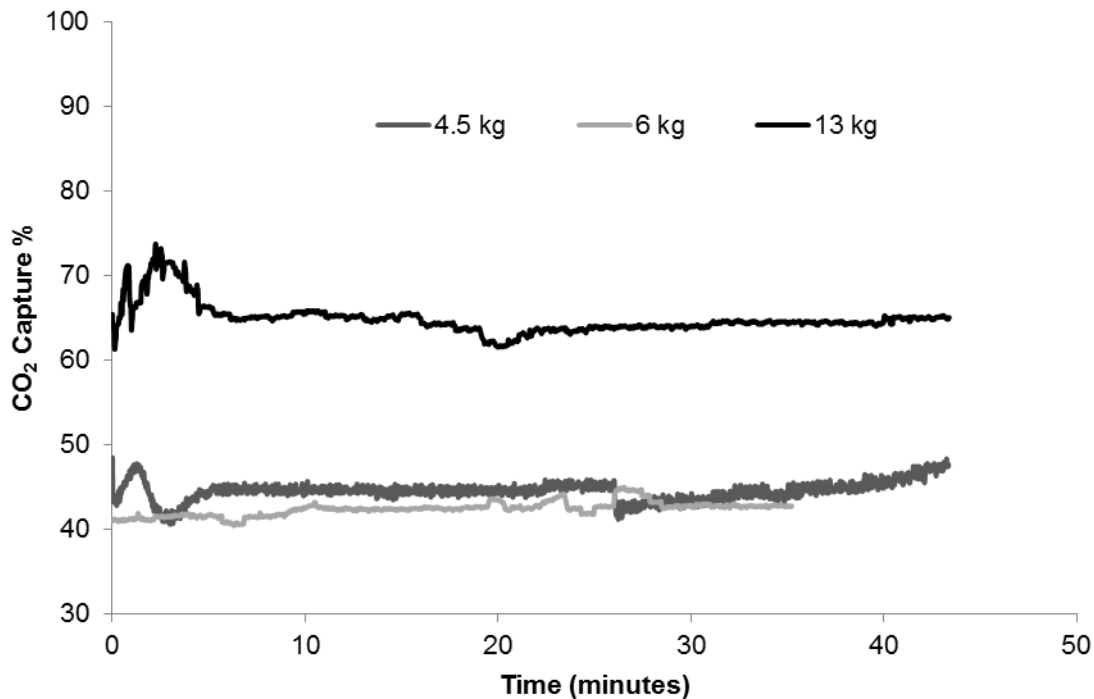


Figure 8-8 Effect of bed inventory on % CO₂ capture efficiency, for bed inventory of 4.5 kg, 6 kg and 13 kg.

8.1.5 Calciner Gas Distributors

The gas distributors (Figure 6-4b) of the calciner frequently became blocked, a phenomenon not observed to the same extent in the carbonator considered due to higher temperatures in the calciner and therefore increased sintering and agglomeration. In addition at the start of each test, solids were added to, and subsequently calcined in the calciner, before then being transferred to the carbonator via the loop seal, meaning that for the start of each test at least, the majority of the solids were present in the calciner and therefore had more opportunity for entering the plenum chamber, in the process known as ‘weeping’. This was also observed in the cold model when there was a sudden stop in the gas flow, for example if the burner should go out, resulting in a decrease in pressure across the distributor, allowing solids to fall through the nozzles.

If the gas distributors became partially blocked, this increased the pressure within the calciner plenum, making it increasingly difficult for the burners to stay lit. Figure 8-9 shows the decrease in plenum pressure as each gas distributor is unblocked, providing evidence that blockage of the nozzles was causing an increase in pressure. In order to account for future blockages, a valve was fitted to the calciner

plenum, thereby decreasing the plenum pressure and allowing the calciner burner to be lit even if some agglomeration of solids around the gas distributors did occur. Once the calciner burner was lit, the valve was then closed to allow testing as normal. Therefore the introduction of the valve greatly improved the reliability of the burner and in turn allowed longer periods of steady state testing to take place. Although this may not be such an issue in industry, this is a factor which has affected this pilot scale work, albeit that it is unlikely to affect smaller scale work due to the lack of a requirement for a burner.

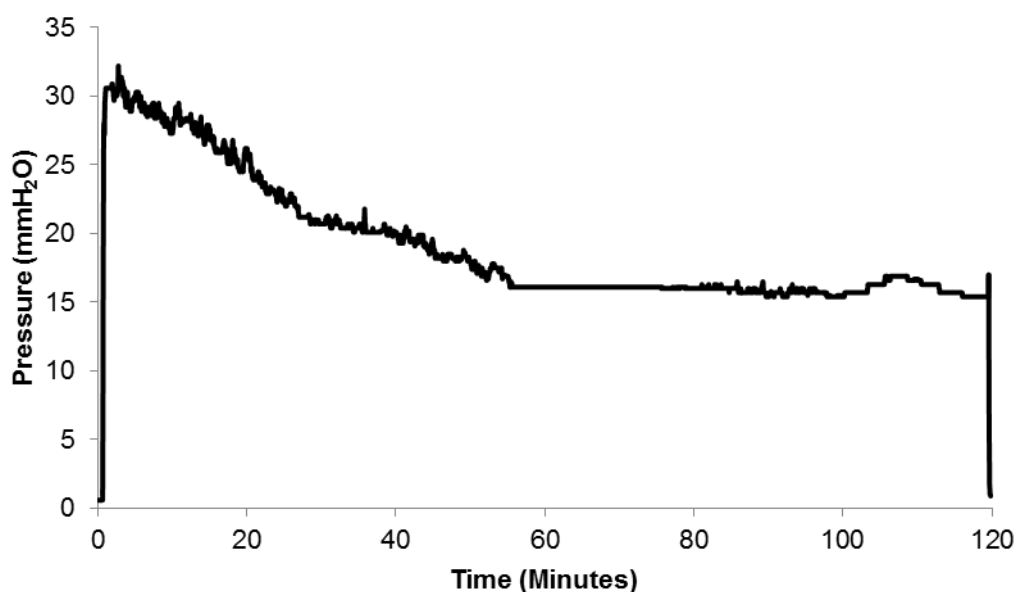


Figure 8-9 Decrease in plenum pressure as calciner gas distributors are individually unblocked.

8.1.6 Lower Loop Seal Standpipe Blockage

Testing with additional steam in the calciner was attempted for looping cycle tests. However, all such tests resulted in a blockage in the standpipe leading from the calciner to the lower loop seal (Figure 8-10a). This is considered to be due to insufficient temperatures in the standpipe, causing formation of Ca(OH)_2 , which is known to decompose to CaO above approximately 450°C , suggesting temperatures across the lower loop seal and its standpipes need to be maintained above this temperature. Images and XRD analysis of the solids causing the blockage are shown in Figure 8-10, with XRD analysis Figure 8-10b confirming the presence of Ca(OH)_2 in the solid sample.

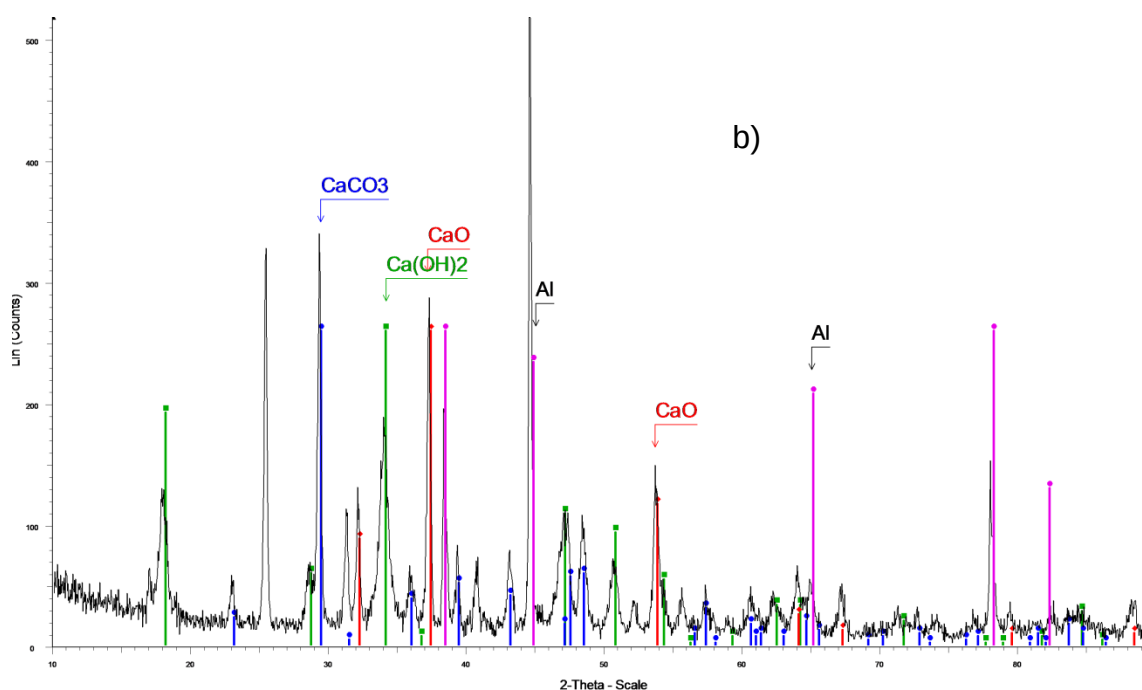


Figure 8-10 a) Image of solid causing LLS blockage; b) XRD analysis of solid causing blockage, confirming presence of Ca(OH)_2 shown in green and identified on figure.

Figure 8-11a shows pressure across the lower loop seal before the blockage was removed, indicating that pressure readings at both the LLS entry and exit were minimal at 3.3 and 1.0 mmH₂O respectively when calciner gas was flowing. After the blockage removed, higher pressure readings were recorded at the LLS, with higher readings at the entry than the exit (7 and 3.9 mmH₂O respectively) as would be

expected, implying the blockage was removed. Similarly, Figure 8-11b shows flow rates through the carbonator and calciner orifice plates before and after removal of the standpipe blockage. Before the blockage was removed, gas flow added to the carbonator was only recorded at the carbonator orifice plate. After the blockage was removed, flow added to the carbonator was recorded at both the carbonator and calciner orifice plates in almost equal amounts, as the LLS was then clear allowing gas flow through to the calciner.

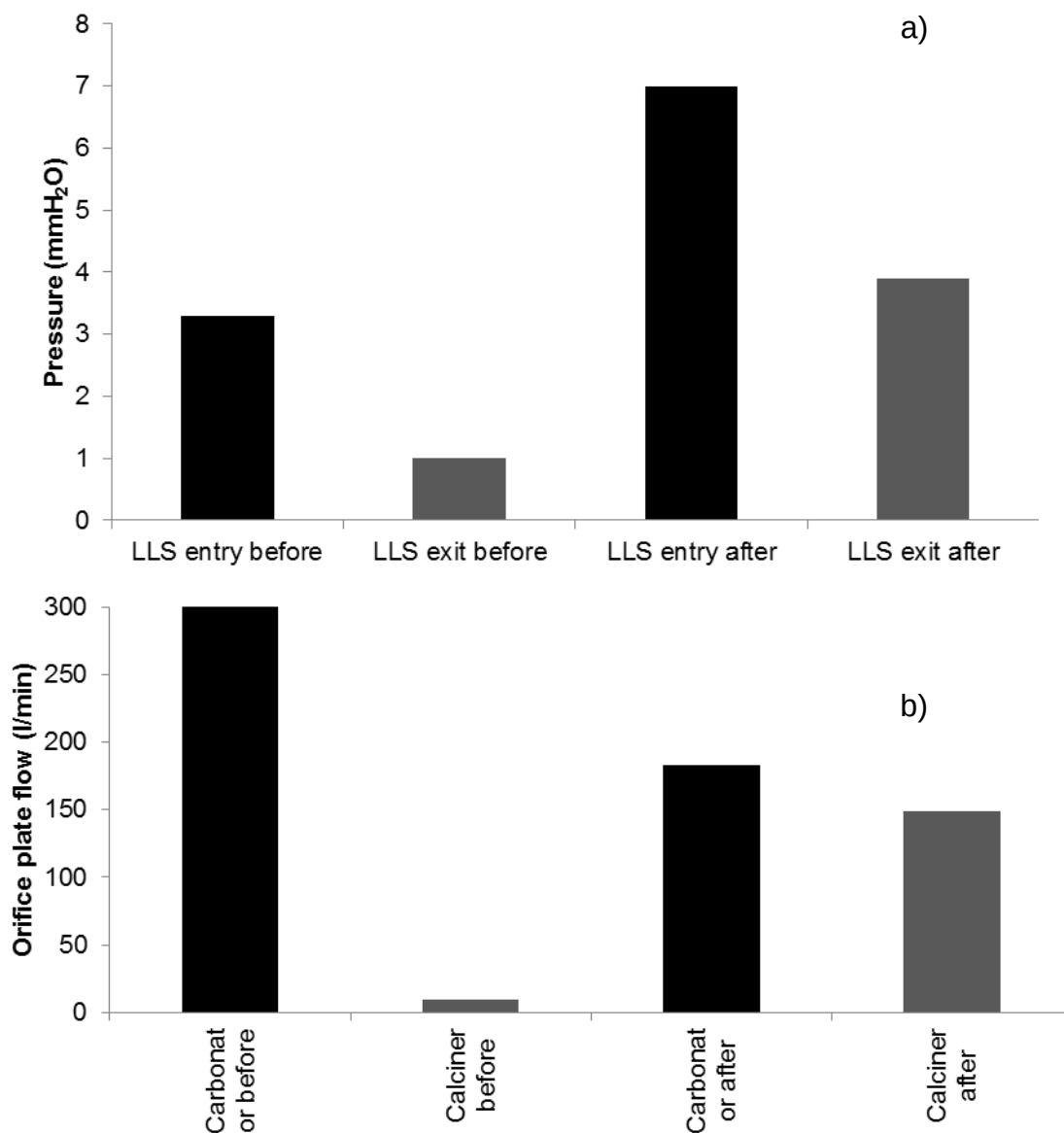


Figure 8-11 a) Lower loop seal entry and exit pressures for calciner gas flow, before and after LLS standpipe blockage was removed. Note different y axis values and units between graphs.

Further, a 90° angle bend in the calciner exhaust proved problematic when attempting to test with additional steam in the calciner, due to a build-up of solids at this point in the exhaust (Figure 8-12). The exhaust was not trace heated, and therefore it is likely that condensation of steam carrying fine particles resulted in the formation of 'putty-like' $\text{Ca}(\text{OH})_2$ blocking the exhaust bend. This caused an increase in pressure in the calciner, and resulted in the calciner burner being unable to light. From this work, it was recommended that a cyclone should be fitted to the calciner exhaust to remove particulate matter, and the 90° angle be removed from the exhaust to prevent particulate build up.



Figure 8-12 Calciner exhaust 90° angle bend blockage during attempted steam tests.

8.1.7 Further Reactor Modifications

In order to try and encourage solids transfer through loop seals, several modifications were made. These included the addition of 'air shakers', which were fitted to the upper and lower loop seal, and created a vibration across the loop seal, which it was intended would enhance solids transfer. Concern regarding the decrease in temperature across the lower loop seal, due to lack of trace heating at this location on the reactor, led to the introduction of heating elements to increase the temperature of gas to the LLS. These were fitted at the entry location for the LLS fluidising gas, and heated fluidisation gas on entry to the loop seal, in a bid to raise the LLS temperature. Figure 8-13 shows the increase in LLS temperature with the addition of the heated elements. A summary of the key reactor and process modifications made throughout the duration of the testing period is provided as Table 8-1, and the improved % CO_2 capture achieved as a result of the modifications is provided in Figure 8-14. The results show that as a result of the physical and

operational modifications made to the reactor, the % CO₂ capture increased from approximately 35 % capture for Test 2, to close to 80 % capture for Test 9. This is as a result of improved thermodynamics in terms of carbonator and loop seal gas temperatures, improved solids circulation rate, and improved space time, as well as increasing sorbent surface area by using a smaller PSD.

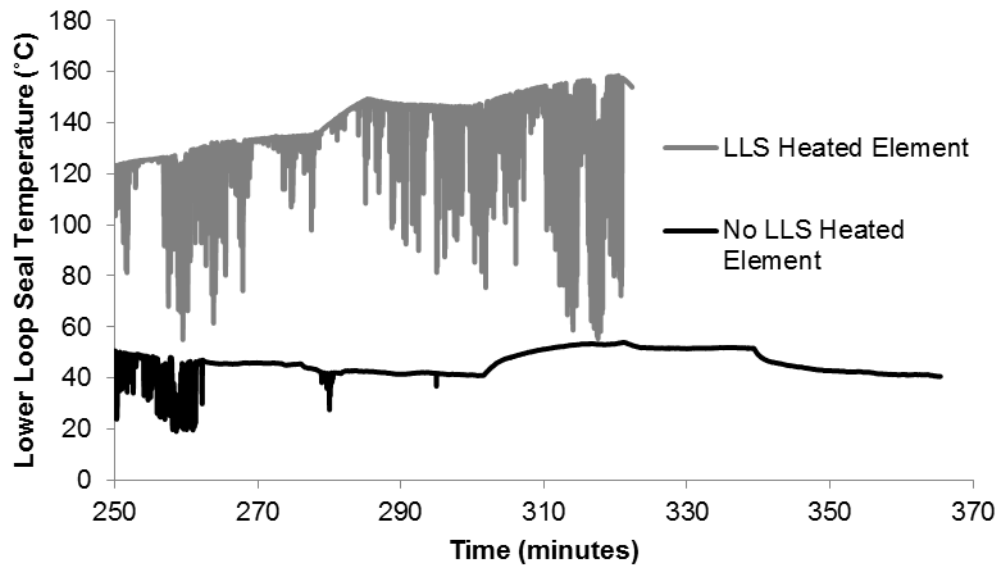


Figure 8-13 Improved lower loop seal temperature as a result heated element additions.

Table 8-1 Test conditions and modifications made in a bid to improve % CO₂ capture efficiency.

Test	Operating Conditions	Value
2	Carbonation temperature	550-600°C
	Sorbent mass in reactor	4.5 kg
	Sorbent PSD	125-250 µm
	Other amendment	Increased trace heating temperature and % CH ₄ in burner
3	Carbonation temperature	650-700°C
	Sorbent mass	4.5 kg
	Sorbent PSD	125-250 µm
	Other amendment	Increased trace heating and CH ₄ flow rate to increase temperature
7	Carbonation temperature	650-700 °C
	Sorbent mass	13 kg
	Sorbent PSD	125-250 µm
	Other amendment	Air shakers added to loop seals to encourage solids transfer
9	Carbonation temperature	600-650°C
	Sorbent mass	13 kg
	Sorbent PSD	106-125 µm
	Other amendment	Heated elements added to lower loop seal to increase temperature

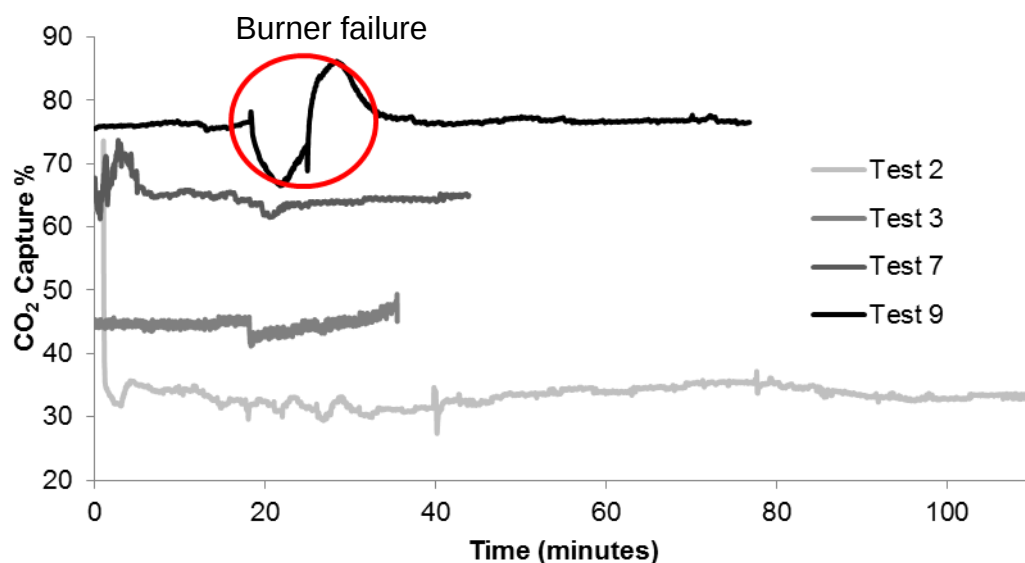


Figure 8-14 Effect of reactor and process modifications on improved CO₂ capture efficiency made over a series of tests, with test conditions and modifications outlined in Table 8-1.

8.1.8 Attrition

The effects of attrition are well documented as one of the primary issues regarding the calcium looping cycle. There is information in the literature looking at how attrition influences PSD and therefore bed inventory, but there appears to be minimal information available regarding how bed inventory may influence attrition. Figure 8-15 shows the difference in particle attrition for a single column test and a looping test, both with a bed inventory of 4.5 kg CaCO₃. The results identify that for the same superficial velocity, particles in the looping cycle test experienced a greater extent of attrition than particles sampled from the single column test. This is likely to be due to the increased forces exerted on the particles as they are cycled in the looping test, from both other particles and reactor walls. Barrett-Joyner-Halenda (BJH) pore volume analysis of the sorbent samples taken from the two tests is provided as Figure 8-16 which shows that the sorbent which underwent looping had a smaller pore volume for a given mean pore diameter. This is almost certainly due the effects of sintering experienced by the sorbent at higher temperatures in the calciner, which were not experienced in the single column batch tests. The increased level of sintering may have led to an increase in the friability of the sorbent due reduced

porosity, and in turn, enhanced attrition. Another more plausible explanation may be that the sorbent that underwent looping was exposed to both higher temperatures, and increased forces, resulting in increased sintering and attrition respectively. This highlights the importance of pilot scale, realistic tests in scaling up the technology for industry.

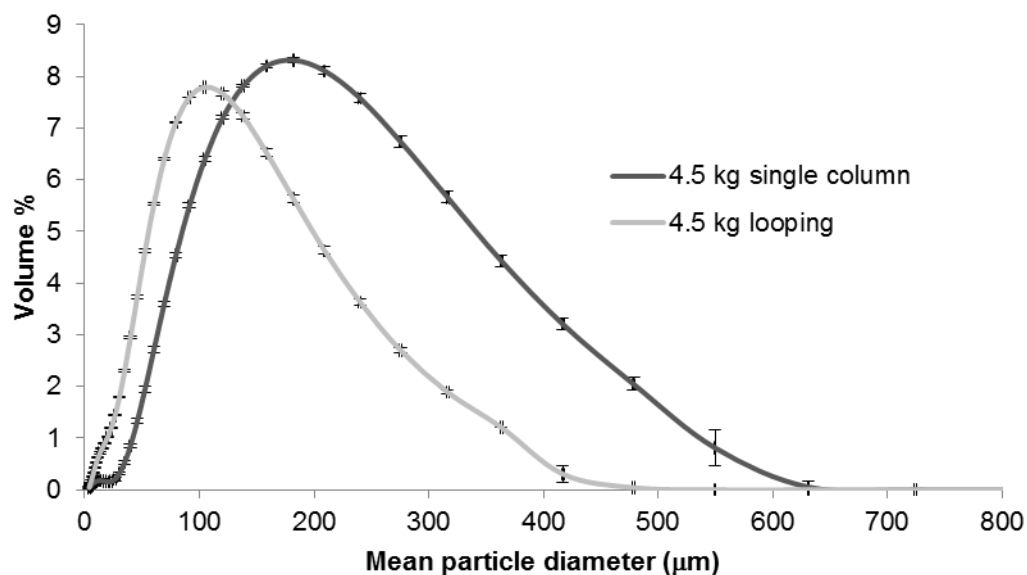


Figure 8-15 Comparison between attrition effects of single column and looping cycle tests with 4.5 kg bed inventory. Standard error bars are present on both curves.

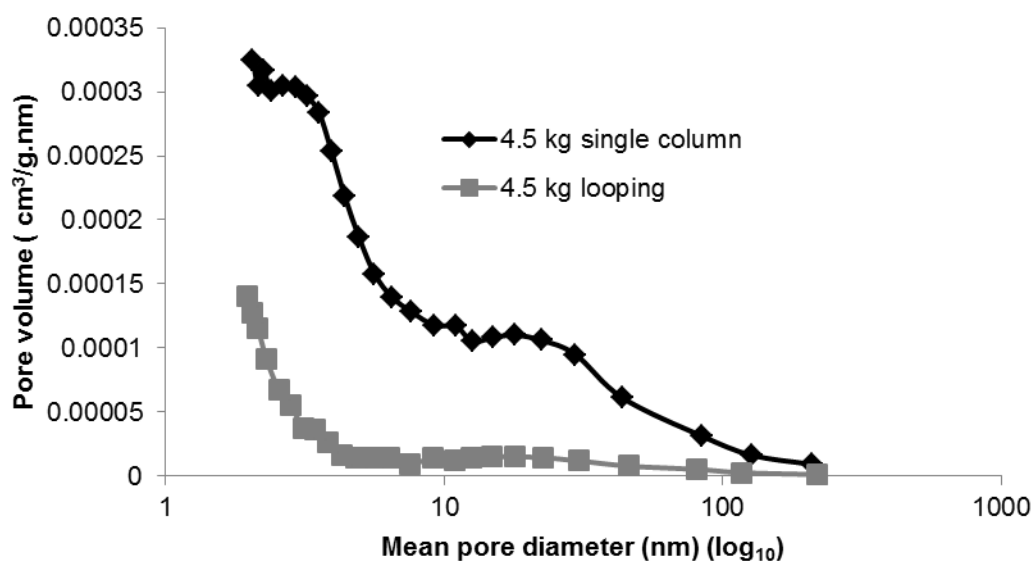


Figure 8-16 Comparison of BJH analysis of samples taken from carbonator after single column and looping cycle experiment.

Figure 8-17 shows the effect of bed inventory on particle attrition. All tests were run for approximately two hours, and samples were taken from the carbonator at the end of each test. It is apparent that samples from the bed inventory of 4.5 kg experienced the greatest amount of attrition. By contrast it appears that the largest bed inventory of 13 kg resulted in particles experiencing the least attrition. This result is unexpected given the same fluidising velocities, as given a greater number of particles present in the reactor, an increase in collisions and therefore attrition would be expected. However, it may be that an increased bed mass resulted in increased sintering of the particles, resulting in a larger mean particle diameter (Figure 8-17). SEM images (Figure 8-18) show reduced porosity on the sorbent samples taken after the test with 13 kg bed inventory, when compared with samples taken from tests run with lower bed inventories. This suggests a greater extent of sintering. BJH analysis of the samples shown as Figure 8-19, shows that samples from the test run with 13 kg bed inventory had the smallest pore diameter and volume, whereas those from the test run with 4.5 kg bed inventory had the largest pore diameter and volume. The larger particle size but smaller pore size achieved by particles in the 13 kg bed inventory suggests that greater sintering was experienced with a larger bed inventory. Although changes in bed inventory will not be of particular concern in industry, due to the large masses required to treat large through flows of flue gas, this work highlights a key issue observed on scale up of the technology from bench

scale to pilot scale. Another reason for the increase in particle diameter in the sorbents sampled after testing, may be due to erosion of the reactor, resulting in small pieces of the reactor within the sorbent sample. This is explained in further detail in section 9.3 but due to the high temperature and high steam conditions, erosion of the reactor to some extent was considered likely, supported by the presence of black particles in the sorbent samples. Although every effort was made to remove these ‘black’ particles prior to sorbent PSD analysis, it is inevitable that some will have remained and been included within the analysis. These may therefore account for the larger particle diameters observed after testing, that weren’t observed prior to.

The attrition rate and extent of attrition based on modification to Vaux’s equations made by Jia *et al.*, 2007 [132] are provided in Table 8-2, along with a comparison of rate and extent values calculated by the same author. Similarly, Jia *et al.*, 2007 [132] concluded that severe fragmentation of limestone occurred in the first one or two calcination cycles, after which attrition rates were more typical of the forces exerted upon such particles. The extent of attrition varied considerably between the different limestone, with NISCO (US) and Tamuin (Mexican) limestone experiencing higher attrition rates than the Canadian Cadomin or Havelock limestone.

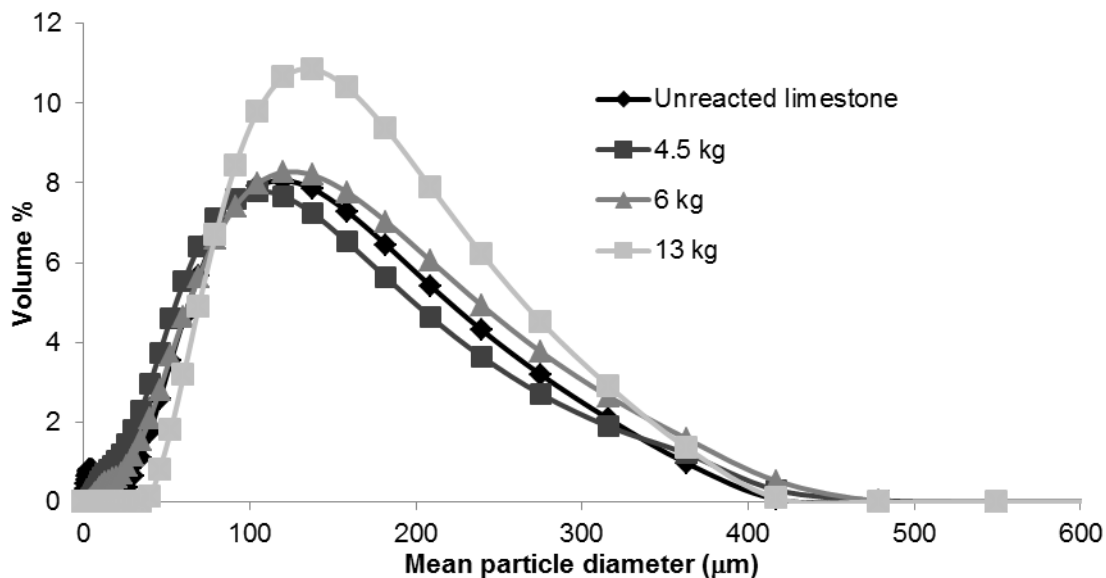


Figure 8-17 Effect of bed inventory on extent of attrition after looping cycle tests.

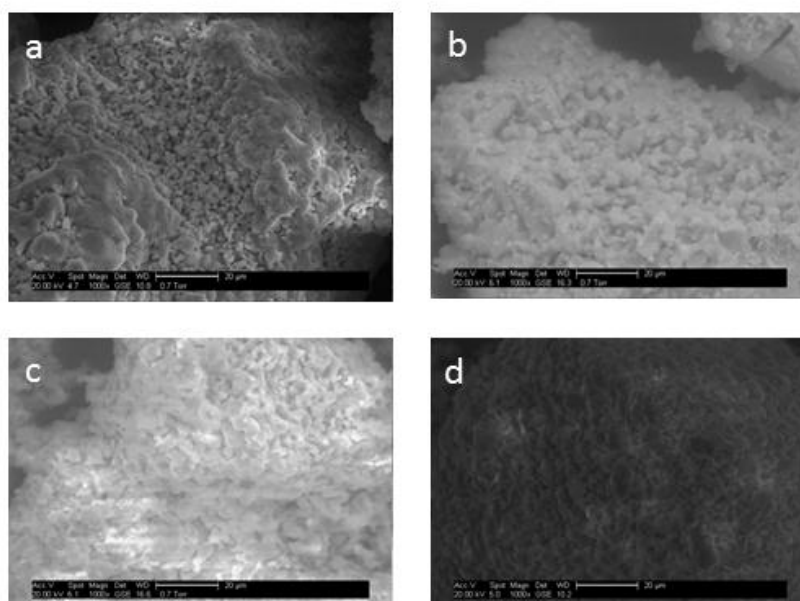


Figure 8-18 SEM analysis of samples taken from carbonator after each test: a) 13 kg bed inventory; b) 6 kg bed inventory; c) 4.5 kg bed inventory; d) unreacted limestone. Magnification 1000x. Average test time 120 minutes.

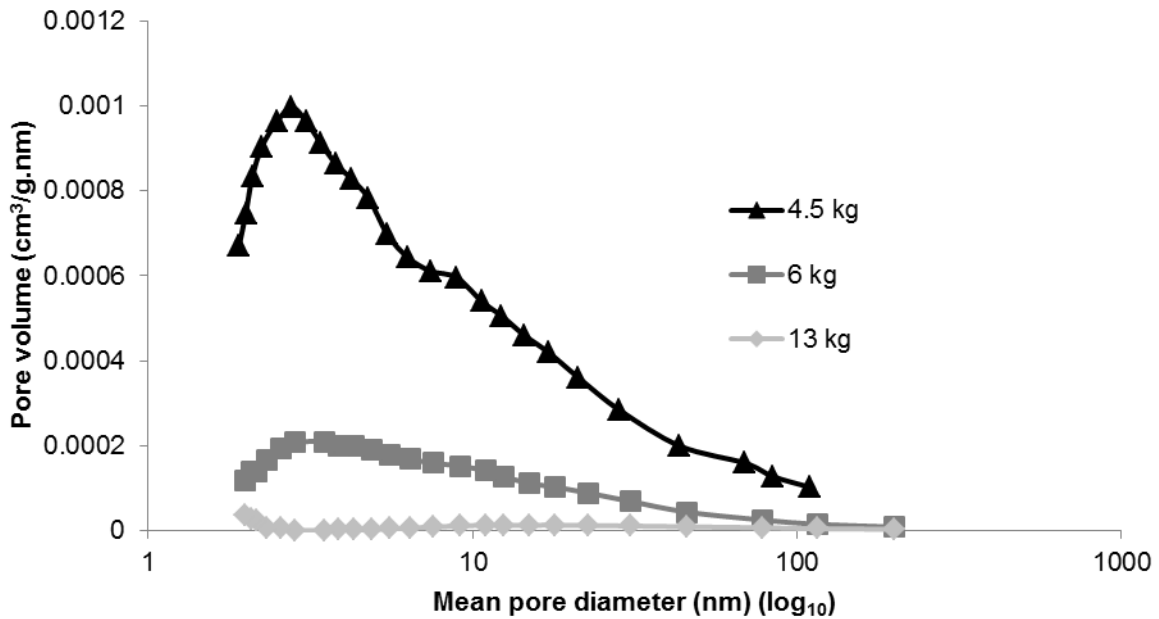


Figure 8-19 Comparison of BJH analysis of sorbent samples taken from tests run with increasing bed inventory.

Table 8-2 Comparison of attrition rate and extent of attrition for Longcliffe limestone, compared with work by Jia *et al.*, 2007 [132].

Limestone		Average rate of attrition, R_a (1/h)	Extent of attrition, A (%)
Longcliffe (this study)	4.5 kg	0.09	5.5
	6 kg	+0.13	+8.4
	13 kg	+0.34	+23
Tamuin		0.032	14.60
TP1		0.002 - 0.004	1.29 - 2.04
TP2		0.005 - 0.008	2.33 - 3.99
NISCO		0.087	39.47
Cadomin		0.013	5.86

+ represents decrease in attrition and increase in particle diameter.

Montagnaro *et al.*, 2009 [299] also modelled the extent of attrition in a FBC on the particle size distribution of a limestone bed, and found attrition had an appreciable effect on changing the PSD of the limestone bed. By contrast however, this work suggests that bed inventory has an impact on attrition, with increasing bed inventory resulting in reduced attrition, possibly as an effect of increased sintering and/ or reactor erosion. González *et al.*, 2010 [88] investigated attrition effects in a pilot

scale, continuous mode calcium looping reactor, for two different limestones from the northwest of Spain. Results identified higher attrition in the initial capture cycles, after which for up to 140 hours there was a negligible change in particle size.

8.1.9 Comparison of results with other pilot scale reactors

A comparison of Cranfield's pilot scale CO₂ capture reactor is made with other pilot scale, looping cycle reactors in Table 8-3 which have been chosen based on the volume of data available in the literature. The maximum % CO₂ capture achieved in the Cranfield reactor as part of this study has increased considerably with reactor and process development, but remains somewhat less than that achieved in the other pilot scale reactors. All of the other three reactors have achieved capture efficiencies of at least 80 %, with the Canmet and IFK reactor achieving values > 90 % capture under stable operation. The CSIC reactor also achieved >90 % capture, although it was noted that this was only possible for short periods due to reduced cyclone efficiency and in turn reduced solids inventory. The maximum capture achieved in the Cranfield reactor when run on a continuous basis is close to 80 %, which is considered lower than the other reactors due to a number of reasons, including that of the calcium looping ratio. Here, the calcium looping ratio (F_{Ca}/F_{CO_2}) is defined as the ratio of calcium looping rate between reactors (mol/h), to CO₂ flow to the carbonator (mol/h) [7]. Charitos *et al.*, 2010 [7] suggest that a calcium looping ratio of at least 14 is necessary to ensure maximum possible CO₂ capture efficiency. For the earlier tests carried out as part of this study, a calcium looping ratio of just 2.6 and 3.5 was achieved for bed inventories of 4.5 and 6 kg respectively. For later tests with 13 kg bed inventory, the calcium looping ratio was increased to approximately 8, which although a much higher figure than previously, is below the figure of 14 proposed by Charitos *et al.*, 2010 [7]. The reason for the reduced looping ratio used here was primarily due to calciner burner failure for bed inventories greater than approximately 13.5 kg. This suggests that the maximum ~80% capture achieved to date in this reactor could be increased with burner modifications and in turn an increased bed inventory of at least 20 kg. Further, the residence time of the particles in the reactor at Cranfield is less than the other pilot scale reactors mentioned in Table 8-3, primarily due to the smaller height of the carbonator, at 4.3 m compared to 5, 6.5 and 12.4 m for the Canmet, INCAR-CSIC and IFK carbonators respectively. Therefore, this reduced the solids inventory in the carbonator and the

residence times, and particles were able to react for a decreased length of time when compared to a taller reactor, before then being transferred to the calciner for sorbent regeneration, resulting in reduced % capture. Alonso *et al.*, 2010 [295] reported improved results when they increased the height of the CSIC carbonator riser from 3.2 m to 6.5 m, and noted much more stable conditions, particularly in terms of carbonator bed inventory and solids circulation rates. In addition, the experiments in this study did not make use of the addition of fresh sorbent throughout the testing period, which also partially accounts for the decrease in sorbent capture capacity over time. This was because of aforementioned issues with the burner. By contrast, it is believed that the other three reactors would have introduced fresh sorbent to achieve maximum capture efficiency by increasing the average carrying capacity of CaO entering the carbonator [291] [293]. A further reason for the reduced % capture in this study may be due to the lower inlet CO₂ concentration of 8 % used compared to the IFK and CSIC reactors, which both operate with approximately 12 and 15 % respectively. The lower % of CO₂ used in this study resulted in increased dilution of CO₂, and therefore a lower partial pressure of CO₂, leading to a lower capture percentage. Normalisation of capture efficiency in order to directly compare results of this work, with that of CSIC and IFK with different CO₂ % inlets, has not been possible due to lack of access to a TGA, required to confirm the fraction of active (i.e. available to carbonate) CaO in the carbonator bed.

Although different limestones have different properties for CO₂ capture, good results have been achieved using Longcliffe limestone in bench scale [150] [121] and pilot scale work to date. Attrition does not appear to be pronounced, however sintering effects do appear to have occurred based on the results from the PSD analysis, although these should be viewed with caution due to potential contamination of samples with reactor material (see chapter 9). Overall limestone type is not considered a factor in the lower capture capacity in this instance.

Table 8-3 Comparison of pilot scale calcium looping reactor at Cranfield, with other pilot scale reactors described in the literature. Adapted from Charitos *et al.*, 2010 [300], Rodriguez *et al.*, 2011 [298], and Lu *et al.*, 2008 [8].

Operating Parameter	Units	Cranfield, UK	Canmet, Canada	INCAR-CSIC, Spain	IFK, Stuttgart
Maximum CO ₂ capture achieved	%	~75	>97	>95	97
Limestone	-	Longcliffe, UK	Canadian	Spanish	German
Mean particle size	μm	90/250	400/800	130/180	170/350
F _{Ca} / F _{CO2}	-	3-8	-	5-10	3-20
Control of F _{Ca} /F _{CO2} between reactors	-	Loop seal	'L' valve and solenoid ball valve	Loop seal	Cone valve
<i>Carbonator characteristics</i>					
Reactor Type	-	EFB	FBC	CFB	CFB
Height	M	4.3	5	6.5	12.4
Diameter	M	0.1	0.1	0.1	0.07
Gas velocity	m/s	0.8	-	1.1-3.5	4.0-6.0
Thermal power	kW _{th}	25	75	30	10
Fluidisation regime	-	Fast	-	Turbulent	Fast
Inlet CO ₂ concentration	Vol %	8	8 / 15-16.5	15	12
Temperature	°C	600-650	580-720	570-720	ca.650
<i>Regenerator characteristics</i>					
Reactor Type	-	BFB	BFB	CFB	BFB
Temperature	°C	ca.900	850-950	850-900	ca. 900
CO ₂ Partial pressure	Bar	<0.3	<0.3	<0.3	<0.3
Residence time	Min	0.5	-	1-5	1-5
Heat supply	-	Electrical heating and natural gas combustion	Electrical heating / biomass with air / oxyfuel combustion with biomass and coal	Electrical heating and air-fired coal combustion	Electrical heating, O ₂ - enriched air (O ₂ = 40% vol), CH ₄ combustion

8.2 Effect of Steam

The effects of steam on pilot-scale calcium looping were investigated in batch experiments. Figure 8-20 shows results for 0 %, 5 %, 10 % and 20 % additional steam, which outlines that 20 % additional steam produced the most improved CO₂ capture results. The CO₂ capture at 40 minutes was 50 % for 0 % additional steam, 85 % for 10 % additional steam, and approximately 97 % for 20 % additional steam. This shows a marked improvement in sorbent capture capacity with increasing amounts of additional steam, with carbonation extended with increasing steam concentration. 0 % steam also showed the fastest initial decrease in CO₂ capture, followed by 5 % additional steam, which unexpectedly showed the lowest % capture. Symonds *et al.*, 2009 [152] ran pilot scale batch tests with 3 kg sorbent, 8 % CO₂ feed, and 17 % H₂O, and too found the capture efficiency and duration to be superior to that when run without steam.

It is apparent from these results that batch testing can achieve much higher levels of initial % CO₂ capture than continuous looping cycle testing, for which the maximum % capture achieved as part of this work was close to 80 %. The reason for this is likely to be due to improved efficiency as the particles remain in the one reactor and therefore the solids and gas are not being circulated.

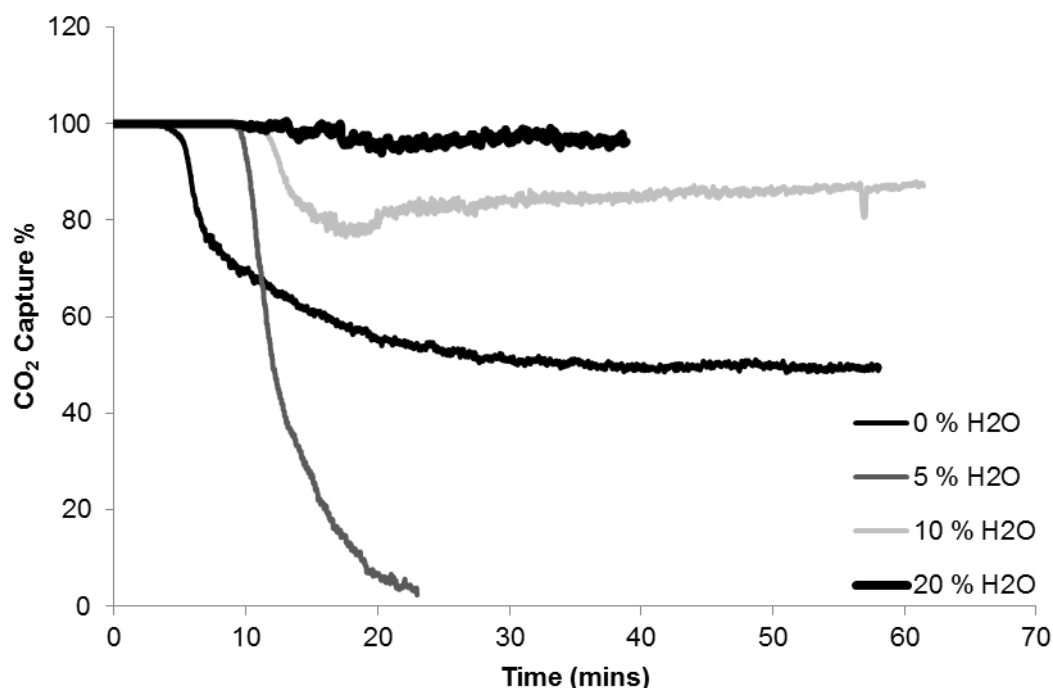


Figure 8-20 Effect of additional steam on CO₂ capture in single column, batch experiments.

EDS analysis (Figure 8-21) of the samples taken from the reactor post-carbonation show decreasing C and O weight %, and increasing Ca weight % with increasing steam concentration for tests run with 5 and 10 % steam when compared with 0 % steam. This implies that carbonation was occurring to a greater extent with increasing steam. The EDS result for 20 % steam was somewhat unexpected, showing the lowest weight % values for each element, other than that achieved when run with 0 % additional steam, and may be due to increased formation of Ca(OH)₂. This is supported by quantitative X-ray diffraction (QXRD) analysis (Figure 8-22) of sorbent tested with 20 % additional steam, and compared with sorbent tested with 0 % additional steam showing a far higher proportion of Ca(OH)₂ in the sample tested with steam, at 1.2 and 40 weight % Ca(OH)₂ for 0 and 20 % additional steam respectively.

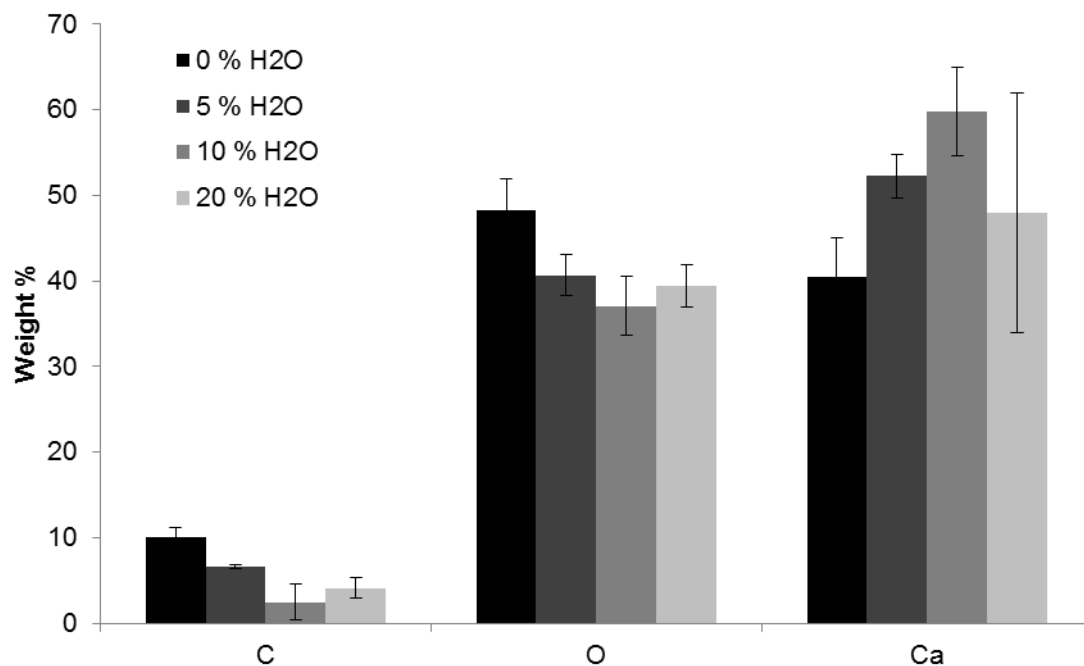


Figure 8-21 EDS analysis of sorbent after testing to show effect of additional steam.

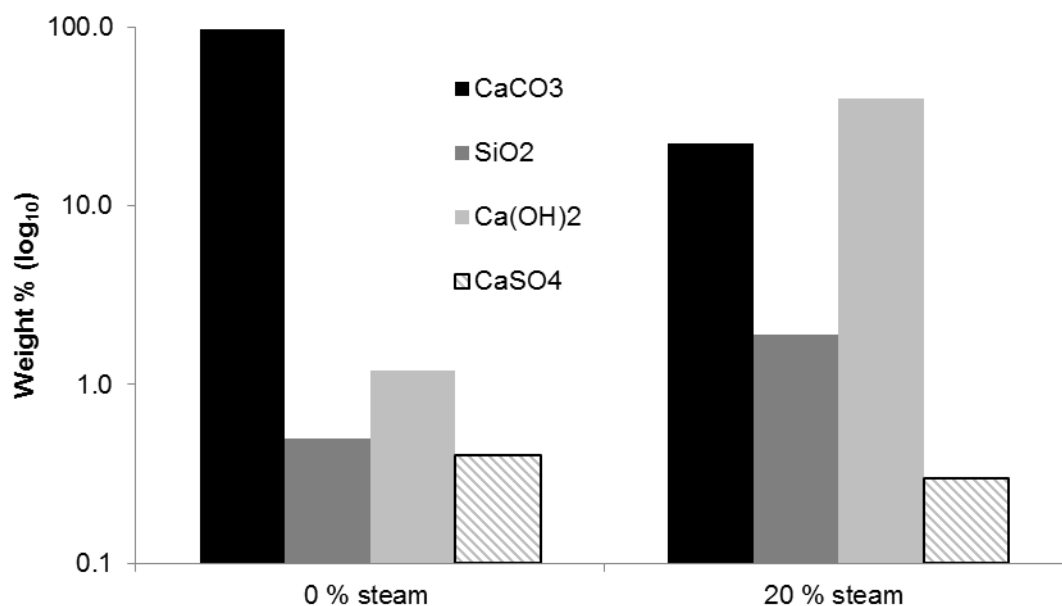


Figure 8-22 QXRD analysis of sorbent tested with 0 % and 20 % additional steam.

SEM analysis of the samples taken from the reactor after testing shows enhanced porosity of the sample run with 20 % steam (Figure 8-23) when compared with the other samples, although it is apparent that cracks may be present in the sorbent. Manovic *et al.*, 2008 [151] suggest that sorbent cracks are important for hydration when pore blockage may occur, but result in particle fragility, suggesting difficulty

with sorbent handling and increased sorbent losses, thus reducing process efficiency.

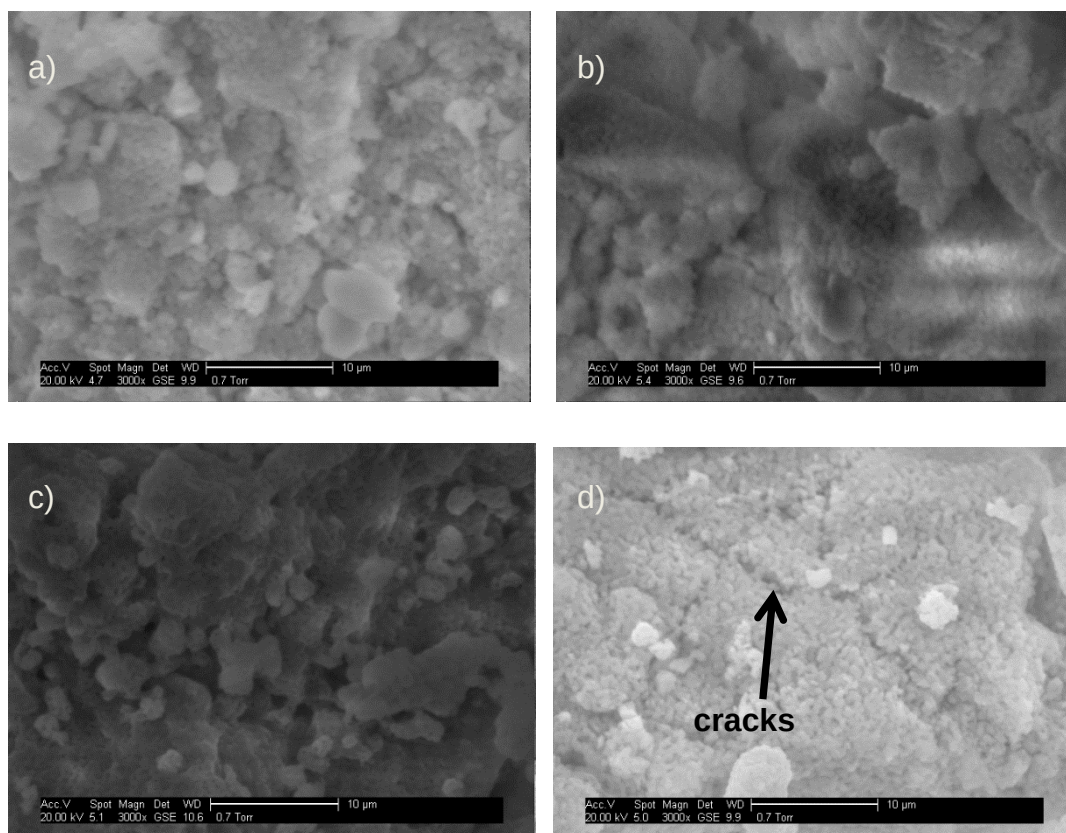


Figure 8-23 SEM analysis of sorbent sampled after testing in single column, for increasing additional steam concentrations: a) 0 % additional steam; b) 5 % additional steam; c) 10 % additional steam; d) 20 % additional steam. Magnification 3000x.

Particle size distribution (PSD) analysis of sorbent sampled from the carbonator at the end of each test with 0, 5, 10 and 20 % additional steam (Figure 8-24), shows that PSD appears to increase with increasing steam concentrations, implying that in this case, steam acts to reduce attrition. It has been noted in the literature that repeated carbonation cycles with steam may act to increase attrition due to crack formation [153]. This does not appear to be the case in these tests, perhaps due to the relatively short period of time over which the batch tests were run. However as mentioned, cracks are apparent in Figure 8-23, suggesting sorbent attrition may occur in longer test runs. As previously mentioned, erosion of the stainless steel 310 reactor may be enhanced with increasing steam concentrations, resulting in particulates in the sorbent samples, and thus causing an apparent increase in particle diameter with increasing steam concentration. Likewise, a combination of

CO₂ and steam is known to enhance sintering effects [301] which may lead to increased particle diameters due to grain growth, although it is unlikely that the increases seen in Figure 8-24, of increases in diameter of approximately 100 μm with each increasing steam concentration test can be attributed to sintering. This is also supported by SEM analysis of the samples (Figure 8-23), which show little apparent sintering, particularly for 20 % additional steam.

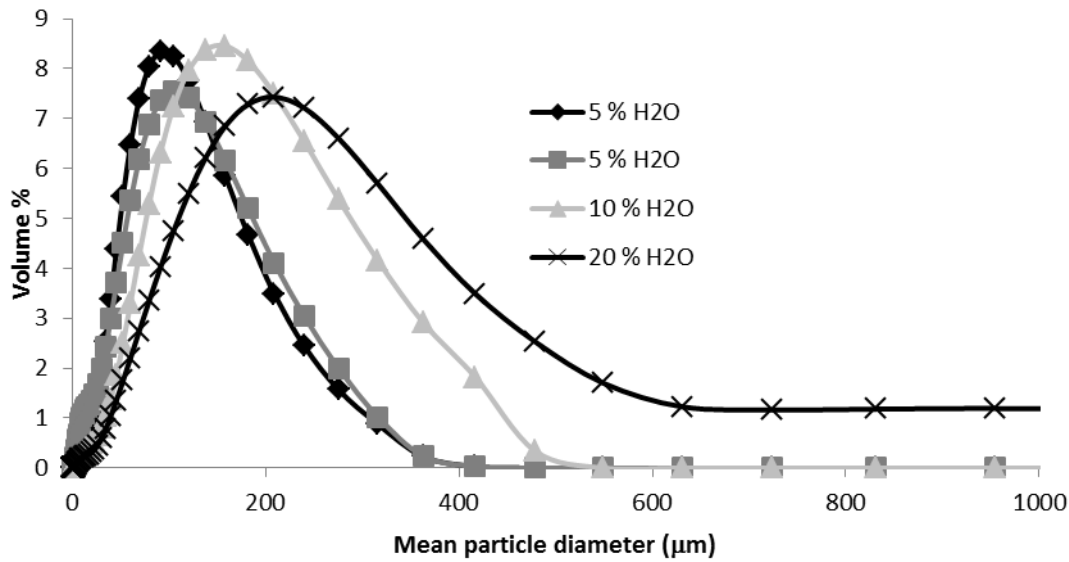


Figure 8-24 PSD analysis of sorbent sampled after tests run with 0, 5, 10 and 20 % additional steam.

BJH analysis of the sorbent samples (Figure 8-25) shows similar pore sizes within each sample, particularly for pores of mean diameter 10-100 nm. Samples tested in 10 % additional steam showed slightly lower mean pore diameter and pore volume than for other samples. This sample also shows a reduced surface area from BET analysis when compared to samples from the other tests (Table 8-4), and although unexpected, it should be noted that the decrease between samples is small. The similar values achieved between samples may be attributed to the large steam volumes from the use of an air fired burner in the carbonator, suggesting that beyond a certain level of steam improvements in sorbent morphology reach a maximum. Bench scale testing carried out by Kavosh (2011) [121] however showed an increase in Longcliffe limestone BET surface area from 5 to 5.3 to 12 m^2/g , for 28 %, 48 % and 78 % steam respectively during calcination, using a sorbent mass of 0.01 kg. The BET surface area value achieved with 28% steam by Kavosh (2011) [121] is comparable to that achieved in this study with 20 % additional steam (i.e. 32 %

steam total) at values of 5 and 4.1 m²/g respectively. The smaller bed inventory used in the bench scale study may result in greater reactivity with steam, and therefore higher pore surface areas achieved.

As noted by Arias *et al.*, 2012 [154], very little work has been carried out looking at the effects of steam in flue gas, due to the predominant use of synthetic flue gases comprising N₂/air and CO₂. Therefore this work provides results from a scenario more similar to that of industry than some other work available in the literature due to the use of an air fired burner to heat the reactor and provide the CO₂-containing flue gas.

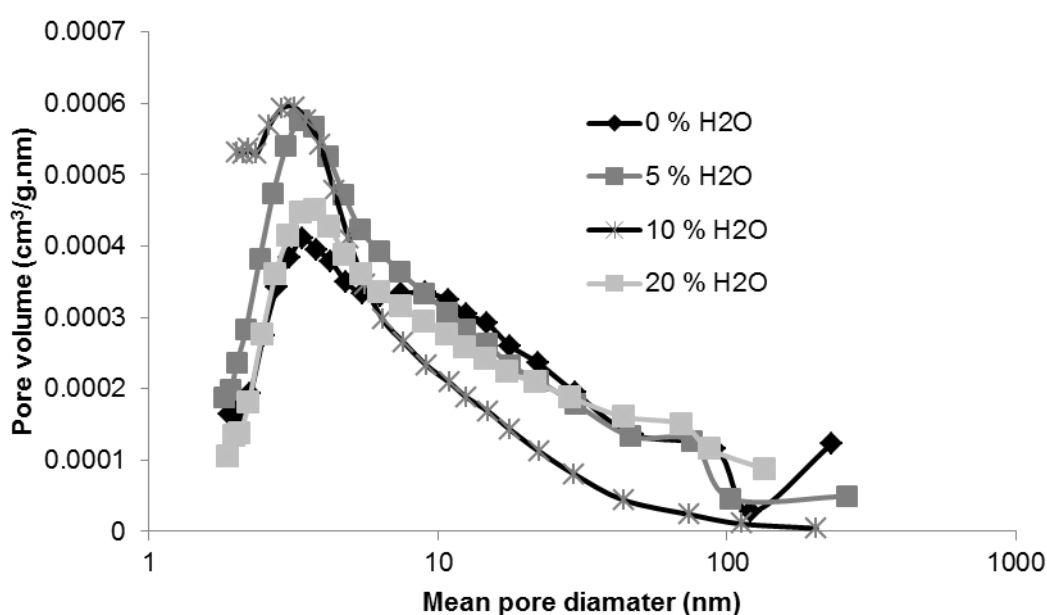


Figure 8-25 BJH analysis of sorbent sampled after tests run with 0, 5 10 and 20 % additional steam.

Table 8-4 Pore surface area and volume analysis of samples from tests in increasing concentrations of additional steam.

Additional steam	S _{BET} (m ² /g)	Pore volume (cm ³ /g)
0 %	4.3	0.02
5 %	4.5	0.02
10 %	3.7	0.01
20 %	4.1	0.024

8.3 Effect of SO₂

The effects of SO₂ on pilot-scale calcium-looping were investigated in both single column batch tests, and looping experiments.

8.3.1 Effect of SO₂ – Single Column Batch Tests

Figure 8-26 shows results from single column batch experiments, which outlines that increasing SO₂ concentrations appears to decrease % CO₂ capture. This is likely to be caused by the well-documented detrimental effect of SO₂ on CO₂ capture, due to the formation of CaSO₄. CaSO₄ has a molar volume of 46 cm³/mol, compared to a molar volume of 37 cm³/mol for CaCO₃ [146], and therefore acts to block pores and impede CO₂ capture. This is supported by Figure 8-27, which shows the average pore diameter of sorbent sampled from the reactor after each test for 0, 1000 and 2000 ppm SO₂, and identifies that increasing SO₂ concentration reduces the average pore diameter, from 55 nm to 28 to 10 nm for 0, 1000 and 2000 ppm respectively.

For 0 ppm SO₂, the % CO₂ capture remained close to 100 % for the longest period of time before beginning to decrease. This is a higher initial capture value than that achieved in continuous looping cycle testing, as shown in section 8.3.2 and for reasons described in section 8.2. However, for 1000 ppm SO₂, this remained at a high level (above approximately 90 %) for the longest period of time before beginning to decrease. Further, the % capture at the end of the test was approximately 36 %, 2 % and 9 % for 0, 1000, and 2000 ppm SO₂ respectively. The fact that the 1000 ppm SO₂ test had a lower final capture % than the 2000 ppm SO₂ test is unexpected, as given the well-documented detrimental effects of SO₂ on carbonation, it would be expected that the 2000 ppm test had the lowest final % capture. A reason for this outcome however could be the positive effect that SO₂ may have in decreasing effects of attrition [123]. This is supported by Figure 8-28 which shows that sorbent from the 0 ppm test experienced the greatest decrease in particle diameter, whilst the sorbent tested with 1000 ppm SO₂ had the largest mean particle diameter and volume when compared with sorbent tested in 0 and 2000 ppm SO₂, suggesting that 1000 ppm SO₂ represents a compromise between pore blockage and attrition. Jia *et al.*, 2007 [132] too found that ‘light’ sulphation of limestone in SO₂ concentration of 1800 ppm resulted in reduced material loss as a result of attrition.

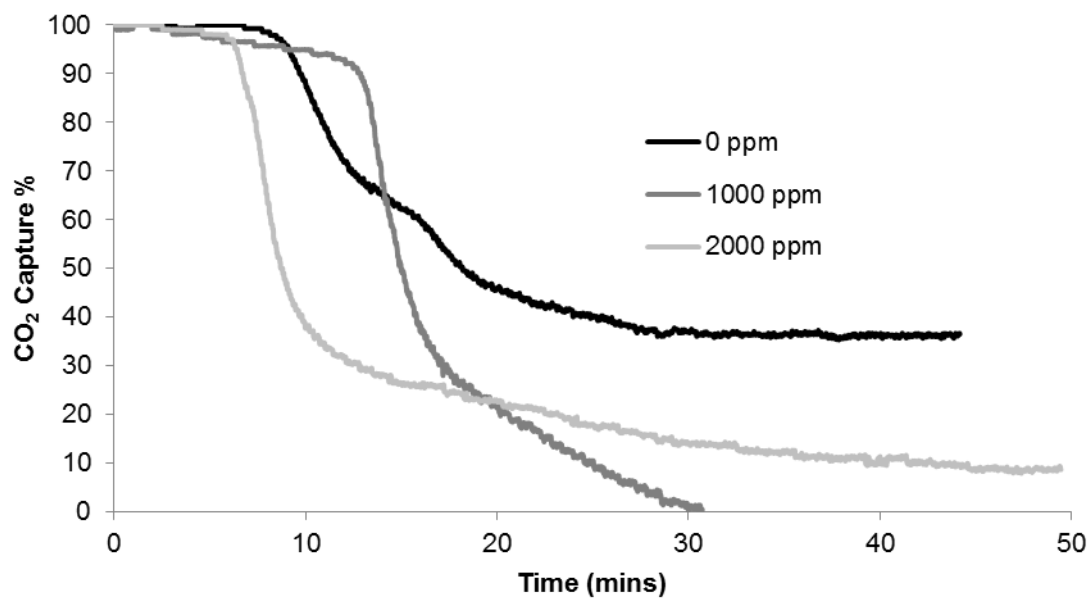


Figure 8-26 Effect of increasing SO₂ concentration on % CO₂ capture.

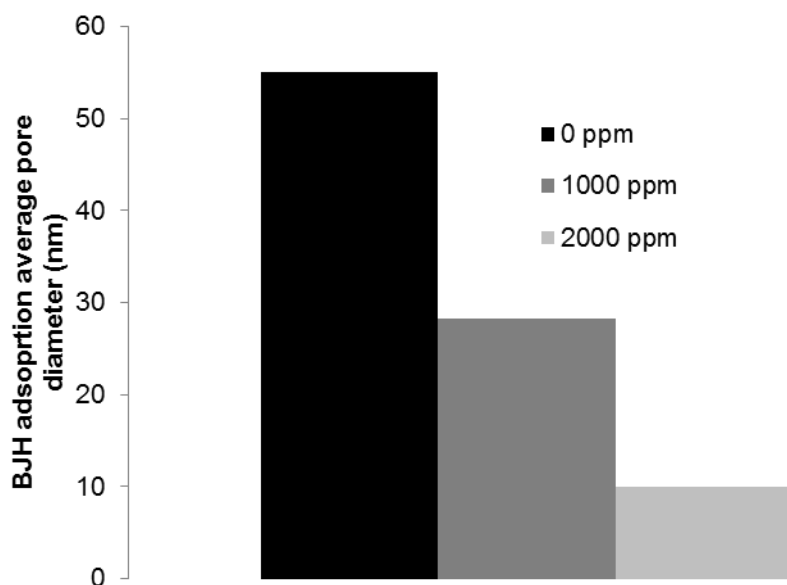


Figure 8-27 BJH analysis showing average pore diameter of sorbent sampled from the reactor after each tests, for 0, 1000 and 2000 ppm SO₂.

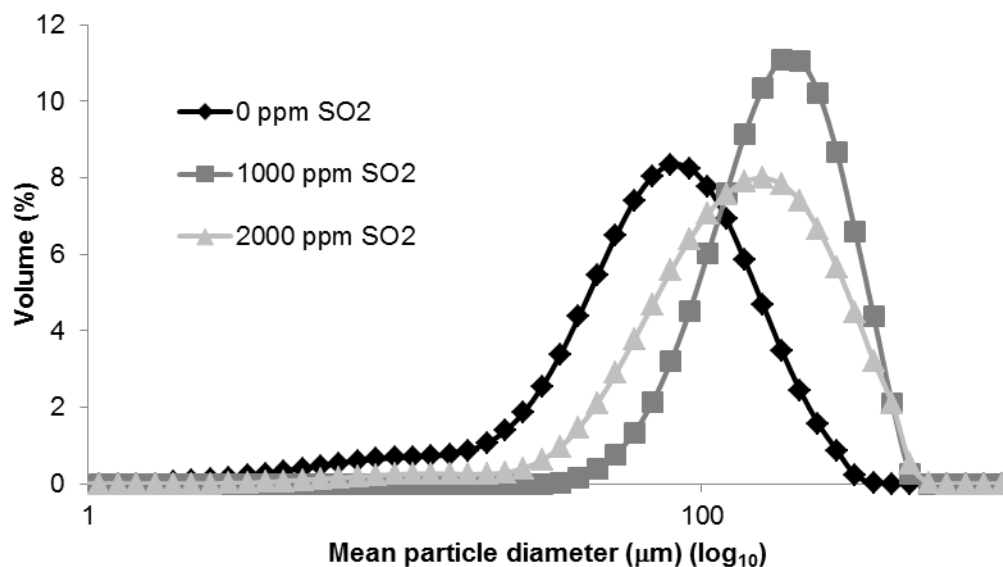


Figure 8-28 PSD analysis of sorbent sampled from the reactor after each tests, for 0, 1000 and 2000 ppm SO₂.

EDS analysis (Figure 8-29) of sorbent after each test suggests reduced carbonation with increasing SO₂ concentration, implied by decreasing weight % of C and O, and increasing weight % of S. However, the weight % of Ca does not increase linearly, as would be expected for reduced carbonation, and instead decreases from 40.5 % at 0 ppm, to 36.7 % 1000 ppm, before then rising to 41 % for 2000 ppm SO₂. This again could be indicative of 1000 ppm producing some form of compromise between pore blockage and reduced attrition effects, or may be attributed to an anomalous reading obtained from the EDS analysis.

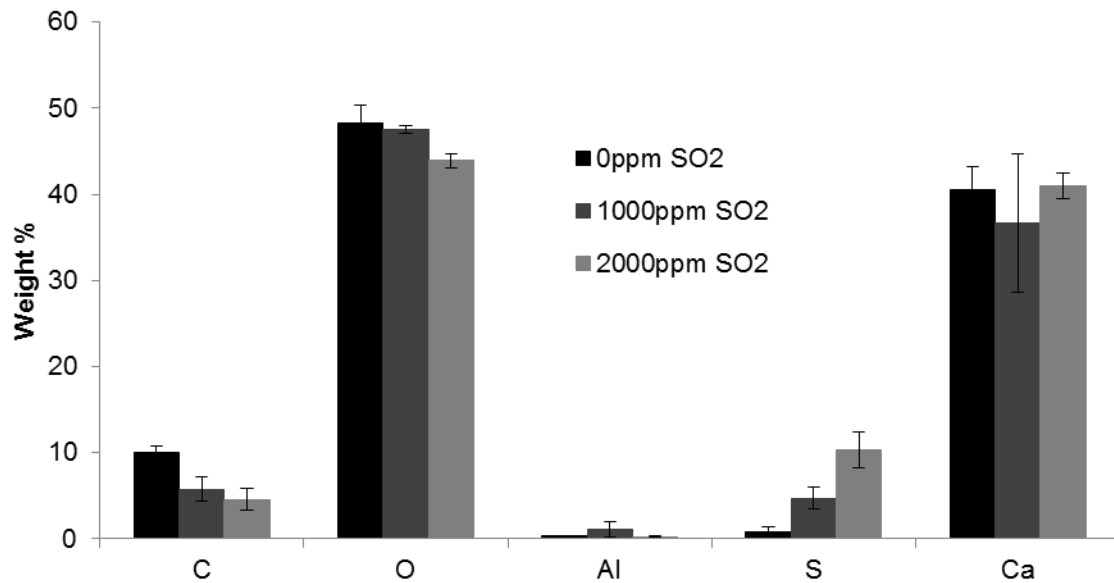


Figure 8-29 EDS analysis of sorbent exposed to increasing SO₂ concentrations in single column experiments.

SEM analysis of the sorbent morphology shows that increasing SO₂ concentrations cause the porosity of the sorbent to decrease (Figure 8-30). This can be explained by the increased molar volume of CaSO₄ over CaCO₃, causing pore blockage. This is also supported by Figure 8-27 in that reactions are limited by pore size, as well as by pore surface area and pore distribution. Pore surface area can be considered the area where reactions can take place, while pore volume is the space in which products can grow. Pore diameter can be defined as the space limitation in a single pore [146].

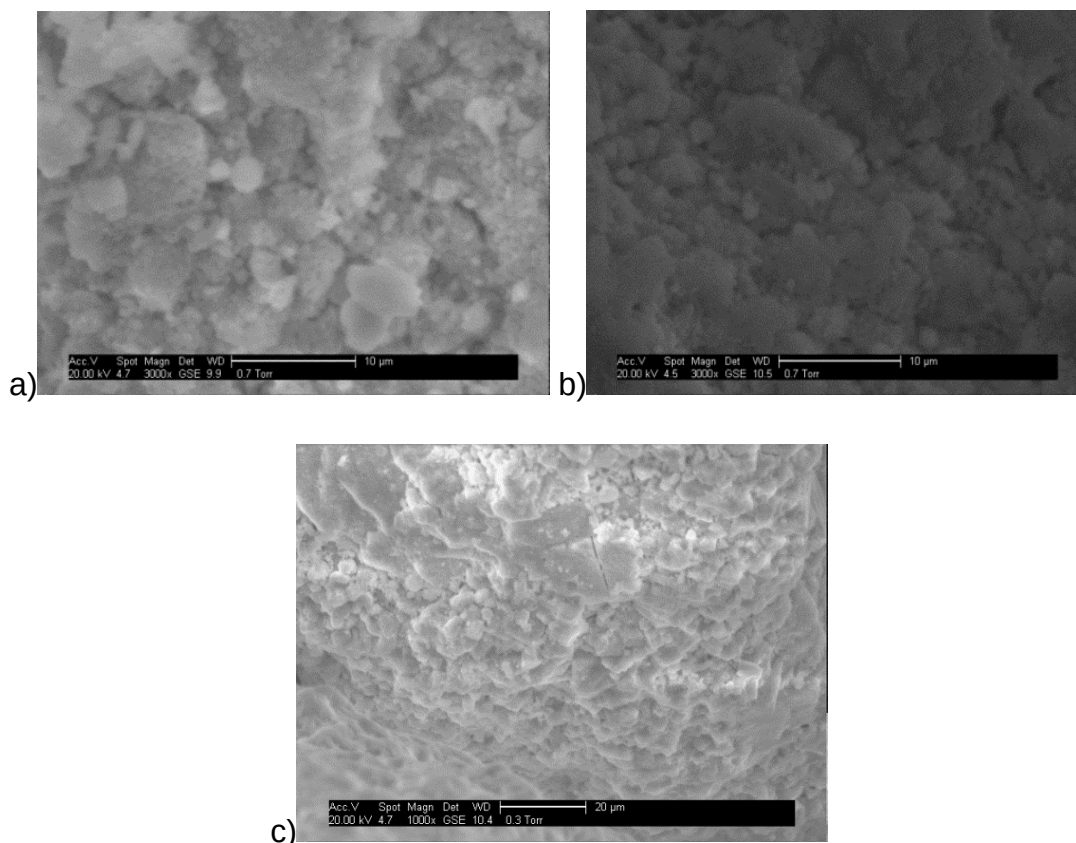


Figure 8-30 SEM analysis of sorbent exposed to increasing SO₂ concentrations in single column experiments: a) 0ppm SO₂; b) 1000 ppm SO₂; c) 2000 ppm SO₂. Magnification 1000x.

8.3.2 Effect of SO₂ – Looping Cycle Experiments

Figure 8-31 shows the effect of increasing SO₂ concentration on the CO₂ capture efficiency of the calcium-looping cycle, which identifies that increasing SO₂ concentration appears to decrease the % capture efficiency, likely due to pore blockage as a result of CaSO₄ formation. This is in accordance with the majority of work available in the literature [112] [302]. However, it is apparent that the % capture for each test shown does not appear to decrease over time with increasing carbonation/calcination cycles, as would be expected from the standard CO₂ capture ‘model’ (Figure 8-32). The reason for this may be due to the quantities of steam produced by the carbonator’s air-fired burner, and the calciner’s oxy-fired burner, at 87 and 108 l/min H₂O in the carbonator and calciner respectively. The effects of additional steam on % CO₂ capture in the calcium-looping cycle have been investigated, and it is apparent from this work and research available in the literature

that addition of steam during carbonation/ calcination improves % CO₂ capture due to the acceleration and enhancement of the fast-diffusion process in carbonation.

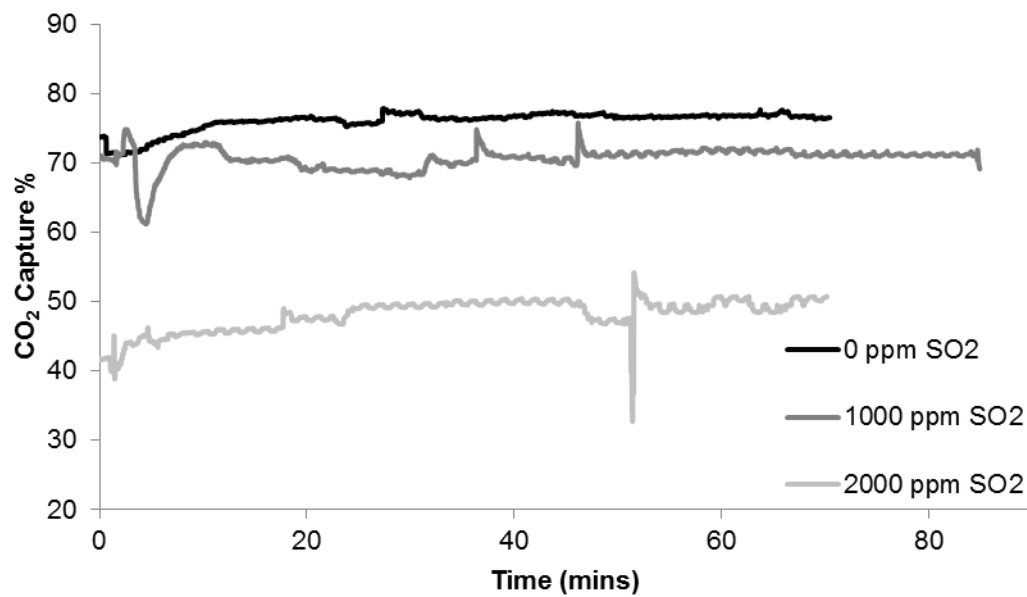


Figure 8-31 Effect of SO₂ concentration on % CO₂ capture during pilot scale calcium-looping.

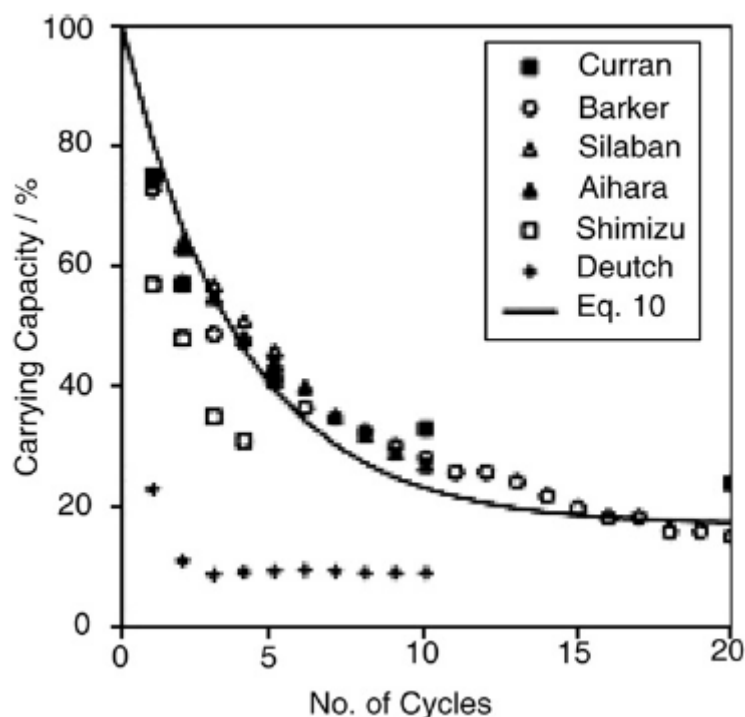


Figure 8-32 Literature and experimental results of carrying capacity and number of carbonation – calcination cycles in bench scale work [90].

With further regard to the reduction in CO₂ % capture proposed due to pore blockage, Figure 8-33 shows the results of BET analysis for sorbent sampled from the reactor after each test which confirms this hypothesis. It identifies that the sorbent tested in 2000 ppm and 1000 ppm SO₂ has a much smaller pore volume than that tested without, implying pore blockage had occurred. The pore diameter for sorbents from all three test scenarios was very similar, with sorbent from 0 and 1000 ppm SO₂ addition tests showing slightly smaller diameters, the smallest of which was approximately 2 nm and can be considered small pores (<6 nm), compared to a close value of 7nm for the 2000 ppm SO₂ test. The pronounced peak in pore volume at a diameter of ~3nm for the 0 ppm test and also to a lesser extent for the 1000 ppm test is interesting. It suggests that the small pores that contribute to pore volume and thus important for CO₂ capture, are filled with increasing SO₂ concentration, and thus in this case it is both the small and large pores that are active in reducing CO₂ capture capacity. This is in contrast to TGA work carried out by Chen *et al.*, 2012 [146] who suggested that decay in activity is largely due to changes in large pores, and also Gullet and Bruce (1987) [303] (from Sun *et al.*, 2007 [112]) who suggested sulphation fills pores of 10-60 nm or larger. In the carbonator, where CaO particles

are transferred in order to be carbonated, sulphation (i.e. sulphation of CaO) is more likely to occur than direct sulphation (sulphation of CaCO_3) because of the larger surface area of CaO. The reason for this filling of small pores may be due to diffusion of CO_2 through the CaSO_4 layer, due to its smaller molecular volume when compared to SO_2 , thereby filling smaller pores, which in the absence of SO_2 is not 'necessary' for it to do. This may be more pronounced at pilot scale than bench scale because of the larger area available over which reactions can take place in a fluidised bed, compared to a fixed bed in a TGA.

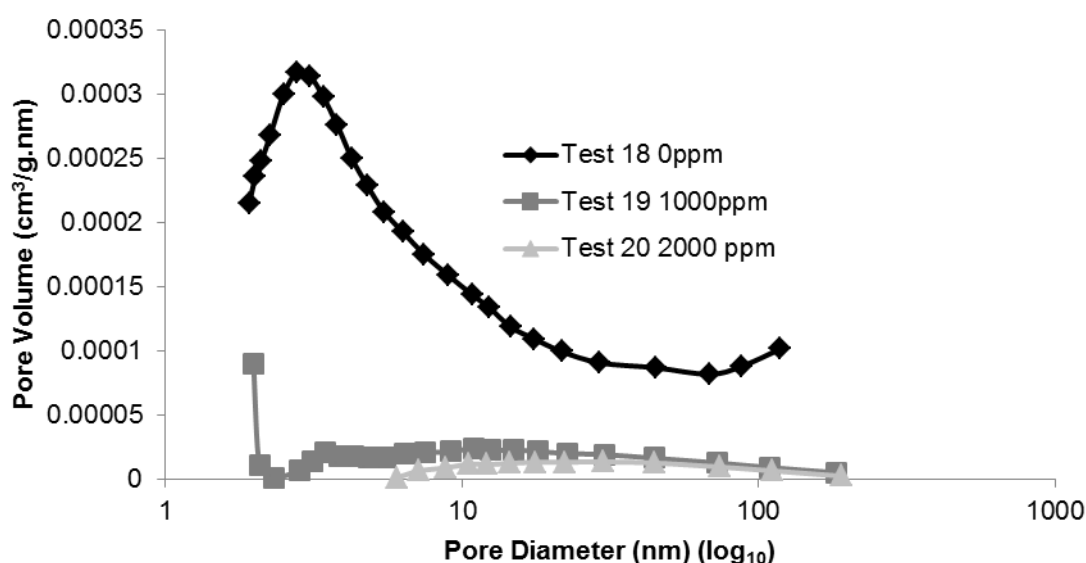


Figure 8-33 BET analysis of sorbent taken from reactor after testing with increasing SO_2 concentrations.

Bench-scale work carried out by Kavosh (2011) [121] for SO_2 concentrations of 200, 2500, and 5000 ppm too confirmed that increasing SO_2 during carbonation and calcination resulted in reduced CaO conversion, and in turn lower % CO_2 capture. A comparison of pore volume, size and surface area for bench scale and pilot scale work is provided as Table 8-5. For both the pilot scale and bench scale tests, as previously mentioned it is clear that increasing SO_2 concentration acts to reduce both pore surface area and pore volume. The pore volume for sorbents from the 1000 and 2000 ppm pilot scale tests is very similar; however the surface area for these tests appears to reduce by almost half from 1000 to 2000 ppm SO_2 . The results from the bench scale tests for the most part appear to fit well into this pattern, with the only anomaly being that the surface area for bench scale tests at 2500 ppm SO_2 is higher than that for pilot scale tests at 2000 ppm SO_2 . However, given that the

differences are small, the overall results suggest that scale up of the calcium looping process is unlikely to affect sorbent pore characteristics in the case of Longcliffe limestone.

Table 8-5 Comparison of sorbent pore characteristics for pilot scale looping tests and bench scale batch tests in increasing SO₂ concentrations, using Longcliffe limestone, adapted from Kavosh (2011) [121].

SO ₂ concentration (carbonation) (ppm)	Pilot scale looping test		Bench scale batch test	
	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	S _{BET} (m ² /g)	Pore volume (cm ³ /g)
0	2.5	0.014	-	-
200	-	-	2.3	0.0030
1000	0.52	0.002	-	-
2000	0.25	0.0019	-	-
2500	-	-	0.3	0.0008
5000	-	-	0.08	0.0004

With regards to attrition, Figure 8-34 shows the results of sorbent PSD analysis after testing, showing very similar PSD for all 3 tests. In this case the sorbent from the 2000 ppm SO₂ test shows a slightly higher extent of attrition than the 1000 ppm, and in turn the 0 ppm test. This is in contrast to single column tests with SO₂ which showed slight a decrease in attrition with SO₂ present. The difference may be due to the looping cycle process, during which particles are subjected to other forces, including gravitational, drag, buoyancy and pressure forces [304], which in single column tests they would not experience, including the abrasive bed, and the reactor walls. This in turn may result in a weaker CaSO₄ surface layer, and / or removal of said layer. Similar results whereby increasing SO₂ caused a slight increase in attrition were found by Coppola *et al.*, 2012 [302] in bench scale, batch tests with 1800 ppm SO₂.

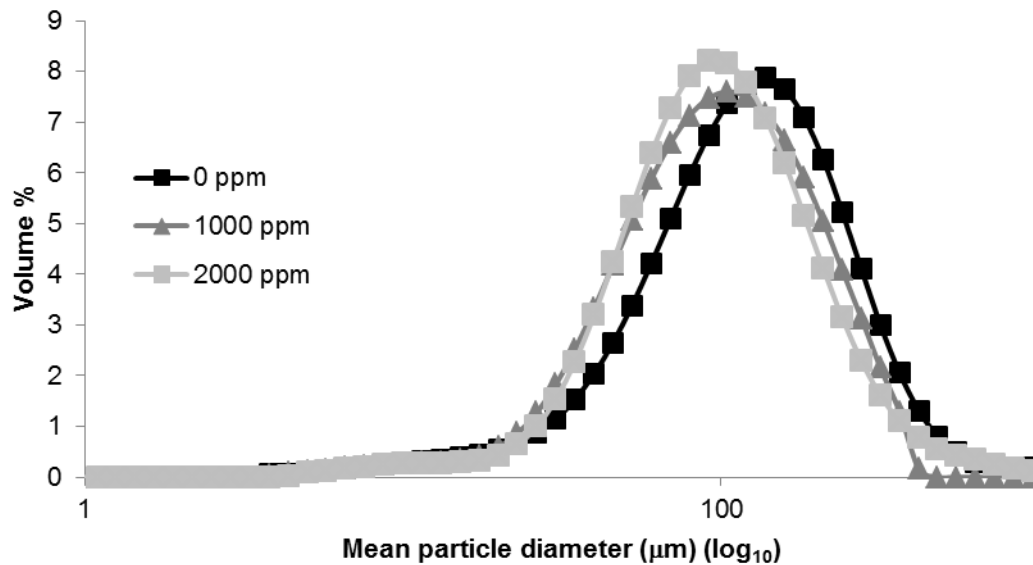


Figure 8-34 PSD analysis of sorbent sampled from reactor after testing with increasing concentrations of SO₂.

SEM images shown in Figure 8-35 of samples taken from the carbonator for tests with 0 ppm, 1000 ppm and 2000ppm (a-c), and also samples from the calciner for the same tests (d-f), identify that increasing SO₂ concentration appears to reduce the porosity of the sorbent, likely due to formation of an impervious CaSO₄ layer. This appears to be particularly so when comparing images from 0 and 1000 ppm tests, whereby for the 1000 ppm carbonator sample in particular, the surface layer appears more apparent than for the 2000 ppm sample. This supports the theory that in the looping cycle tests a weaker CaSO₄ surface layer is formed, resulting in increased attrition.

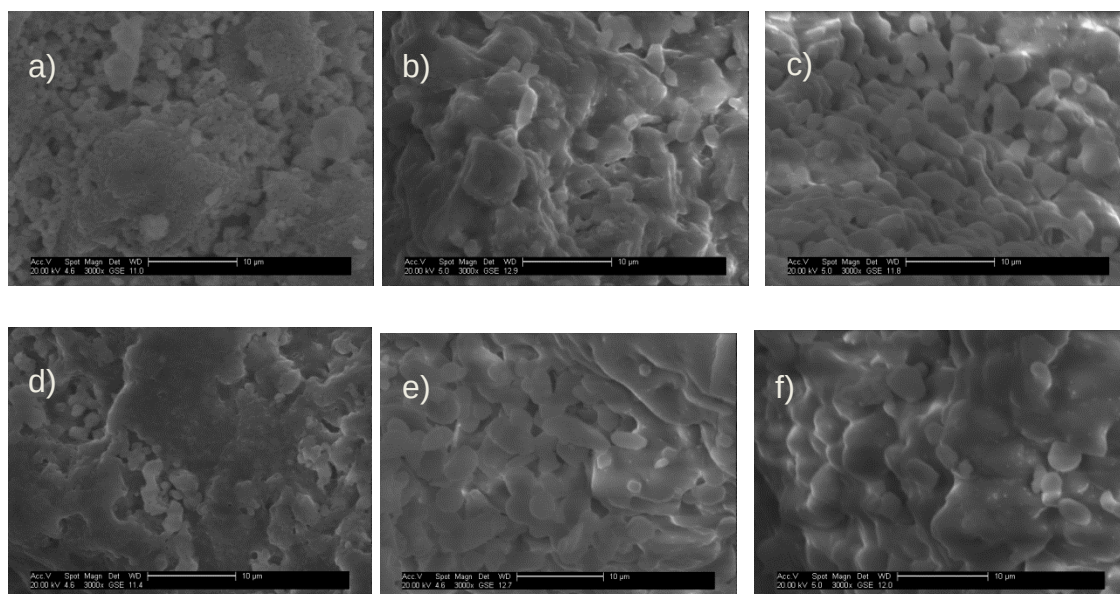


Figure 8-35 SEM analysis of sorbent from the carbonator after testing for 0, 1000 and 2000 ppm SO₂ (a-c), and from the calciner after testing for 0, 1000 and 2000 ppm SO₂ (d-f). Magnification 3000x.

8.4 Conclusion

CO₂ capture tests have been carried out in a pilot scale reactor employing the calcium looping cycle in continuous mode. A maximum CO₂ capture % of close to 80% has been achieved in this reactor, following a number of process and reactor modifications, including, but not limited to, modification of carbonator temperature, enhanced heating of the lower loop seal inlet gases through the addition of heated elements, and also addition of air movers to encourage solids transfer. It is considered that a higher % capture could be achieved with further modifications to improve the solids inventory, solids circulation rate and residence time of solids in the reactor, as well as improvements to the burner reliability. The effects of additional steam have been investigated in pilot scale batch experiments which showed that increasing steam concentrations have a beneficial effect on CO₂ capture due to enhanced diffusion, supported by SEM and BET analysis. The effects of SO₂ have also been investigated at the pilot scale in both batch and continuous experiments, and it was found, in accordance with work available in the literature, that SO₂ has a detrimental effect on CO₂ capture. This is supported by PSD, BET, EDS, QXRD and SEM analysis of sorbent samples subsequent to testing. Interestingly, the large water content present in the reactor from the use of an air and oxy-fired burner

seems to have a positive effect in maintaining the CO₂ capture % achieved by the sorbent.

This work has made a contribution to knowledge in terms of achieving a good level of CO₂ capture % in a pilot scale reactor that had not been operated in continuous looping mode prior to this work. Although the % capture achieved is lower than that achieved in other pilot scale reactors, namely those at Canmet [8], CSIC [300] and IFK [300] [298], reasons for why this is so have been proposed. It is widely acknowledged in the literature that further work is required at the pilot scale in order to facilitate scale up of the technology to demonstration scale, and therefore this work makes a significant contribution to this, particularly with the identification of the importance of residence time and high temperature maintenance. Results have also been compared with those carried out at bench scale, which have confirmed the importance of a lower carbonator temperature at the pilot scale level, compared to bench scale. Attrition of Longcliffe limestone does not appear to be of particular issue in this case, with PSD seeming to increase with increasing bed inventory. However, this is attributed to sintering, and also highlights the importance of reactor and component corrosion, and the potential implications that this may have in contaminating sorbent and artificially increasing PSD. Beneficial effects of steam have been realised, particularly in maintaining % capture in the presence of SO₂. This has important implications for industry in that inherent steam in flue gas will have in general a positive effect on the calcium looping cycle. This work therefore meets Objectives 2a, 2b and 2c.

9 RESULTS AND ANALYSIS: ELEMENT PARTITIONING

This chapter provides the experimental results from the elemental analysis carried out on solid and flue gas-derived samples from the calcium looping cycle. This includes off-line sampling, as well as on-line gas sampling using a mobile Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). An analysis of the results is provided, including suggested mechanisms to account for the results found, and potential implications for cement production using calcium looping cycle derived CaO. The results and analysis of thermodynamic equilibrium modelling undertaken to investigate effects of bed inventory and SO₂ concentration is also provided in this chapter.

The work outlined in this chapter has been submitted for publication in the following research papers:

- A. Cotton, K. Patchigolla, J.E. Oakey (2013) 'Minor and Trace Element Emissions from Post-Combustion CO₂ Capture from Coal: Experimental and Equilibrium Calculations' *Fuel*, Accepted, In Press.
- A. Cotton, K.N. Finney, K. Patchigolla, R.E.A. Eatwell-Hall, J.E. Oakey, J. Swithenbank, V. Sharifi (2013) 'Quantification of trace element emissions from low-carbon emission energy sources: I. Ca-looping cycle for post-combustion CO₂ capture; and II. Fixed bed, air blown down-draft gasifier' *Revised manuscript incorporating reviewer's comments resubmitted to Chemical Engineering Science*.

9.1 Elemental Content in Raw Limestone Sample

ICP-MS analysis of unreacted Longcliffe SP52 limestone was carried out to determine the presence of element impurities. The major, minor and trace elements are given in Table 9-1, with the results for the complete elemental analysis presented in Figure 6-6. Throughout the literature, there are varying definitions for major, minor and trace element [305]. In this case, major elements are defined as those of concentration > 10 ppm, minor elements of concentration between 1 and 10 ppm, and trace elements of concentration < 1 ppm. Calcium was reported to be 'over-

range' (above the detection limit) as this is the majority constituent. The results confirm the presence of a variety of contaminant elements, with Mg present at the highest concentration at 5749 ppm. This is to be expected given the presence of a dolomitic fraction ($\text{CaMg}(\text{CO}_3)_2$) in most natural occurring limestones. Other elements found in high concentration include Sr, Al, Fe, Mn, K and Ba, at concentrations of 736, 415, 355, 268, 224, and 136 ppm respectively. Included within the analysis are a number of heavy metals, including Pb, U and Zn albeit at relatively low concentrations of 26.21, 1.31 and 10.5 ppm respectively.

Table 9-1 Identification of major, minor, and trace elements in the limestone powder sample used in the calciner-carbonator reactor.

Major > 10 ppm	Li, Na, Mg, Al, P, K, Ti, Cr, Mn, Fe, Zn, Ga, Br, Sr, Y, Ba, Pb
Minor (1-10 ppm)	V, Co, Ni, Cu, Zr, Mo, Cd, Sn, La, Ce, Pr, Nd, Sm, Gd, Dy, U
Trace (<1 ppm)	Be, Sc, Ge, As, Se, Rb, Nb, Ru, Pd, Ag, In, Sb, Te, I, Cs, Eu, Tb, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Pt, Au, Hg, Tl, Th

9.2 Effect of Bed Inventory

Experiments were carried out to identify the effect of bed inventory in the reactor on elemental concentration of solid sorbent in the reactor, and the mean values of gaseous major element emissions from the carbonator. Bed inventories of 4.5, 6 and 13 kg were used for looping cycle tests. Results are shown based on the major, minor and trace elements as provided in Table 9-1. Elements which were determined to be of concentration <0.1 ppm in solid samples have not been included, as they are considered to be of insignificant concern both in terms of environmental and industrial processes. They are provided in Table 9-2 below. Hg is included in this table, but it is an element known to cause adverse health and environmental effects. However, concentrations of Hg in this study were identified as being of less than 0.001 ppm, and therefore data for it has not been included within figures in this chapter. In the case of the minor and trace concentrations identified in the unreacted limestone, concentrations of all in the flue gas were <0.1 ppm, and therefore graphs for these elements have also not been provided.

Table 9-2 Elements found in samples in concentrations < 0.1 ppm, and not considered in analysis.

Elements of concentration <0.1 ppm and not included in analysis	Ga, V, Ge, Ru, Rh, Pd, A, I, Xe, Cs, Tb, Ho, Tm, Lu, Hf, Ta, Re, Os, Ir, Pt, Au, Hg, Tl, Bi, Th.
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9.2.1 ICP-MS analysis

9.2.2 Major elements

Figure 9-1a shows the major element concentration for solid samples taken from the carbonator. Samples were acid digested and analysed using ICP-MS, and compared with acid digestion blanks in order to obtain the final values. The effect of bed inventory is apparent in this case, with concentrations of Fe in particular increasing from 319 ppm to 4598 ppm for bed inventories of 4.5 kg and 13 kg respectively. Similarly, concentrations of Cr, Mn, Zn and Pb also increased with increasing inventory. For Cr, no positive recording was made for the lowest bed inventory of 4.5 kg, but recordings were made at 6kg and 13 kg. For Mg, Al, Si, Ti, Sr and Y concentrations appeared to slightly decrease with increasing bed inventory. Figure 9-1b provides values for those major elements which decreased in concentration in the sorbent sample after testing, when compared with the acid digestion blank. It is clear that for each of the major elements to which this occurred, (C, Na, P, Br, S) that increasing bed inventory resulted in an increase in concentration.

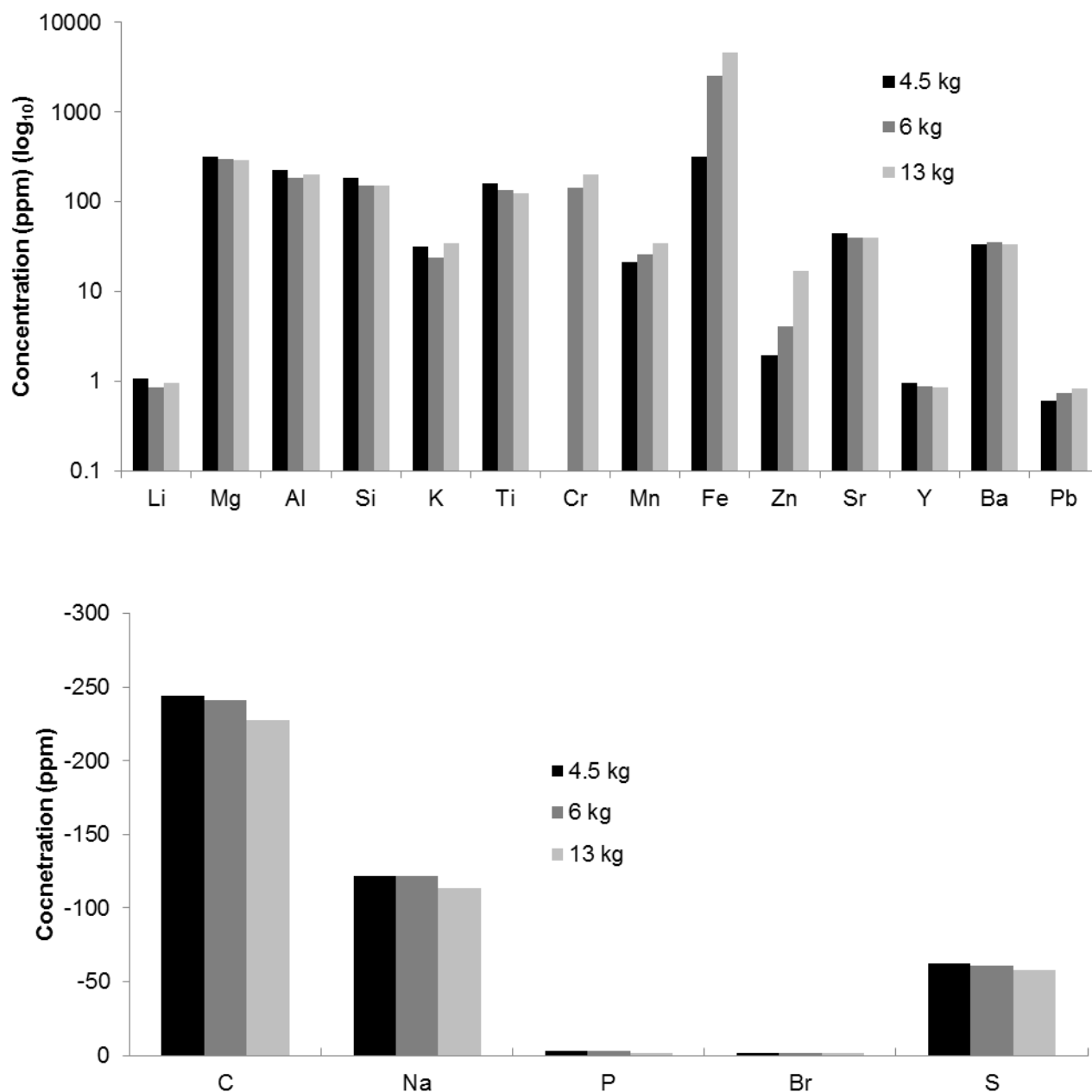


Figure 9-1 Effect of bed inventory on a) increase of solid major elemental concentrations; and b) decrease of solid major elemental concentrations, for bed inventories of 4.5 kg, 6 kg and 13 kg CaCO_3 . Note change in y axis values between the graphs.

Results of ICP-MS flue gas analysis provided in Figure 9-2 show that most of the major elements present in the carbonator flue gas increase with the mass of the limestone in the reactor. However, some elements are only present for the largest bed inventory of 13 kg e.g. Ti, Cr, Mn. However, all elements included within the figure can be considered to be at very low concentrations of <2 ppm.

Those elements at the higher concentrations in the flue gas include Na, Si, K, Zn, and Br. For Na in particular which was present in low concentrations in the solid, this suggests that some of it may be partitioning to the flue gas for bed inventories of 6 and 13 kg.

For Na, Al, K and Fe, the lowest bed inventory of 4.5 kg resulted in a concentration in the flue gas which was less than that of the blank sample (Figure 9-2b), values which then increased for the higher bed inventories (Figure 9-2a). This suggests that a certain amount of these elements is being absorbed, perhaps by the sorbent in the case of Fe, or by the reactor itself. In the case of P, decreased values compared to the blank were found for bed inventories of 4.5 kg and 13 kg, but an increased value for 6 kg inventory. However, the values are very low at < 0.01 ppm and this anomalous result may be due to analytical errors. Overall, although concentrations in the flue gas are small at < 2 ppm, increasing bed inventory does appear to increase the concentration of the majority of major elements present in the flue gas.

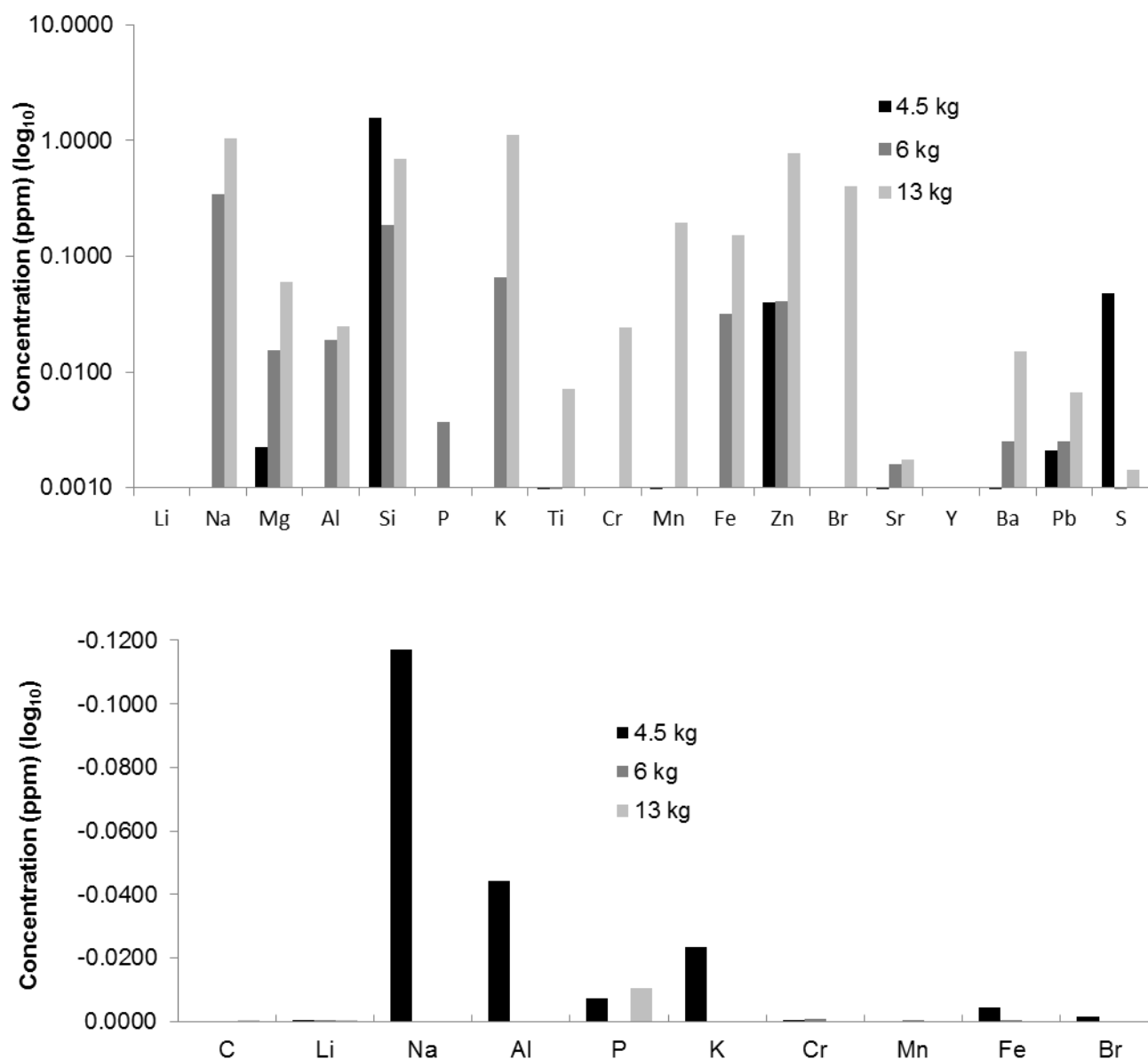


Figure 9-2 Effect of bed inventory on a) increase of flue gas major elemental concentrations; and b) decrease of flue gas major elemental concentrations for bed inventories of 4.5 kg, 6 kg and 13 kg CaCO_3 . Note change in y axis values between the graphs.

9.2.3 Minor Elements

Figure 9-3 shows the concentrations of minor elements in the solid sorbent. Increasing bed inventory resulted in increasing values observed for Co, Ni, Cu, Mo, Cd, and Sn (Figure 9-3a). In the case of Cu and Sn, values were obtained that were lower than that of the blank, at -0.66 and -0.1 ppm respectively (Figure 9-3b) for a bed inventory of 4.5 kg, which then increased to values of 22 and 0.22 ppm

respectively for 13 kg. In the case of Gd, Dy and U, small decreases in concentration were found for an increasing inventory, however values are low at < 1 ppm and the changes observed are small. The remaining elements (Zr, La, Ce, Pt, Nd) recorded an increase in concentration for 6 kg over 4.5kg, and then a decrease from 6 kg to 13 kg. All minor element flue gas concentrations were <0.1 ppm and therefore have not been provided.

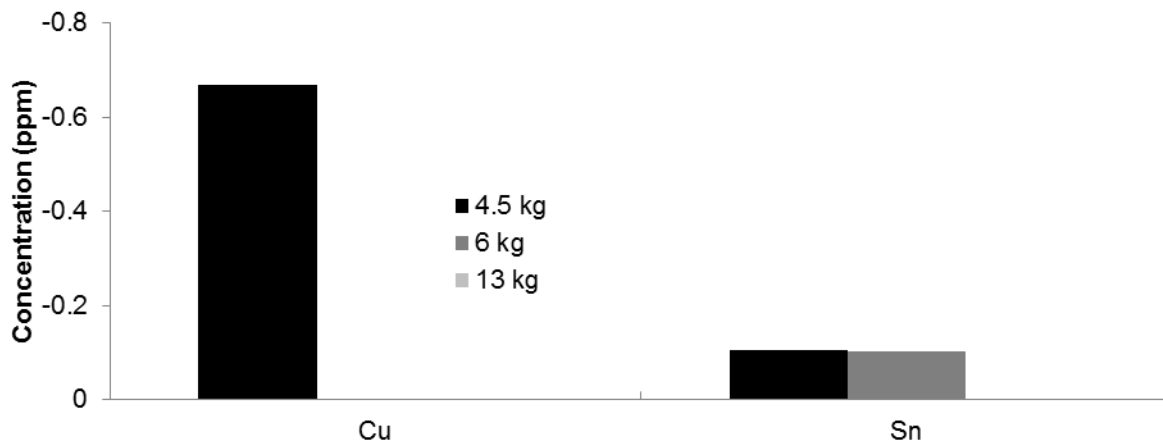
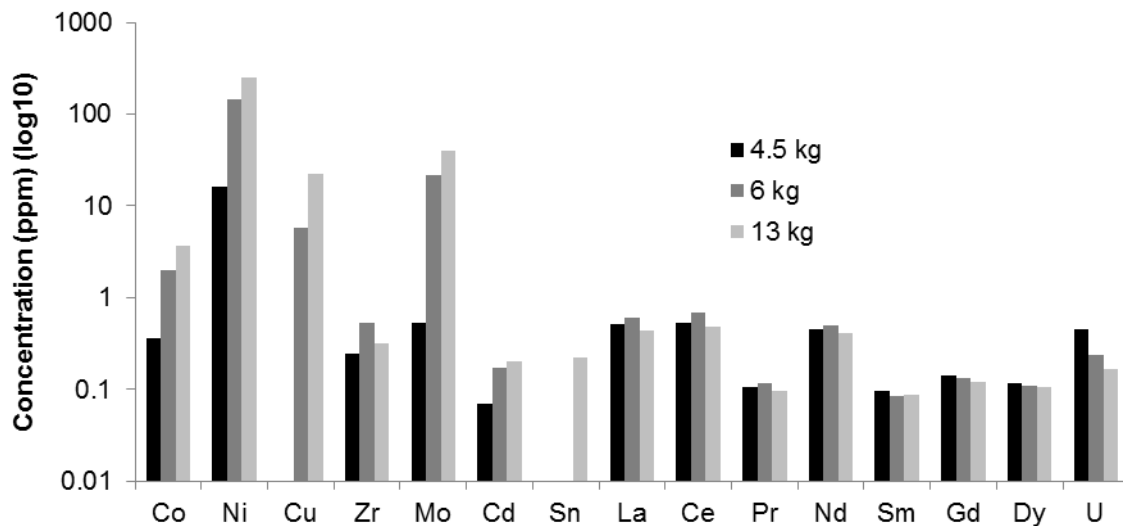


Figure 9-3 Effect of bed inventory on a) increase of solid minor element concentrations, and b) decrease of solid minor element concentrations, for bed inventories of 4.5 kg, 6 kg and 13 kg CaCO_3 . Note change in y-axis values between the two graphs.

9.2.4 Trace Elements

Figure 9-4 shows solid concentrations of trace elements, of which only Rb, Nb and W were found at concentrations greater than 0.1 ppm. W showed the greatest change, with concentration increasing from 0.06 to 0.42 to 0.74 ppm for inventories 4.5, 6 and 13 kg respectively. All trace element flue gas concentrations were <0.1 ppm and therefore have not been provided here.

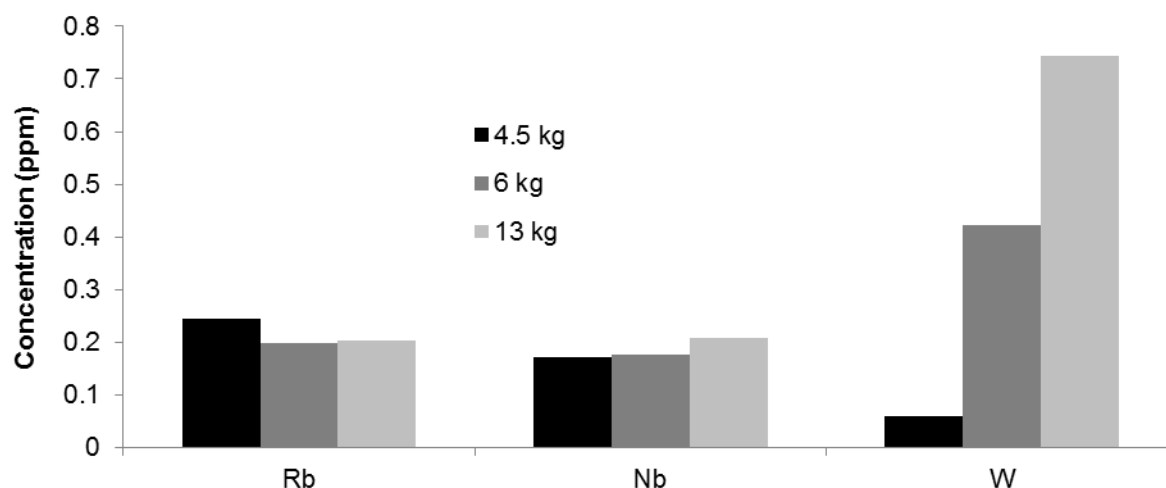


Figure 9-4 Effect of bed inventory on increase of solid trace elemental concentrations, for bed inventories of 4.5 kg, 6 kg and 13 kg CaCO_3 .

As expected for major, minor and trace elements, the concentration is generally higher by several orders of magnitude for solids samples compared to flue gas samples. It is clear that in the cases where elemental concentration decreased with increasing bed inventory, this is mostly seen for period 3 elements (Mg, Al, Si), and some lanthanide rare earth metals (Sm, Gd, Dy, Rb) and U.

The geochemistry of limestone is complex, with various hydrous and anhydrous forms of the mineral available. Naturally formed CaCO_3 (termed ' CaCO_3 I' for the purposes of this study) generally has a rhombohedral-hexagonal lattice system, and is stable at atmospheric pressures, and Longcliffe SP52 can be assumed to be in this form. Other forms of CaCO_3 (II-V) are formed over ranges of both increasing temperature and pressure [306].

Each Ca^{2+} in the CaCO_3 structure is bonded with six oxygen atoms, resulting in a charge of +1/3 per bond. Similarly, the O in each CO_3 group is bonded with two Ca^{2+} ions, meaning each CO_3 group is coordinated to six Ca ion. This provides alternating layers of Ca and CO_3 groups [307] (Figure 9-5).

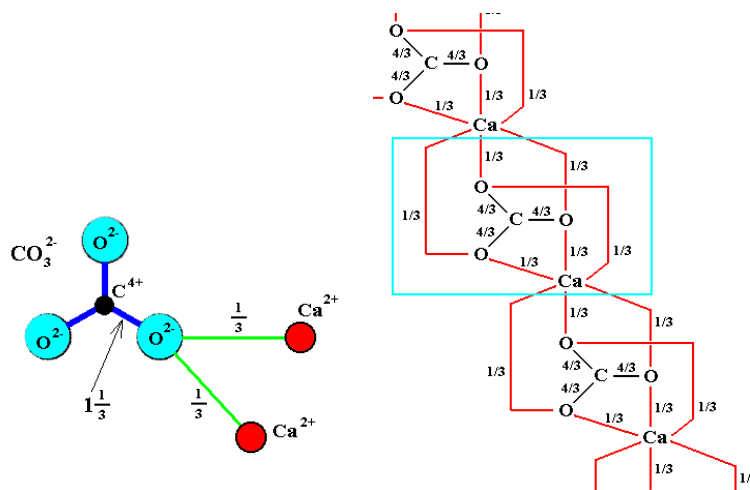


Figure 9-5 Calcite structure: a) single molecule showing stereometric relationships between atoms; b) alternate calcium cations and carbonate anions, showing each Ca ion bonded to 6 O ions [308].

Contaminant elements have three possible locations for bonding in CaCO_3 [309]:

- Substitution via cation exchange for Ca^{2+} occurs for 90-95% of contaminant elements e.g. Fe, Mn, Sr;
- Adsorption onto crystal faces to balance charge imbalances e.g. Na, K; and
- Inclusion of additional mineral phases within the CaCO_3 .

Due to the hexagonal structure of the crystals, spaces between the cations allow elements with an ionic radii smaller than Ca^{2+} , such as Fe, Mn, Cd, Co, Ni, Zn, Cu to be incorporated with the crystal structure.

For the cases where elemental concentration increased with increasing bed inventory, the elements concerned were mostly those of low volatility (Be, Cr, Mn), transition metals (Fe, Co, Ni, Cu, Zn, Nb, Mo, Rh, Cd, W), and group 6 metals (Pb, Sn). Elements that have low volatility are most likely to partition to solid phases within the reactor, and therefore it would be expected that the concentration of the low volatility elements would increase for a greater bed inventory. The transition metals have high melting points because of strong metallic bonds resulting from the presence of unpaired electrons, resulting in low volatility. Most also have a charge of $2+$, allowing substitution for Ca^{2+} within the CaCO_3 lattice. Iron oxides are also able to sequester transition metal cations and thus are able to immobilise other transition metal contaminants [310], thus accounting for the general increase in transition metal concentration with bed inventory.

For Pb and Sn, of which Pb is considered to be a Group II element, and Sn is considered to be between Group I and Group II, both are emitted mostly in coal fly ashes in coal combustion [311], and therefore could be considered to partition to the solid phase in the calcium looping cycle.

Further, it was noted that non-volatile elements have been found more likely to condense out with particulate matter, resulting in an increase in trace element concentration with a decrease in sorbent size [13; 264]. An increase in bed inventory is likely to result in increased attrition, and therefore an overall decrease in PSD, due to the greater number of collisions that are likely to occur between particles. Sager *et al.*, 1999 [256] found that introduction of limestone increased Pb, Cd and Mn emissions, but these were immediately sorbed from the vapour phase onto particulates.

With regards to the elemental species that decrease in concentration with increasing bed inventory, Mg, Al and Si oxides are generally considered primary components of limestone in addition to Ca. However, no Si was detected from ICP-MS analysis of unreacted limestone, which can be attributed to low Si detection limits on the ICP-MS in question; although EDS analysis shows decreasing Si concentrations with increasing bed inventory (Figure 9-6). MgO and Al₂O₃ can be considered to have extended ionic structures, whilst SiO₂ has an extended covalent structure, meaning that all have high melting and boiling points, requiring large amounts of energy to volatilise them. Therefore, they are considered to be of low volatility, but the increase of these elements in the flue gas analysis suggests that they are being removed from the sorbent under the high temperature conditions.

The literature suggests that limestone can be used to capture Ni, Pb and Cd, thus accounting for the increased concentration of these three elements with increasing bed inventory [312]. By contrast, it has also been suggested that interaction, and therefore capture of Ni with Ca-bearing materials is of minor significance [313] although it would appear that this is not the case in this study.

With regard to the lanthanides, when investigating limestone formation and rare earth element prevalence, Nagarajan *et al.*, 2007 [314] found a negative correlation of rare earth elements and CaO. It is suggested that in general the absorption of lanthanide cations is weak, and therefore they have low molar absorption

coefficients, due to shielding of the $4f$ orbitals by the filled $5s$ and $5p$ sub-shells [315]. The low cation exchange capacity of the lanthanides may explain the small decreases in concentration in limestone, with increasing bed inventory.

9.2.5 Mass Balance

A mass balance for the carbonator is provided as Table 9-3, calculated based on the incoming and outgoing concentrations of elements. It shows that partitioning was always higher to the solid samples than in the flue gas samples, with very low concentrations partitioning to the flue gas in all cases.

Table 9-3 Mass balance for effect of bed inventory, showing elemental partitioning between solid and gaseous phase.

			Major Elements														
		Units	Li	Na	Mg	Al	Si	P	K	Ti	Cr	Mn	Fe	Zn	Br	Sr	Y
4.5 kg	Solid samples in	ug/min	1275.699	-146458	380561.4	271745.8	220610.8	-3397.42	38136.24	190323.7	0	25249.51	383901.2	2344.059	-2236.7	53738.15	1143.107
	Gaseous samples out	ug/min	-1.1E-05	-0.0406	0.000781	-0.01538	0.547387	-0.00255	-0.00809	0.000153	-0.00022	5.21E-05	-0.00153	0.013862	-0.00057	0.000252	-1E-06
	Mass Balance closure (out/in)	n/a	-9E-09	2.77E-07	2.05E-09	-5.7E-08	2.48E-06	7.5E-07	-2.1E-07	8.04E-10	0	2.06E-09	-4E-09	5.91E-06	2.55E-07	4.69E-09	-9.1E-10
6 kg	Solid samples in	ug/min	1006.732	-146268	362501.7	225106.8	181554.6	-3410.96	28652.52	160520.8	170327.7	31202.58	3026590	4816.438	-2206.5	48049.55	1050.646
	Gaseous samples out	ug/min	-2E-05	0.119243	0.005338	0.00655	0.064094	0.001281	0.022625	0.000123	-0.00029	-0.0002	0.010926	0.014225	-1.5E-05	0.00056	-1.2E-05
	Mass Balance closure (out/in)	n/a	-2E-08	-8.2E-07	1.47E-08	2.91E-08	3.53E-07	-3.8E-07	7.9E-07	7.67E-10	-1.7E-09	-6.3E-09	3.61E-09	2.95E-06	6.61E-09	1.17E-08	-1.2E-08
13 kg	Solid samples in	ug/min	1146.613	-136231	350820.9	238635.9	180748.1	-1919.96	40808.64	150490.5	243975.7	41403.88	5514952	20423.48	-2081.45	48024.37	1012.59
	Gaseous samples out	ug/min	-0.00012	0.35837	0.020767	0.008507	0.241046	-0.0036	0.382791	0.002462	0.008477	0.067894	0.053066	0.271775	0.139514	0.000604	-1E-05
	Mass Balance closure (out/in)	n/a	0	-2.6E-06	5.92E-08	3.56E-08	1.33E-06	1.88E-06	9.38E-06	1.64E-08	3.47E-08	1.64E-06	9.62E-09	1.33E-05	-6.7E-05	1.26E-08	-9.9E-09
			Minor Elements														
		Units	V	Co	Ni	Cu	Zr	Mo	Cd	Sn	La	Ce	Pr	Nd	Gd	Dy	U
4.5 kg	Solid samples in	ug/min	0	435.3898	19692.76	-803.412	297.7981	644.396	82.84071	-124.975	619.4009	634.1599	128.3079	543.9397	170.9185	141.6386	537.2744
	Gaseous samples out	ug/min	0	-0.00022	-0.00415	0.001208	-0.00093	0	4.27E-05	0.00172	-3.5E-07	-1E-05	-6.9E-07	-2.1E-06	0	0	-1E-06
	Mass Balance closure (out/in)	n/a	0	-5.1E-07	-2.1E-07	-1.5E-06	-3.1E-06	0	5.15E-07	-1.4E-05	-5.6E-10	-1.6E-08	-5.4E-09	-3.8E-09	0	0	-1.9E-09
6 kg	Solid samples in	ug/min	0	2423.014	173928.6	6961.409	648.8454	26191.47	207.593	-123.288	738.317	828.2583	141.3699	607.7495	158.7476	132.681	282.5049
	Gaseous samples out	ug/min	-1E-05	-0.00029	-0.01179	0.001385	-0.00173	-6.9E-07	3.26E-05	0.000758	-1.4E-06	-8.5E-05	-5.2E-06	-1.7E-05	0	0	-2.4E-06
	Mass Balance closure (out/in)	n/a	0	-1.2E-07	-6.8E-08	1.99E-07	-2.7E-06	-2.6E-11	1.57E-07	-6.1E-06	-1.9E-09	-1E-07	-3.7E-08	-2.8E-08	0	0	-8.6E-09
13 kg	Solid samples in	ug/min	0	4460.402	302682.4	26986.38	385.2317	48063.8	244.7849	272.0325	533.4318	572.8632	117.4082	494.2219	145.5418	125.8261	197.6001
	Gaseous samples out	ug/min	0.000995	0.008477	0.015103	0.039212	0.000118	1.18E-05	0.000174	0.003293	-4.5E-06	-0.00016	-2E-05	-8.9E-05	0	0	0
	Mass Balance closure (out/in)	n/a	0	1.9E-06	4.99E-08	1.45E-06	3.06E-07	2.45E-10	7.12E-07	1.21E-05	-8.5E-09	-2.9E-07	-1.7E-07	-1.8E-07	0	0	0
			Trace Elements														
		Units	Rb	Nb	W												
4.5 kg	Solid samples in	ug/min	291.8469	204.9593	71.17635												
	Gaseous samples out	ug/min	-8.7E-06	3.47E-07	4.51E-06												
	Mass Balance closure (out/in)	n/a	-3E-08	1.69E-09	6.34E-08												
6 kg	Solid samples in	ug/min	237.6517	210.411	506.5362												
	Gaseous samples out	ug/min	-1.8E-05	-2.1E-06	3.82E-06												
	Mass Balance closure (out/in)	n/a	-7.6E-08	-9.9E-09	7.54E-09												
13 kg	Solid samples in	ug/min	244.1204	249.6585	892.9666												
	Gaseous samples out	ug/min	3.61E-05	0	-0.00023												
	Mass Balance closure (out/in)	n/a	1.48E-07	0	-2.6E-07												

9.2.6 SEM-EDS Analysis

SEM-EDS analysis of sorbent sampled from the carbonator after each test was undertaken to determine the percentage weight of the elemental species present. The results as shown in Figure 9-6 confirm that increasing bed inventory generally increases the presence of Al, Fe and Cu. Al was identified in the unreacted sample at a weight % of 0.34, but this increased to similar values of 0.67 and 0.66 % for 4.5 kg and 6 kg samples respectively, with a much higher value of 3.98 % for 13 kg sample of sorbent. This increase in Al % weight with increasing sorbent mass may be because there is a greater amount of Al present originally, or because the limestone acts as a sorbent for Al, which is also considered the case for Fe and Cu. Al is also known to form Ca aluminates, which are constituents found in cement. The EDS results indicate similar quantities of C, O and Ca between tests, although values for the samples that had undergone testing are slightly lower for C and O, and slightly higher for Ca, compared to the unreacted limestone sample, implying that the small change was a result of chemical reactions. Although the values are small, a steady decrease in Si weight % was recorded with increasing sorbent mass, implying removal of Si from limestone in the capture process. However the lowest value was recorded for the unreacted limestone.

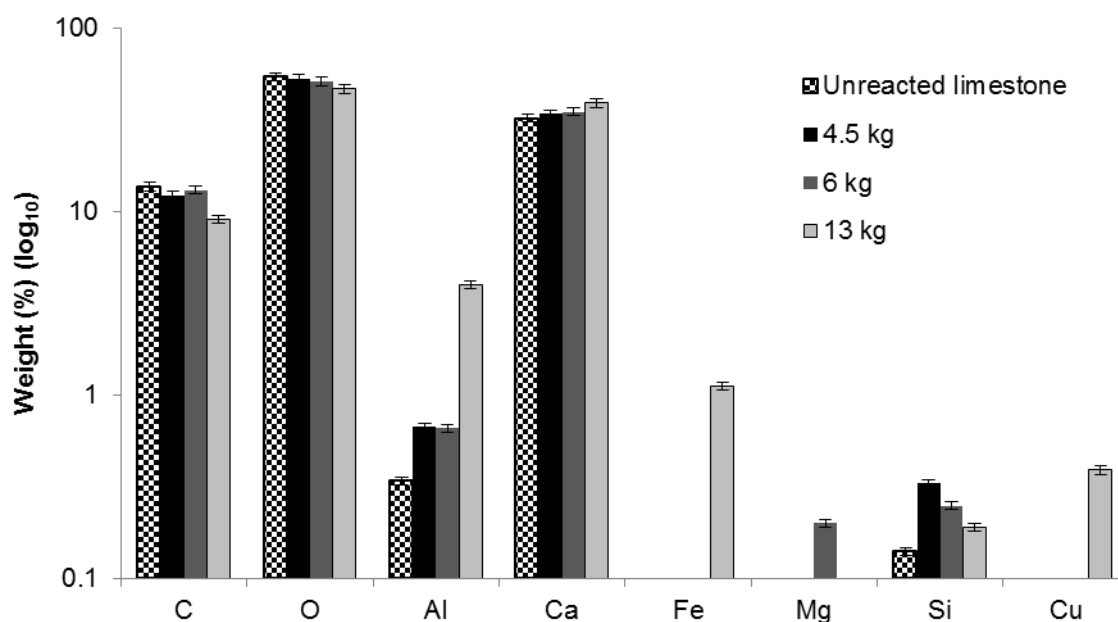


Figure 9-6 SEM-EDS analysis of solid sorbent taken from the carbonator after testing with increasing bed inventory, for bed inventories of 4.5, 6 and 13kg.

9.3 Experimental Elemental Partitioning – Effect of Additional Steam

Single column experiments were undertaken to investigate the effect of steam on trace element partitioning in the calcium looping cycle. A number of issues were encountered when running tests as a looping cycle with steam, including cementation of solids in the lower loop seal standpipe, perhaps due to insufficient temperatures, and blockage of the exhaust, hence the decision to undertake the experiments in a single column. However, running single column tests required pre-calcination of limestone samples in a furnace at 950°C for 12 hours, and this may affect capture capacity of the sorbent. Some literature reports suggest precalcination can improve capture capacity [160] [316] [317] due to formation of a ‘rigid interconnected CaO skeleton’ [119], whilst others suggest that precalcination provides no improvement [318] [319]. As a result, this has required consideration when analysing results from single column batch tests and looping cycle tests.

9.3.1 Major Elements

Figure 9-7 shows the major elements present in solids taken from the carbonator after testing. It is apparent that increasing steam concentration results in an overall increase trace element concentration in the sorbent for Cr, Mn, Fe, Zn and Ba

(Figure 9-7a). For the remaining elements (Mg, Al, Si, K), there is some small change in concentration with increasing steam, but generally concentrations decrease once additional steam is introduced and remain fairly constant irrespective of the quantity of steam introduced. For these elements a very small increase for 10 % additional steam is observed when compared to 5 % and 20 % additional steam. Figure 9-7b shows those elements present in decreasing concentrations when compared to the blank. The low concentration of C is unexpected given that it is a major component of limestone and may be an analytical error. However, the concentration of C in the sorbent does increase for additional steam, implying that steam improves carbonation.

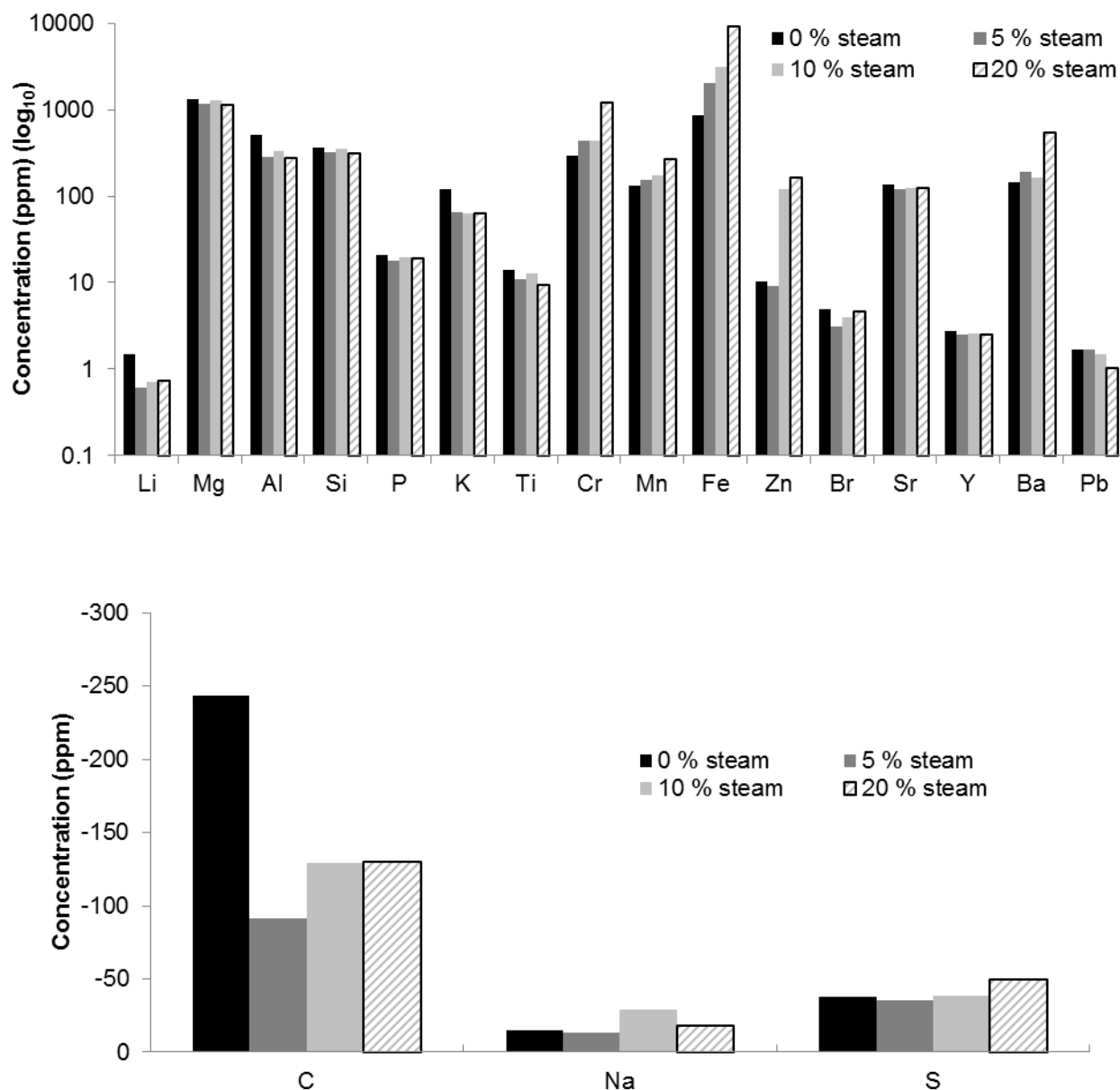


Figure 9-7 Effect of additional steam on a) increase in solid major element concentrations; and b) decrease in solid major element concentrations, for 3 kg bed inventory, and additional steam concentrations of 0, 5, 10 and 20 %. Note change in y axis values between the graphs.

Figure 9-8 shows the major element concentrations in acid solutions through which the carbonator flue gas had passed. It shows that a variety of trace elements are present in the flue gas, although there appears to be little apparent trend in terms of how the trace elements are emitted. In some cases, 10% additional steam appeared

to result in higher trace element emissions than for 20 % additional steam, as is the case for the elements Si and Zn. For several elements, 5% steam resulted in a decrease in flue gas element concentration, as is the case for Al, Si, and K. Concentrations of all elements in the flue gas are low at < 1.3 ppm.

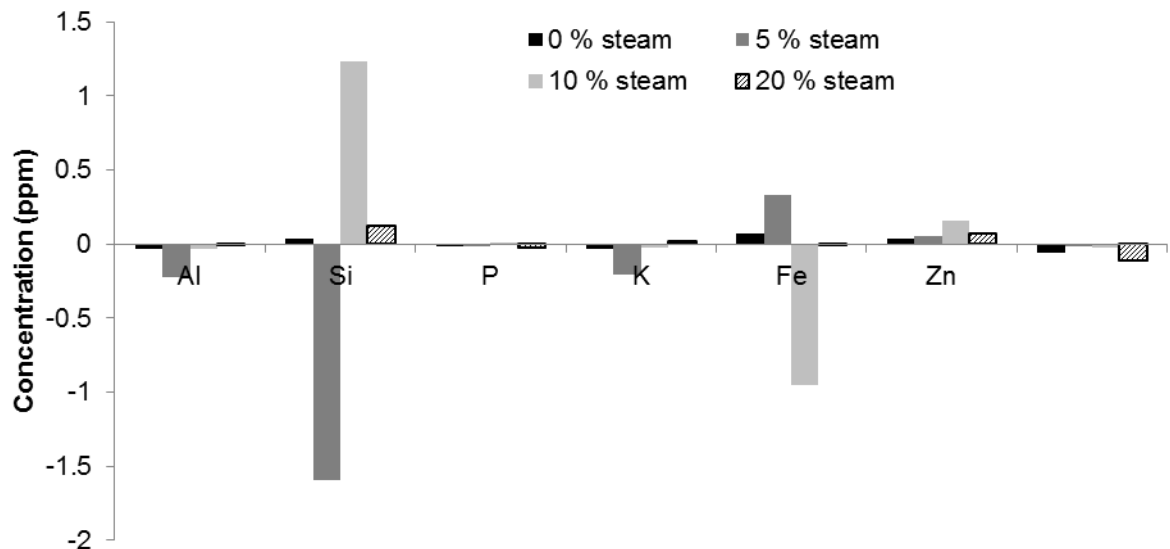


Figure 9-8 Effect of additional steam on flue gas major element concentrations for 3 kg bed inventory and additional steam concentrations of 0, 5, 10 and 20 %.

9.3.2 Minor Elements

Figure 9-9 shows the solids minor element concentrations for increasing concentrations of additional steam. For Co, Ni and Mo, concentration clearly increased as % additional steam increased. Ni had a value of 72 ppm for 0 % steam, which increased to 932 ppm for 20 % additional steam. For the majority of elements (Zr, Cd, La, Ce, Pr, Nd, Sm, Gd, Dy, U) however there was little change between concentrations with and without additional steam, although a slight decrease from 0 % to 5 % steam can be observed.

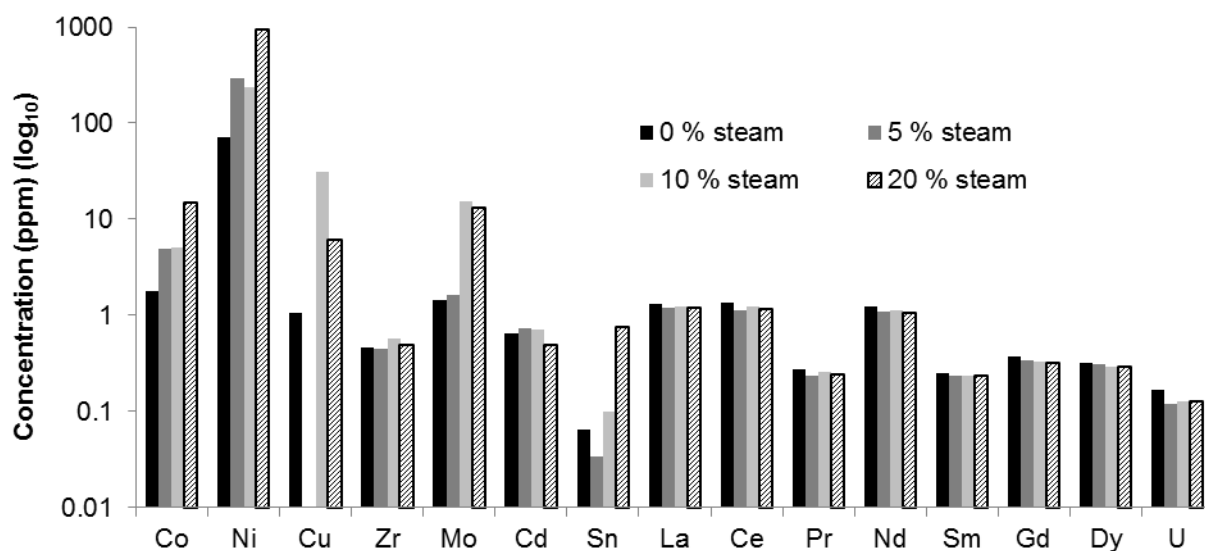


Figure 9-9 Effect of additional steam on solid minor element concentrations, for 3 kg bed inventory and additional steam concentrations of 0, 5, 10 and 20 %.

9.3.3 Trace Elements

The effect of additional steam on sorbent trace element concentration is seen in Figure 9-10. For the elements Ba and W, there is a clear, albeit small, positive relationship between increasing steam and element concentration. For Rb, Er and Yb there is minimal change in concentration for all additional values of steam.

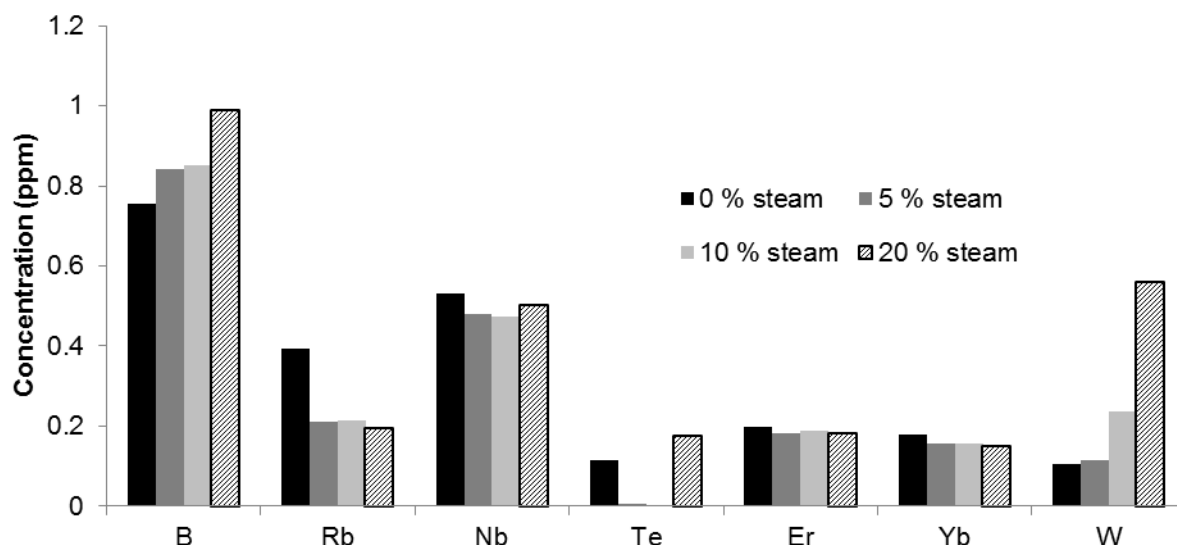


Figure 9-10 Effect of additional steam on solid trace elemental concentrations, for 3 kg bed inventory and additional steam concentrations of 0, 5, 10 and 20 %.

Those elements that appear to increase in concentration in the sorbent as a result of increasing steam concentration are again the transition elements, including Cr, Mn, Fe, Zn, Co, Ni, Cu, Mo and W. As mentioned, the transition elements have low volatility and therefore are most likely to partition to solid phases. In addition, the reactor is made from 310 stainless steel the composition of which is provided in Table 9-4. The reactor materials are comprised of Fe, Cr and Ni in the largest quantities, and concentrations of which were also present in high quantities (9207, 1257 and 932 ppm respectively with 20 % additional steam) in the sorbent samples, and increased with increasing steam concentration. It may be that increasing steam concentration leads to enhanced oxidation of the reactor, leading to corrosion and thus increasing concentrations of those elements in the sorbent samples. Stainless steel alloys with high concentrations of Cr and Ni are considered to have higher corrosion resistance in wet air, in part due to formation of a Ni-enriched layer forms [320] [321]. Whilst this may initially protect the alloy, this layer may eventually itself corrode with increased use, leading to increasing Fe, Mn, Cr and Ni concentrations within the particulate limestone sorbent. Similarly, oxidation in steam of 300-series stainless steel is known to promote formation of a Cr-rich oxide scale on the surface of the alloy. However, the rapid use of Cr in forming a protective scale when the alloy

is first exposed may result in a reduction in Cr in the subjacent alloy surface [322]. If the protective scale is lost before further Cr has been able to diffuse from the bulk of the alloy, then the steel would be prone to further rapid oxidation [322]. The high temperature, high steam and abrasive bed may contribute to corrosion of the reactor and its components.

Table 9-4 Chemical composition of 310 stainless steel from which the reactor is made.

Element	Fe	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	B
Weight %	53.22	0.048	0.32	1.43	0.023	0.0008	24.34	20.10	0.32	0.2	0.0006

Those elements whose concentrations in the sorbent are shown to decrease with increasing steam concentration are Li, Mg, Al, Si, K, Ti, Pb, Rb. The majority of decreases are small in value, although Al concentration in the sorbent with 0 % steam was 507 ppm, which decreased to 277 ppm with 20 % additional steam. Pb is considered a volatile element, and therefore concentration of which in the sorbent is expected to decrease as it partitions to the gaseous phase. Steam addition during carbonation retains finer pores, and thus reduces diffusion resistance through the carbonate layer [150]. Other than Ca, Mg, Al and Si can be considered to be predominant components of limestone, and therefore it may be that with finer pores retained, there is a greater volume over which the ions can exchange for Mg, Al and Si from within the lattice structure.

The remaining elements appear to show little change in concentration in the sorbent as a result of increasing steam concentration.

9.3.4 SEM-EDS Analysis

Figure 9-11 shows SEM-EDS analysis of sorbent samples from the single column tests. Results show that increasing steam generally appears to improve the extent of calcination of samples, shown by decreasing weight % of C and O, and increasing weight % of Ca. However, for 20 % steam, the opposite effect seems to occur. This may be because there is an optimum amount of steam which enhances calcination, beyond which negative effects occur. Although steam acts to improve CO₂ capture efficiency of the calcium looping cycle, it has been suggested that additional steam may enhance attrition in multiple hydration cycles due to crack formation [153],

although in this case single column tests did not employ multiple cycles. The addition of 20 % steam appears to greatly enhance the weight % of Fe present in the sorbent at 6.1 %, which was not identified for the other tests. This result may be due to enhanced corrosion of the stainless steel reactor and its components, particles of which may have been sampled along with the sorbent. The presence of S can be attributed to contamination from previous tests run with SO₂ in the same reactor, and is unlikely to have arisen only from the steam tests.

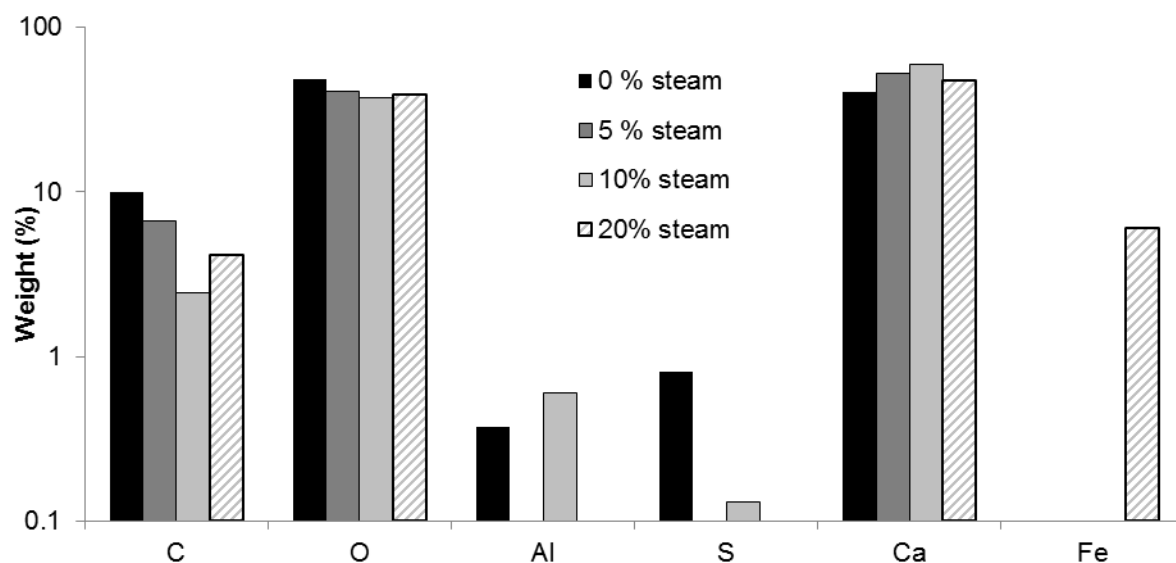


Figure 9-11 SEM-EDS analysis of solid sorbent taken from the carbonator after testing with increasing additional steam concentrations of 0, 5, 10 and 20 %.

9.4 Experimental Elemental Gaseous Emissions – Effect of SO₂ Concentration

SO₂ is prevalent in coal combustion systems and therefore its effects on elemental partitioning have been investigated in both single column and looping CO₂ capture experiments.

9.4.1 Single column tests

9.4.1.1 Major Elements

Figure 9-12 outlines the effect of SO₂ on trace element concentration in the sorbent. The results show that 1000 ppm SO₂ causes a decrease in elemental concentration for all elements except Li. This too is shown in Figure 9-12b for S, which shows a reduced value for S at 1000 ppm SO₂, when compared to 0 and 2000 ppm SO₂.

Despite this, EDS analysis (Figure 9-18) shows an increase in S with increasing SO₂ concentration. This suggests that S is being removed from the sorbent at 1000 ppm.

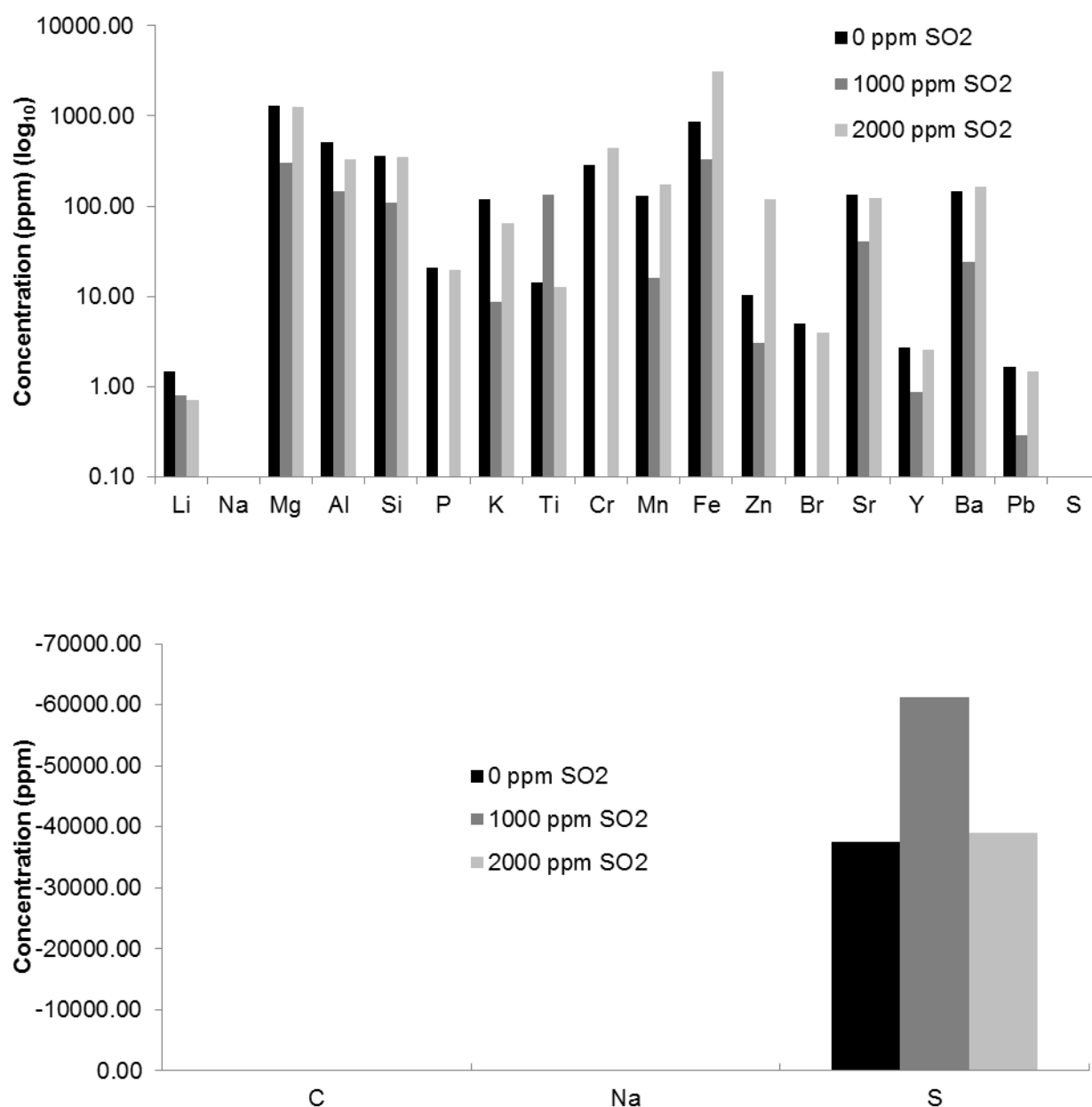


Figure 9-12 Effect of SO₂ on a) increase in solid major elemental concentrations; and b) decrease in solid major elemental concentrations for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO₃. Note change in y axis values between the graphs.

The effect of SO₂ concentration on gaseous major element release was also investigated, results of which are provided as Figure 9-13. The results confirm that

1000 ppm SO₂ concentration generally acts to increase major element emissions, particularly for Na, Si, Fe, Zn and Br. However, there are some elements which are the exception to this, including Mg which in fact increases in flue gas concentration as SO₂ concentration increases. The larger molar volume of CaSO₄ (46 cm³/mol) compared to CaCO₃ (37 cm³/mol) may reduce ion-exchange and covalent bonding within the pore structure, causing enhanced elemental release in the majority of cases. The fact that emissions do not increase linearly with increasing sorbent mass or SO₂ concentration implies that the chemistry of the system is complex.

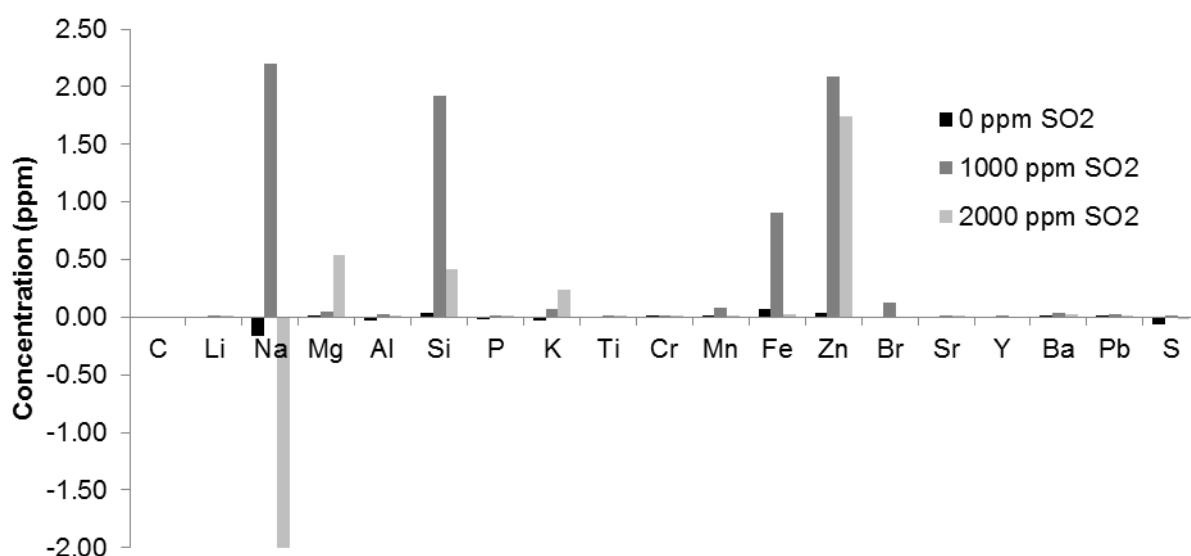


Figure 9-13 Effect of SO₂ concentration on flue gas major element concentrations for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO₃.

9.4.1.2 Minor Elements

Figure 9-14 provides results of the effect of SO₂ on minor element concentration in solids. Similar trends are apparent as for the major elements, in that 1000 ppm SO₂ appears to have a strong and reducing effect on minor element concentration. The exceptions to this are for the elements Mo and U which show an increase and decrease respectively in concentration with increasing SO₂ concentration. Despite the low values achieved, the flue gas minor element concentrations are provided in Figure 9-15, which show that for Co, Ni, Cu and Sn in particular, an increase in concentration is apparent at 1000 ppm SO₂.

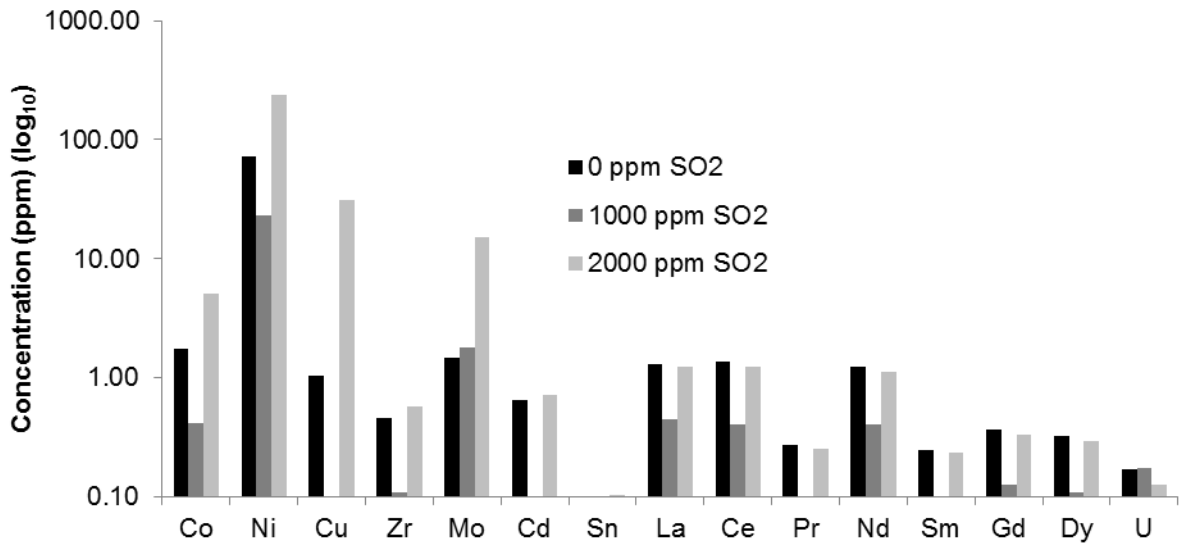


Figure 9-14 Effect of SO₂ concentration on solids minor element concentrations for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO₃.

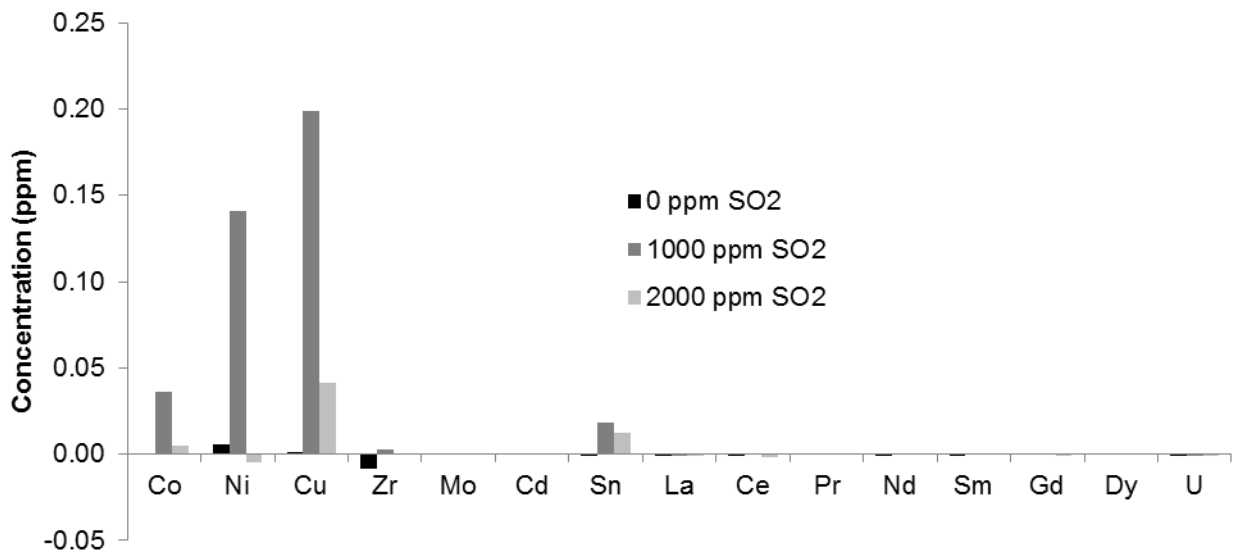


Figure 9-15 Effect of SO₂ concentration on flue gas minor element concentrations for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO₃.

9.4.1.3 Trace Elements

Figure 9-16 shows that for trace elements, 1000 ppm SO₂ results in a lower elemental concentration in the sorbent than for 0 and 2000 ppm SO₂. The exception

to this is for Be which shows a reduction in concentration with increasing SO₂ concentration.

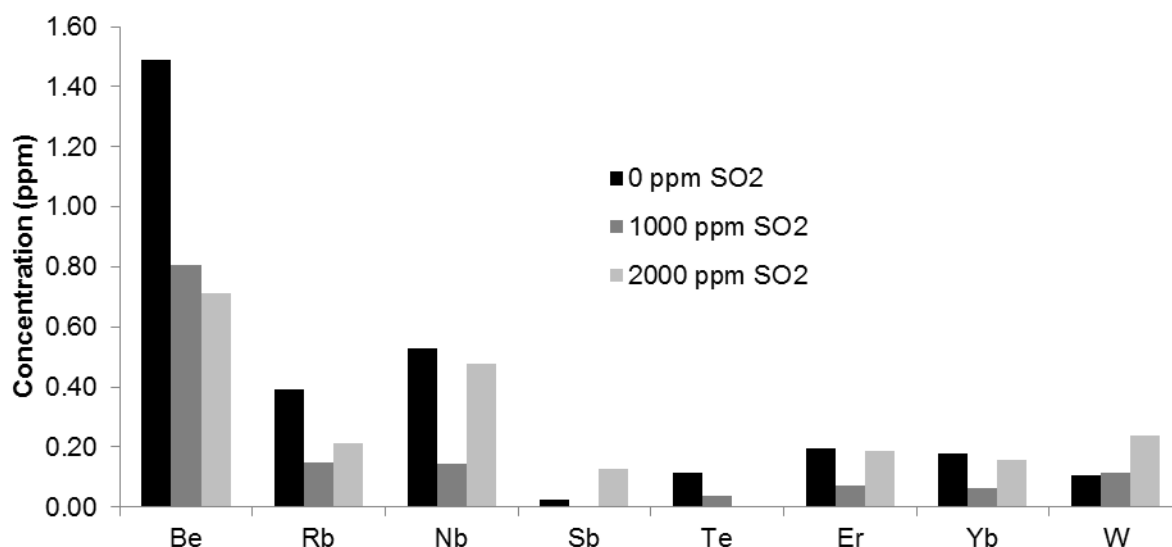


Figure 9-16 Effect of SO₂ concentration on solids trace element concentrations for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 3 kg CaCO₃.

The effect of 1000 ppm SO₂ on elemental concentration in the sorbent and also the flue gas, when compared to that of 0 and 2000 ppm is unexpected. SO₂ is known to reduce attrition effects experienced by limestone sorbents. Figure 9-17 shows PSD analysis of sorbent samples taken from the carbonator after testing, which shows a similar and larger PSD for sorbent tested in 1000 and 2000 ppm SO₂, than in 0 ppm SO₂. It may be the case that at 1000 ppm SO₂, a ‘compromise’ is reached between blocking of pores as a result of sulphation, and extent of attrition, resulting in a decrease for the most part in sorbent elemental concentration due to enhanced ion exchange over a greater surface area. At higher SO₂ concentrations of 2000 ppm, greater pore pluggage occurs, leading to retention of impurities within the limestone structure. With regards to Se, Agnihotri *et al.*, 1998 [323] investigated simultaneous capture of SO₂ and SeO₂ by CaO, for SO₂ concentrations of 1-4 ppm, and found that pore blocking due to CaSO₄ rendered CaO inaccessible for trace metal species. By contrast, for investigations into SeO₂ capture by CaO at SO₂ concentrations of between 24 and 2675 ppm, Li *et al.*, 2006 [259] concluded that the product layer of CaSO₄ formed on the CaO surface had no obvious effect on the ability of CaO to

absorb SeO_2 . It is apparent however in this study that SO_2 concentration does have an effect on sorbent elemental concentration. For several elements, and particularly in the case of Na, Si, Zn, Co, Ni, and Cu, the decrease in sorbent concentration coincides with an increase in flue gas concentration, although the decrease in sorbent concentration appears not to equal the increase in flue gas concentration, suggesting that the metals are being sorbed elsewhere, including onto the reactor itself.

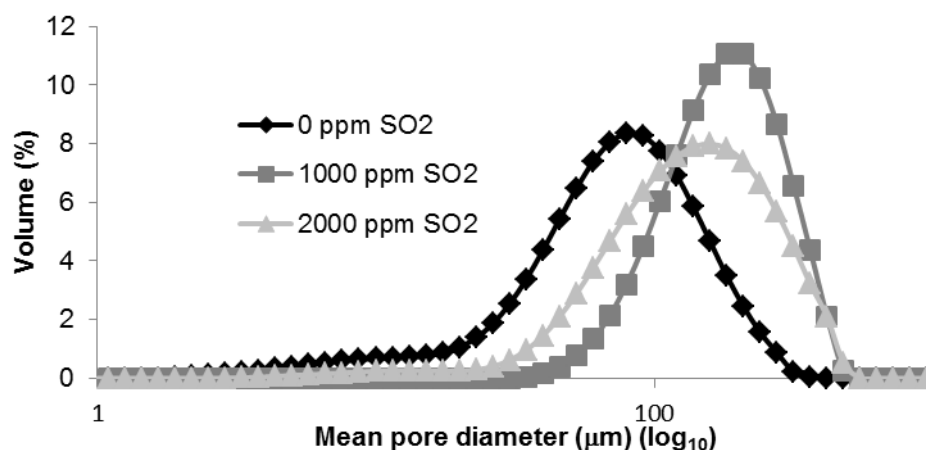


Figure 9-17 Effect of SO_2 (single column batch tests) on particle size distribution of sorbent samples from carbonator, for SO_2 concentrations of 0, 1000 and 2000 ppm SO_2 .

9.4.1.4 SEM-EDS Analysis

Figure 9-18 confirms that SO_2 concentration appears to have had an effect on C, O and Ca weight %, with C and O decreasing with increasing SO_2 , and Ca increasing slightly with increasing SO_2 . This suggests that the presence of SO_2 decreases the extent to which CaO is able to convert to carbonate in the reactor. It is widely accepted that the presence of SO_2 during the carbonation reaction produces CaSO_4 on the sorbent particle pore surfaces, which reduces the extent to which CO_2 can diffuse into pore space and react to form CaCO_3 [9]. As expected, the weight % of S present in the sorbent samples increased from 0.81 % to 4.73 %, to 10.32 % for SO_2 concentrations of 0, 1000 and 2000 ppm respectively, with a value of 0 % for unreacted limestone. The value of 0% for unreacted limestone, but the presence of S identified during ICP-MS analysis (Figure 6-6) may be due to the higher range that ICP-MS analysis can undertake. In terms of other element species, an SO_2 concentration of 1000 ppm appears to result in higher weight % values for Al, Fe, Mg

and Si, than for SO₂ concentrations of 0 ppm and 2000 ppm SO₂, with Fe, Mg and Si not present at other SO₂ concentrations. This result is unexpected, but it may be that, as mentioned previously in section 3.2 the higher concentration of SO₂, and in turn CaSO₄, results in greatly reduced available pore space and therefore bonding between these species, when compared to 1000 ppm SO₂. In turn, it may be that the presence of 1000 ppm SO₂ causes some corrosion of the stainless steel reactor itself, resulting in small deposits on the sorbent particles, although it would be expected that if this were the case, higher values would also be achieved for 2000 ppm SO₂. Miller *et al.*, 2002 [244] investigated the influence of SO₂ on trace element behaviour during wood-bark combustion, and concluded that SO₂ increased emissions of Cd, but reduced emissions of As and Hg. Overall, it is apparent that the interactions that take place in the presence of SO₂ are complex.

The SEM-EDS analysis provides useful data, but due to it having a smaller range than ICP-MS, cannot show data for elements below a certain concentration, and therefore shows data for fewer elements than ICP-MS. Nonetheless, EDS data is useful in outlining trends for the elements which are analysed, and for supporting results achieved using ICP-MS.

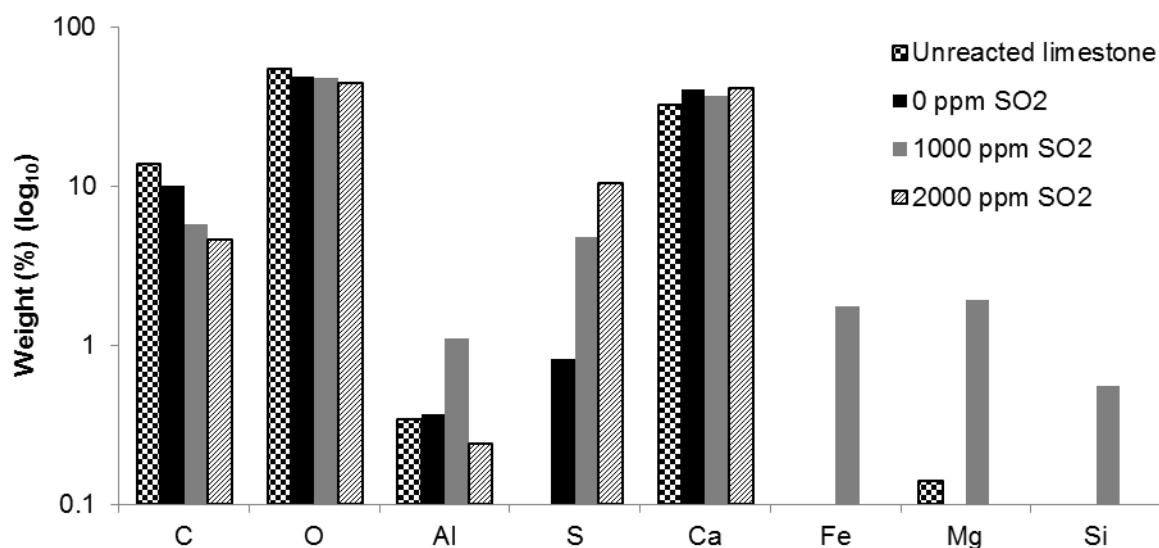


Figure 9-18 SEM-EDS analysis of solid sorbent taken from the carbonator after testing with increasing SO₂ concentrations of 0, 1000, and 2000 ppm SO₂.

9.4.2 Looping Cycle Tests

9.4.2.1 Major Elements

Figure 9-19 shows that increasing SO₂ concentration has some effect on major element concentration in solids. Concentrations of Mg, Al, Si, P, K, Br, Sr, Y, Ba and Pb appear to decrease as SO₂ concentration increases. However, there appears to be little difference between concentrations for 1000 and 2000 ppm, the greatest change in concentration being from 0 to 1000 ppm SO₂. The trend in the batch experiments whereby concentrations of elements at 1000 ppm were generally lower than at 0 and 2000 ppm, is also seen for some elements in the looping cycle test including Cr, Mn and Fe, but not to the same extent as was seen in the batch tests. Ti shows the same trend for looping tests as for single column tests, with 1000 ppm SO₂ showing higher concentrations of Ti (135 ppm for single column, 407 ppm for looping test) compared to 0 and 2000 ppm SO₂ at values close to 10 ppm Ti in both tests. Zn is the only major element showing a clear increase in concentration with SO₂, increasing from 9.4 to 14.1 to 66.8 ppm for SO₂ concentrations of 0, 1000 and 2000 ppm respectively.

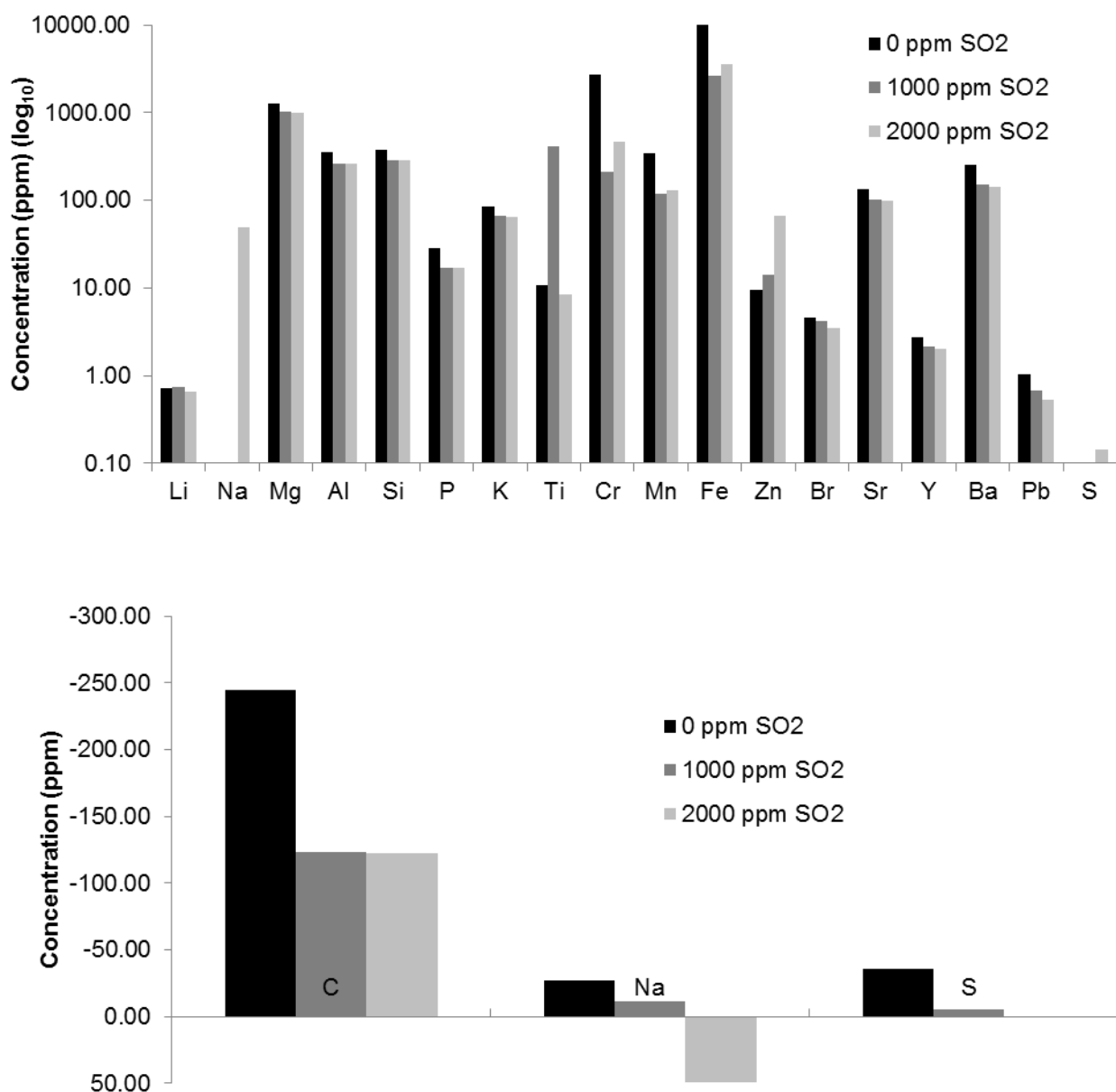


Figure 9-19 Effect of SO₂ on a) increase of solid major elemental concentrations; and b) decrease of solid major elemental concentrations for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 13 kg CaCO₃. Note change in y axis values between the graphs.

Figure 9-20 shows how gaseous major element concentrations were affected by flue gas SO₂ concentration. Concentrations of all were very low at <1 ppm, with Fe and Si present in the highest concentrations at 0.63 and 0.51 ppm respectively. For several elements, 1000 ppm SO₂ resulted in either the highest concentrations, as was the case for Na, Al, and Si, or the lowest concentrations, as was the case for Fe, when compared to 0 and 2000 ppm SO₂.

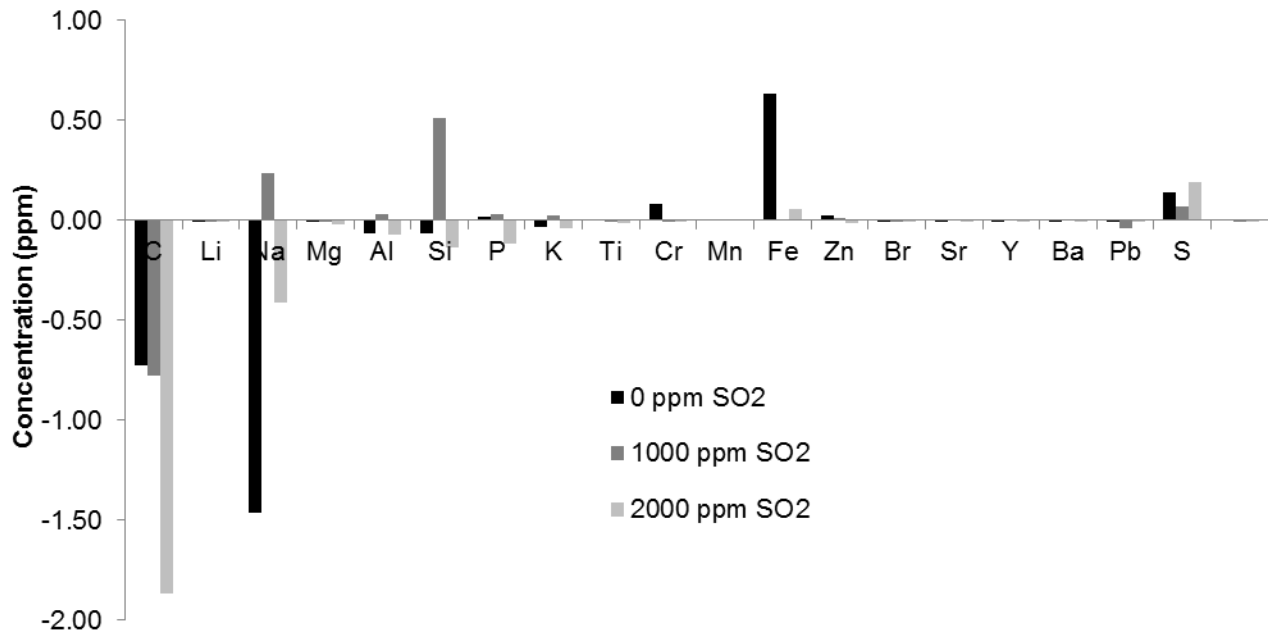


Figure 9-20 Effect of SO₂ on increase of flue gas major elemental concentrations for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 13 kg CaCO₃.

9.4.2.2 Minor Elements

1000 ppm SO₂ concentration in looping cycle tests again appears to have some influence in reducing the concentration of some minor elements, when compared to 0 and 2000 ppm SO₂ (Figure 9-21). This is the case for the elements Co, Ni, Zr, Mo, Cd, Sn and Ce. For the remainder of the elements shown, there was a small decrease in value with increasing SO₂, other than for Cu which saw a small increase in value from 9.74 to 14.13 ppm for 0 ppm and 2000 ppm SO₂ respectively.

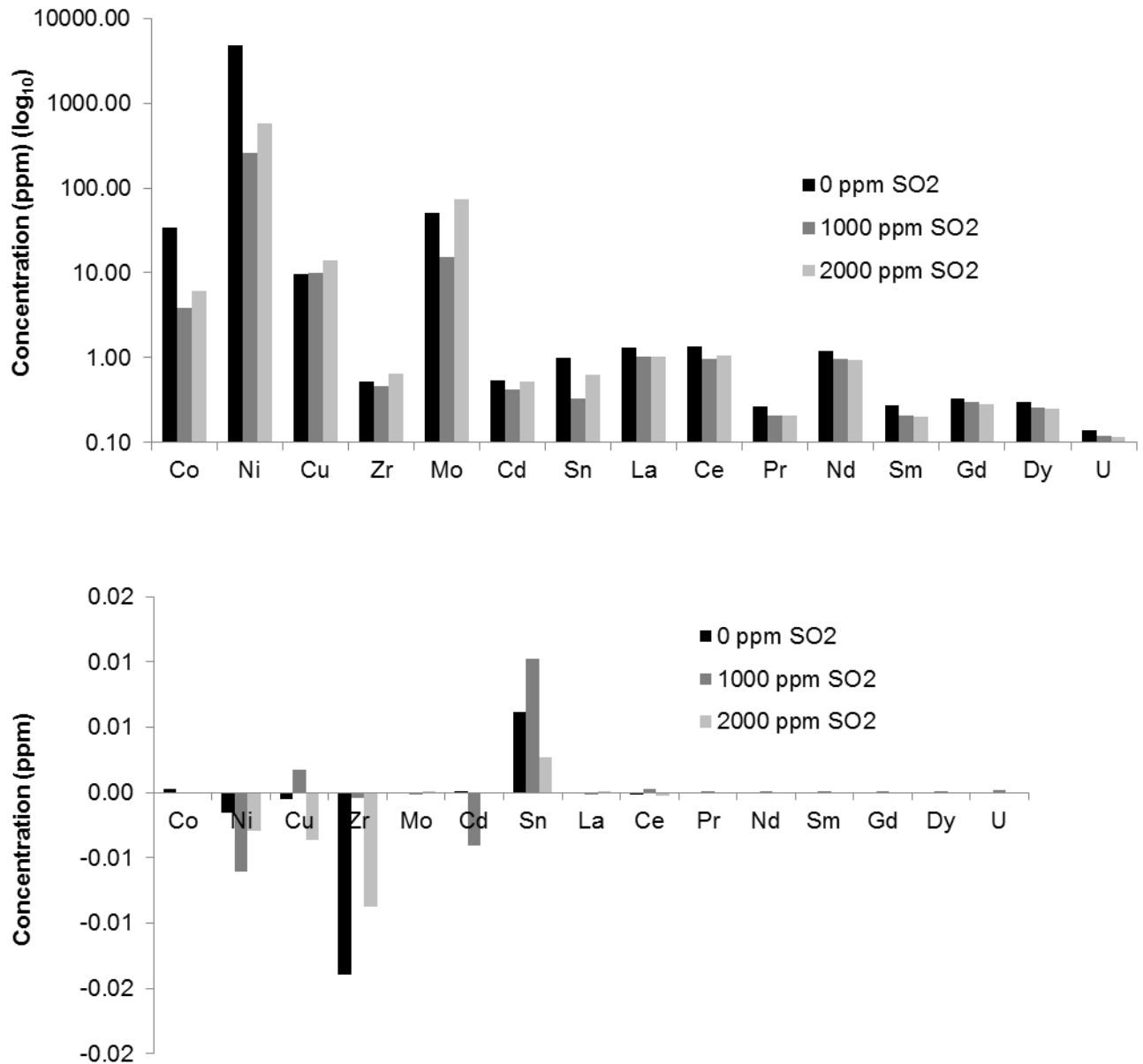


Figure 9-21 Effect of SO₂ on a) increase of solids minor elemental concentrations; and b) increase and decrease of flue gas minor elemental concentrations, for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 13 kg CaCO₃. Note change in y-axis values between graphs.

9.4.2.3 Trace Elements

Figure 9-22 shows that increasing SO₂ concentration does influence trace element sorbent concentration, and for B in particular, concentrations rose from 2 ppm to 2.6 ppm for 0 and 1000 ppm SO₂ respectively. W experienced a decrease with increasing SO₂ concentration from 1.3 ppm to 0.08 ppm for 0 and 1000 ppm SO₂

respectively. Although trends are apparent for the trace elements, concentrations are low, reducing the reliability of the results and in turn the trends observed.

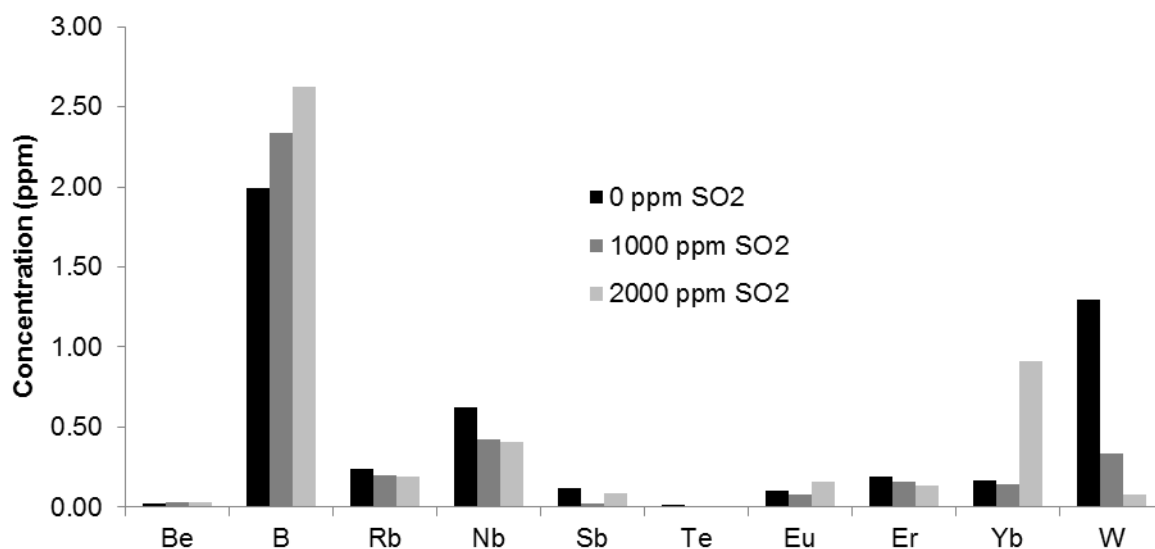


Figure 9-22 Effect of SO₂ on increase of solids trace elemental concentrations for SO₂ concentrations of 0 ppm, 1000 ppm and 2000 ppm, and bed inventory of 13 kg CaCO₃.

The results shows that as with single column batch tests, looping cycle tests carried out in the presence of increasing concentrations of SO₂ resulted in, for the most part, a decrease in elemental concentrations in both solid sorbent and flue gas samples. A small number of elements appeared to increase in concentration with increasing SO₂ concentration, including Zn, Cu, B and Yb. Iron cation exchange sites may account for the increase in concentration of the transition metals Zn and Cu.

Figure 9-23a shows a slight decrease in mean pore diameter for increasing concentrations of SO₂, indicating that SO₂ had a minor negative effect on particle attrition. Similar results were found by Coppola *et al.*, 2012 [302] (Figure 9-23b) when investigating effects of SO₂ concentration (110 and 1800 ppm) on limestone attrition, of limestone particle size 0.4-0.6 mm in a bench scale bubbling fluidised bed reactor. Although results between tests are very similar, the slight decrease in particle size with increasing SO₂ is in contrast to the reported beneficial effects of SO₂ with regards to attrition, and may be due to incomplete sulphation occurring, meaning that the sorbent strength as a result of CaSO₄ formation had not reached its optimum. The slight decrease in particle size may allow for a greater surface area over which contaminant elements can react, and thus reducing in concentration. This

in turn suggests that should sulphation fully occur, this would result in an increase in trace metal concentration in the sorbent. The difference in PSD results between batch and looping tests may be a result of enhanced attrition due to greater abrasive action in looping cycle tests compared to single column batch tests. Similarly, sulphation reactions in the batch tests may have occurred more readily than in looping tests due to a smaller volume of the reactor within which the reactions were occurring.

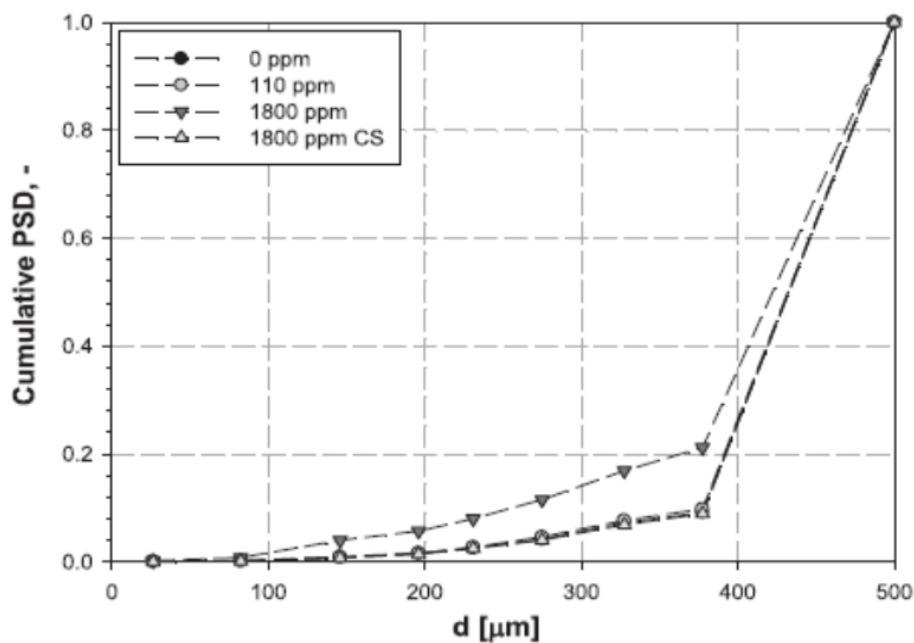
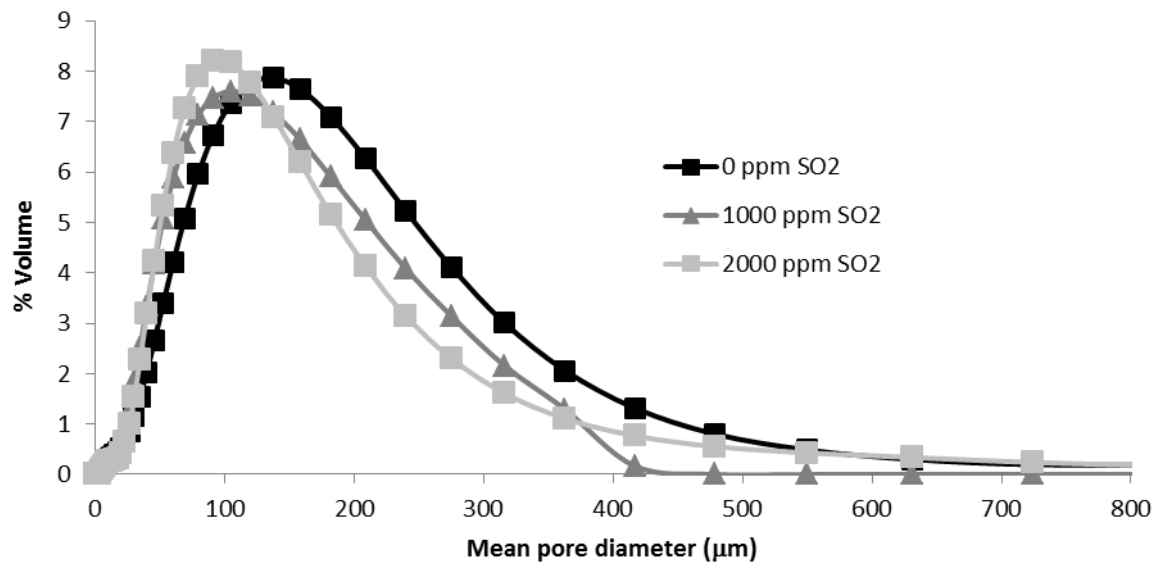


Figure 9-23 a) Effect of SO₂ (looping cycle) on particle size distribution of sorbent samples taken from carbonator after testing; b) effect on SO₂ on cumulative PSD of Italian limestone [302].

9.4.2.4 Mass Balance

A mass balance showing effects of increasing SO₂ concentration on elemental partitioning for the carbonator is provided as Table 9-5, calculated based on the incoming and outgoing concentrations of elements. A mass balance closure value of 1 indicates outgoing concentrations equal to incoming concentrations, and as shown

by the low closure values, partitioning was always higher to the solid samples than in the flue gas samples, with very low concentrations partitioning to the flue gas.

Table 9-5 Mass balance for effect of SO₂ concentration during looping cycle experiments, showing elemental partitioning between solid and gaseous phase.

	Major Elements	Units	C	Li	Na	Mg	Al	Si	P	K	Ti	Cr	Mn	Fe	Zn	Br	Sr	Y	Ba	Pb	S	Ga
0 ppm	Solid samples in	ug/min	-294050	868.1511	-32777.2	1526918	426314.2	449530.5	34032.52	101167.9	12874.59	3284404	413667.7	21054172	11329.86	5540.994	159610.7	3240	302223	1260.119	-42992.9	600.2386
	Gaseous samples out	ug/min	-0.25149	-5.9E-06	-0.50866	-0.00182	-0.02364	-0.02194	0.006793	-0.01158	0.001732	0.028169	0.000131	0.219586	0.009444	-0.00042	-5.2E-06	-9E-06	-5.4E-05	-0.00163	0.048683	6.94E-07
	Mass balance closure (out/in)	n/a	8.55E-07	-6.8E-09	1.55E-05	-1.2E-09	-5.5E-08	-4.9E-08	2E-07	-1.1E-07	1.35E-07	8.58E-09	3.17E-10	1.04E-08	8.34E-07	-7.5E-08	-3.3E-11	-2.8E-09	-1.8E-10	-1.3E-06	-1.1E-06	1.16E-09
1000 ppm	Solid samples in	ug/min	-148240	886.2451	-14059.9	1229014	316214.9	343609.3	20566.01	80207.19	488837.3	252730	144306.9	3125555	16916.68	4952.253	123817.9	2591.146	180717.2	821.9763	-6529.8	0
	Gaseous samples out	ug/min	-0.27001	-0.0006	0.08294	-6.9E-06	0.010574	0.177463	0.011236	0.00778	-0.00082	-9.5E-05	0.000126	0.001092	0.004723	-0.00095	6.07E-05	6.94E-06	0.000477	-0.01281	0.024124	-1E-06
	Mass balance closure (out/in)	n/a	1.82E-06	-6.8E-07	-5.9E-06	-5.6E-12	3.34E-08	5.16E-07	5.46E-07	9.7E-08	-1.7E-09	-3.8E-10	8.7E-10	3.49E-10	2.79E-07	-1.9E-07	4.9E-10	2.68E-09	2.64E-09	-1.6E-05	-3.7E-06	0
2000 ppm	Solid samples in	ug/min	-147286	796.3449	58844.77	1181614	309987.9	348231.2	20374.41	78204.23	10020.1	565774.1	155200.5	4243807	80212.22	4237.35	118559.7	2445.003	169228.3	633.695	172.7013	0
	Gaseous samples out	ug/min	-0.64789	-2.9E-05	-0.14338	-0.00635	-0.02401	-0.04789	-0.04158	-0.01329	-0.005	-0.00027	8.71E-05	0.019299	-0.00582	-0.00071	-0.00028	-1.1E-05	-0.0005	-0.00206	0.067261	-5.9E-06
	Mass balance closure (out/in)	n/a	4.4E-06	-3.7E-08	-2.4E-06	-5.4E-09	-7.7E-08	-1.4E-07	-2E-06	-1.7E-07	-5E-07	-4.8E-10	5.61E-10	4.55E-09	-7.3E-08	-1.7E-07	-2.3E-09	-4.4E-09	-3E-09	-3.3E-06	0.000389	0
	Minor Elements	Units	V	Co	Ni	Cu	Zr	Mo	Cd	Sn	La	Ce	Pr	Nd	Sm	Gd	Dy	U				
0 ppm	Solid samples in	ug/min	0	40468.87	5836673	11689.38	625.0497	61476.98	637.9324	1196.899	1556.183	1612.962	323.499	1428.072	328.7475	398.4095	359.2843	165.8052				
	Gaseous samples out	ug/min	-1.1E-05	8.19E-05	-0.00053	-0.00018	-0.00485	-7.6E-06	1.08E-05	0.002141	0	-4.3E-05	-1.4E-06	-5.9E-06	-6.9E-07	-1E-06	-1E-06	-1.1E-05				
	Mass balance closure (out/in)	n/a	0	2.02E-09	-9.1E-11	-1.6E-08	-7.8E-06	-1.2E-10	1.69E-08	1.79E-06	0	-2.6E-08	-4.3E-09	-4.1E-09	-2.1E-09	-2.6E-09	-2.9E-09	-6.5E-08				
1000 ppm	Solid samples in	ug/min	0	4569.012	312779.5	11942.85	548.3004	18301.66	510.1186	398.419	1233.913	1163.953	249.4862	1169.644	246.166	356.4427	308.3004	143.2411				
	Gaseous samples out	ug/min	0	-1.7E-05	-0.00209	0.000596	-0.00015	-5.4E-05	-0.00141	0.003546	-6.6E-05	8.05E-05	2.43E-06	6.94E-06	6.94E-07	2.43E-06	6.94E-07	7.91E-05				
	Mass balance closure (out/in)	n/a	0	-3.8E-09	-6.7E-09	4.99E-08	-2.7E-07	-3E-09	-2.8E-06	8.9E-06	-5.3E-08	6.92E-08	9.74E-09	5.93E-09	2.82E-09	6.81E-09	2.25E-09	5.52E-07				
2000 ppm	Solid samples in	ug/min	0	7425.7	685066.4	16961.28	775.7853	88517.42	630.04	743.5751	1250.029	1260.308	246.9446	1125.757	238.7207	343.8035	297.43	137.0645				
	Gaseous samples out	ug/min	0	-3.5E-07	-0.00102	-0.00126	-0.00304	1.11E-05	-1.4E-05	0.000943	1.8E-05	-9.8E-05	-3.1E-06	-1.1E-05	-3.1E-06	-1.7E-06	-2.8E-06	-2.7E-05				
	Mass balance closure (out/in)	n/a	0	-4.7E-11	-1.5E-09	-7.4E-08	-3.9E-06	1.25E-10	-2.2E-08	1.27E-06	1.44E-08	-7.7E-08	-1.3E-08	-1E-08	-1.3E-08	-5E-09	-9.3E-09	-2E-07				
	Trace Elements	Units	Rb	Nb	W																	
0 ppm	Solid samples in	ug/min	289.6223	747.674	1557.614																	
	Gaseous samples out	ug/min	-1.9E-05	-1.7E-06	-1.4E-06																	
	Mass balance closure (out/in)	n/a	-6.6E-08	-2.3E-09	-8.9E-10																	
1000 ppm	Solid samples in	ug/min	236.4427	510.83	403.3992																	
	Gaseous samples out	ug/min	1.01E-05	-6.9E-07	-1.9E-05																	
	Mass balance closure (out/in)	n/a	4.26E-08	-1.4E-09	-4.8E-08																	
2000 ppm	Solid samples in	ug/min	230.9537	489.7773	1090.348																	
	Gaseous samples out	ug/min	-1.8E-05	0	-3.8E-06																	
	Mass balance closure (out/in)	n/a	-7.7E-08	0	-3.5E-09																	

9.4.3 SEM-EDS Analysis

Results of SEM-EDS analysis (Figure 9-24) for sorbent taken from the carbonator after each test with additional SO₂, shows that increasing SO₂ results in a greater weight % of C and O, but a decrease in weight % of Ca. Although there is a substantial change in elemental weight % between 0 and 1000 ppm SO₂, there is little change in elemental weight % between 1000 and 2000 ppm SO₂. The results suggest that solids had carbonated to a greater extent in the presence of SO₂. Although the CO₂ capture results (see Section 8.3) show that SO₂ has a detrimental effect on CO₂ capture, the result achieved here is unexpected given the widely reported negative effects of SO₂ on carbonation, and is contrary to the single column SO₂ results achieved in the same reactor. When compared to single column batch tests, the use of the looping cycle is likely to have beneficial effects in improving the extent to which the sorbent is carbonated due to enhanced fluidisation and therefore potential for reaction.

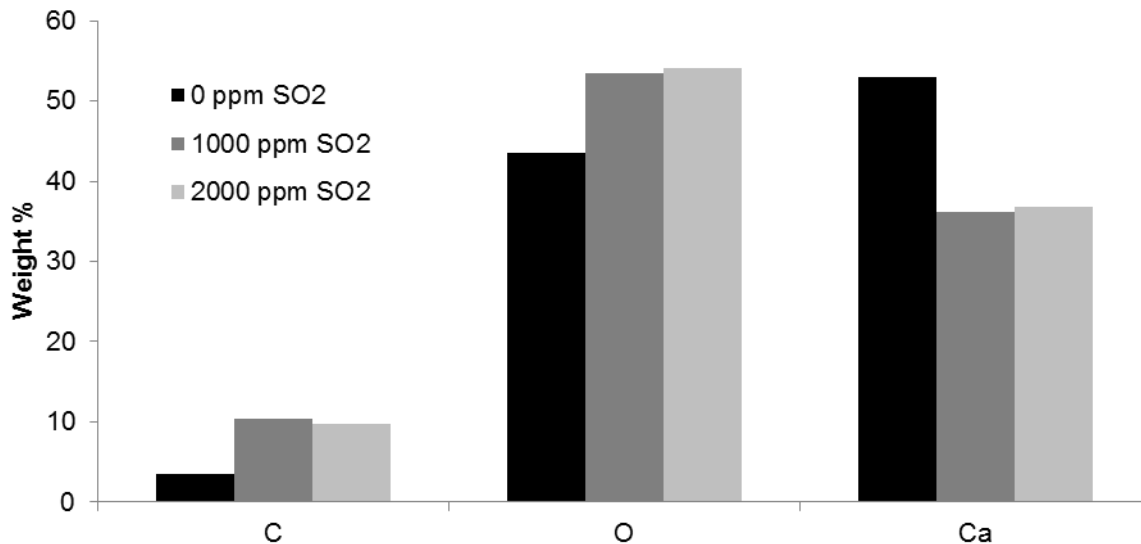


Figure 9-24 SEM-EDS analysis of sorbent taken from carbonator at the end of each test, for increasing SO₂ concentration of 0, 1000 and 2000 ppm SO₂.

9.5 Statistical Analysis

Statistical analysis has been carried out on elemental concentrations for both the solid and flue gas samples. In an ideal situation, repeats of each test would be

carried out in order to identify the variance of samples from which then to carry out an advanced statistical test such as analysis of variance (ANOVA), from which to identify if difference in values between tests was statistically significant. However, due to financial and time limitations, test repeats were not possible. Analysing more than one sample from the same test in order to achieve repeat values would also not have been helpful, because samples would have been from the same test, rather than from separate tests. Therefore, the decision was made to carry out a statistical 'multi-variate analysis technique' known as 'principal component analysis' (PCA), to allow identification of a difference in data sets between tests for indicative purposes. PCA transforms a number of possibly correlated variables within a data set, into a smaller number of uncorrelated variables called 'principal components' that will express as much of the total variance in a data set as possible [324]. This allows identification of other underlying variables which may represent further correlation in the data, and also reduces the dimensionality of the data set in question.

All PCA analysis results are provided as Appendix F. Based on the PCA results, further work outside the remit of this thesis would focus on those correlations identified from the PCA results, and in turn carrying out the required test repeats so that the more advanced ANOVA tests could be carried out on the data. Figure 9-25 is provided as an example and shows results of PCA analysis for increasing bed inventory and elemental concentration in solids. Firstly, the sum of Factor 1 bed inventory (82.5 %) and Factor 2 elemental concentration (17.49 %) is almost 100 %, showing that there is a high correlation between the two variables, implying reliable results. The results show a strong relationship between 4.5kg bed inventory, and Mg, Al, Si and Ti, implying that the highest values achieved for these elements will be for 4.5 kg. By contrast, an inverse relationship is suggested between 4.5 kg inventory and the elements Cr, S and Na, and in particular C. Figure 9-25 shows that C was found in negative concentrations, for which 4.5 kg had the lowest value. For bed inventories of 6 and 13kg, a strong relationship with Fe is apparent, implying high concentrations, whilst an inverse relationship is shown with Sr, Ba and Mn in particular. These results correspond with those shown in Figure 9-1, and are useful for supporting the work undertaken in confirming correlation between bed inventory and elemental concentration.

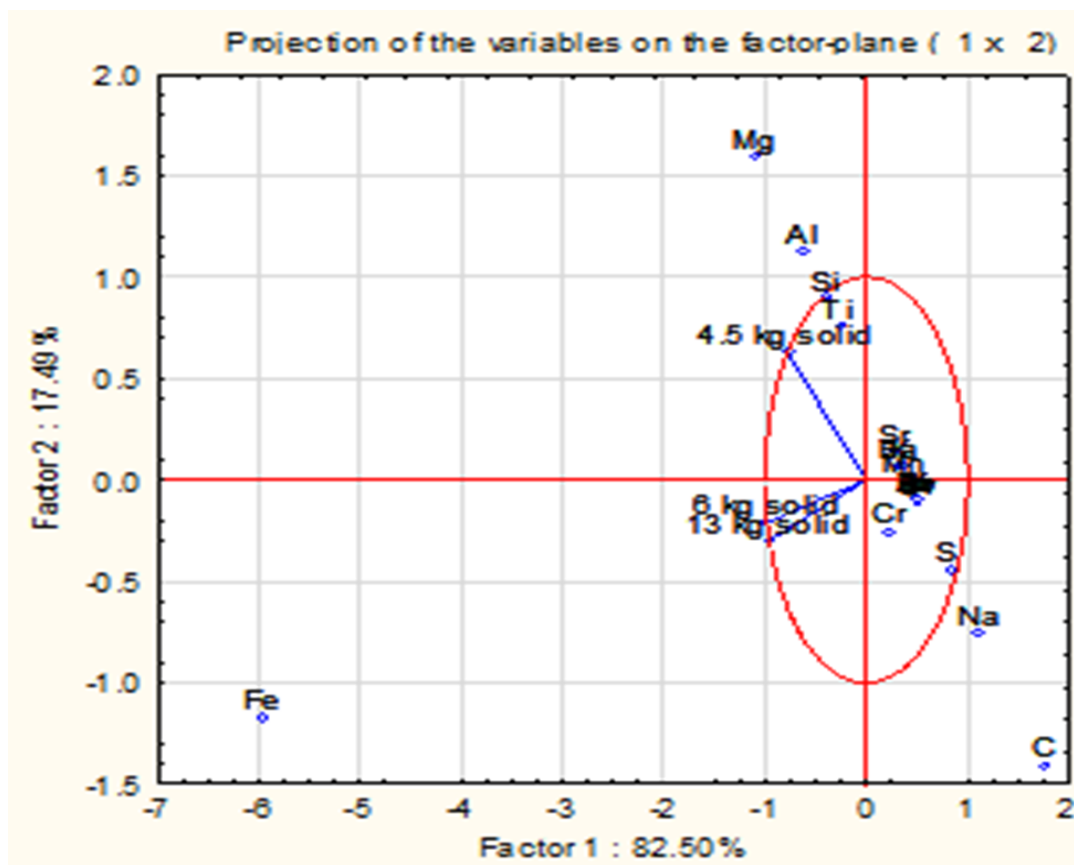


Figure 9-25 PCA analysis suggesting relationships between varying bed inventories of 4.5, 6 and 13 kg, and solids elemental concentrations.

9.6 Comparison of solid element concentrations with those found in cement

A comparison of solid elemental concentrations with those typical of cement [233] is provided in Table 9-6. Those elements found to be higher than those typical of cement are highlighted in grey. The results show that the majority of elements in sorbents analysed as part of this work are equal to or lower than average concentrations found in cement. However, there are several elements whose concentration in the limestone sorbent exceeds average cement or clinker concentrations. The maximum concentration of Cr for the additional steam and SO₂ looping cycle tests was 1207 and 2737 ppm respectively, and was found to exceed the average cement/clinker concentration of 20-450 ppm. Chromium exists as a number of oxidation states in clinker, determined by O₂ concentrations in the kiln. Cr in cement is known to accelerate hydration of paste and improve early strength, although 28 and 90 day strengths are not so improved, and it is thought that Cr may

enhance sulphate expansion and increase cement shrinkage [233]. As previously mentioned, the increased Cr levels during the additional steam test and SO₂ looping test may be a result of reactor and component corrosion. The CO₂ capture reactor is constructed from 310 stainless steel, which comprises 24.34 %wt Cr. Degradation of the reactor after multiple tests was observed by small black particles in the samples, which would act to introduce Cr into the sorbent sample.

Concentrations of Zn in the sorbent sample from the additional steam test were slightly increased over average cement Zn concentrations. Up to 1 % Zn in cement is known to cause reduced cement strength and retard hydration [233], however the concentrations at which Zn was found in the sorbent sample are unlikely to cause issues environmental / health issues. The reason for the elevated Zn concentrations is unknown, but may be due to enhanced cation exchange on reaction sites within the limestone due to retention of finer pores as a result of the use of additional steam.

Ba was also found at a higher concentration for the additional steam test than for all other tests, and was at a concentration almost double that of the average for cement. Barium activates hydraulicity and improves cement strength, and therefore can be considered to have a positive effect on cement properties [233], and therefore is not considered to be of concern with regards to use of spent sorbent for cement manufacture. Further its low volatility means that it is considered of minor environmental concern.

Ni was found present at elevated concentrations in samples from all tests carried out in this study, compared to an average cement concentration of 31 ppm. The highest concentration was in the sample taken from the SO₂ looping test at a concentration of 4864 ppm. The additional steam, bed inventory and single column SO₂ tests recorded maximum values of 932, 252, 240 ppm respectively. Ni is known to enhance cement strength, and soluble salts of which act as accelerators. However, such elevated concentrations may result in volatile Ni compounds, such as NiCO₃, present in kiln dust which could pose a risk to the environment and /or health. Ni is present in 310 stainless steel at 20.1 wt%. Given the high concentrations of both Ni and Cr for additional steam tests, it could be concluded that steam acts in the degradation of the reactor and components, resulting in high concentrations in the

sample, of elements present in 310 stainless steel. Corrosion of the reactor and components is outside the remit of this thesis, but further work could focus on this topic and the influence it may have on element concentrations of sorbent samples.

9.7 Comparison of flue gas elemental concentrations with those of cement works and lime kiln emissions limits

Table 9-7 provides a comparison of the elemental concentration of flue gas from the different tests, with those best available technique (BAT) emissions limits set by the UK Environment Agency for cement works and lime kilns [231] [232]. The results show that all of the flue gas element concentrations for the tests carried out as part of this study, are below the BAT emissions limits for Hg, Cd, Tl and Group 3 elements. This implies that should spent sorbent from the calcium looping cycle be subsequently used for cement manufacture in a bid to reduce CO₂ emissions and minimise waste, then elemental emissions in flue gas should not be of concern. However, it should be noted although the values were based on daily averages, or averages of at least half an hour and not longer than eight hours, the bed inventories used in this study range from 3 to 13 kg, whereas those from a cement works / lime kiln would use far greater quantities of solids. Similarly, the predicted input to the calciner for a theoretical 500 MW plant, is 939.5 kg/s of which 22.5 kg/s would be fresh CaCO₃ [103], and indicates the large quantities of limestone required for the Ca-looping process. Therefore, although all emissions in this study are below BAT limits, the results achieved imply that monitoring and filtration methods are likely to be required from industry employing Ca-looping as a CO₂ capture method, to ensure that emissions levels meet regulatory standards.

Table 9-6 Comparison of maximum element concentration in solid sorbent for each test, compared with typical concentration in cement. Those concentrations found to be higher in this study than in typical cement concentrations are highlighted in grey.

Element	Typical concentration in cement / clinker (ppm) [233]	Max. concentration in sorbent (ppm)			
		Bed inventory (looping cycle) tests	Additional steam (single column) tests	SO ₂ (single column) tests	SO ₂ (looping cycle) tests
Li	Up to 10,000	1	<1	1.5	0.7
Mg	10000 – 50000	317	1302	1302	1272
Al	10000 – 50000	226	507	507	355
Si	>50000	184	324	361	286
K	10000 – 50000	34	119	119	84
Ti	200 – 10000 (as TiO ₂)	159	14	136	407
Cr	20 – 450	203	1207	436	2737
Mn	~10000 (as Mn ₂ O ₃)	35	269	175	344
Fe	>50000	4596	9257	3136	17545
Zn	149	17	163	120	66
Sr	900 (as SrO)	45	135	136	133
Y	Trace amounts	<1	3	3	3
Ba	280	36	543	164	251
Pb	12	<1	2	2	1
C	>50000	-224	-91	-243	-123
Na	10000 – 50000	-122	-15	-15	49

Element	Typical concentration in cement / clinker (ppm) [233]	Max. concentration in sorbent (ppm)			
		Bed inventory (looping cycle) tests	Additional steam (single column) tests	SO ₂ (single column) tests	SO ₂ (looping cycle) tests
P	2000 (as P ₂ O ₃)	<1	21	20	28
Br	5 – 10	-1.7	4	5	5
S	10000 – 50000	-162	-35	-37468	<1
Co	130 (as CoO)	3.7	15	5	34
Ni	31	252	932	240	4864
Cu	90 (as CuO)	22	31	31	14
Zr	5000	<1	<1	<1	<1
Mo	500	40	13	15	74
La	Trace amounts	<1	1.3	1.3	1.3
Ce	Trace amounts	<1	1.1	1.4	1.3
Nd	Trace amounts	<1	1	1.2	1.2
Be	3 ppm	<1	<1	1.5	<1
B	3 ppm	<1	<1	<1	2.6

* Chakarvarti *et al.*, 1979 [325]

Table 9-7 Comparison of maximum element concentration in flue gas for each test, compared with best available technique emissions limits for a cement works and lime kiln [231] [232].

Element	Cement works / Lime kiln BAT concentration limits (ppm) [231] [232]	Maximum flue gas elemental concentration for different tests (ppm)			
		Bed inventory	Additional steam	SO ₂ (single column)	SO ₂ (looping)
Hg & compounds	<0.006	<0.006	<0.006	<0.006	<0.006
Cd & compounds	<0.01	<0.01	<0.01	<0.01	<0.01
Tl & compounds	<0.06	<0.01	<0.01	<0.01	<0.01
Sb	<0.1	<0.01	<0.01	<0.01	<0.01
As	<0.2	<0.01	<0.01	<0.01	<0.01
Cr	<0.2	0.02	<0.01	0.01	0.08
Co	<0.2	<0.01	<0.01	0.04	<0.01
Cu	<0.2	<0.01	<0.01	0.2	<0.01
Pb	<0.06	0.006	<0.01	0.02	-0.04
Mn	<0.2	0.2	<0.01	0.09	<0.01
Ni	<0.2	<0.01	<0.01	0.14	-0.01
V	<0.2	<0.01	<0.01	<0.01	<0.01

9.8 ICP-OES analysis of gas samples

A mobile Spectro CIROSCCD ICP-OES gas analyser was used to continuously monitor gas emissions and analyse the flue gas composition from the carbonator, and subsequently the calciner sample line, for 75 minutes each. This work was undertaken in accordance with Sheffield University, and therefore the text in this section on this collaborative work is included within the joint journal paper by Cotton *et al.*, 2013 (submitted) which was based on the report of this work by Finney *et al.*, 2012 [237].

9.8.1 Elements detected in Carbonator and Calciner

Table 9-8 outlines the modal average and maximum intensities (the count rates, in counts per second (cps)) of each elemental species recorded during the measurements from both the carbonator and the calciner flue gas. Higher count rates (the maximum or peak values, which are significantly above the average intensity reading) indicate the presence of an element. Seven different elements were identified from the ICP-OES, of which three elements were present at two different spectral intensity lines.

Table 9-8 Modal average and maximum intensities of elements found in both the carbonator and calciner flue gases; all values are count rates per second.

Adapted from Finney *et al.*, 2012 [237].

Element / Wavelength	Carbonator (cps)		Calciner (cps)		Technical Note
	Modal Average	Maximum	Modal Average	Maximum	
Ag 328.068	500-950	~1400	300-600	~1500	Prevalence higher for carbonator, but intensity peaks high for calciner
Al 309.271	400-750	~2750	900-1200	~4500	Higher intensity and average counts in calciner
Al 396.152	2200-2500	~2700	10,500-11,000	~13,000	
Ca 315.887	1700-2000	~2100	1000-2500	26,000	Higher intensity and variation in calciner
Cr 205.552	500-650	~750	1300-1600	~2500	Higher count rates recorded for calciner
Na 588.995	107,000-111,000	207,500	30,000-33,000	~280,000	Higher levels recorded in the carbonator
Na 589.592	3500-3900	4250	7000-8000	~9900	
S 142.503	750-1000	~1100	11,000-13,000	~35,000	Higher count rates in calciner
S 182.034	500-1200	~1400	7000-9000	~19,000	
Si 251.612	2300-2500	~44,000	2200-2400	~365,000	

The results show that overall, elemental count rates were higher for the calciner than for the carbonator. The exceptions to this were Ag at spectral line 328.068 and Na at spectral line 588.995, which both had a higher modal average count rate in the carbonator than the calciner, but the maximum intensity for both was higher in the calciner than in the carbonator.

9.8.2 Elements Detected by ICP-OES in the Carbonator Sample Only

A number of elements were detected in the carbonator sample only. There were no elements that were detected in the calciner samples only, that were not also present in the carbonator. The elements found in the calciner have been presented in Table 9-8. Table 9-9 provides the modal average and maximum (peak) intensity readings taken from ICP-OES analysis of the carbonator flue gas.

Table 9-9 Modal average and maximum intensities of elements found only in the carbonator flue gases; all values are count rates, not concentrations, and do not taken into account background readings, as no instrument calibration took place. Adapted from Finney *et al.*, 2012 [237].

Element / Wavelength	Carbonator (cps)		Technical Note
	Modal average	Maximum	
Br 144.990	300-500	~680	Little variation in spectral line
Fe 373.486	550-700	900	Mean value of 600 cps
K 766.491	400-600	~750	Mean value of 475 cps
Ni 221.648	650-800	~30,100	Very high, short-lived peak count rate recorded
P 177.495	100-200	~280	Count rates for P 178.287 were greater
P 178.287	350-450	~850	
S 147.399	250-450	~680	Count rates for S 180.731 varied significantly, decreasing over time. Peak value for the first isotope was recorded when the lowest value was taken for the second isotope.
S 180.731	400-1600	~1850	
Sb 252.852	550-700	~27,000	Peak value coincides with other high/low readings for other elements
Sc 335.373	450-700	~1200	Peak value for the first isotope was recorded at the lowest value for the second isotope
Sc 355.855	5400-6000	6600	
Si 288.158	1650-2000	~43,500	A high maximum count rate of ~43,500 cps was seen at the same point in the test for other high/low readings for other elements
Ti 334.941	1600-1800	~2200	Maximum value was not greatly above the average values

Generally, the count rate intensities were much higher in the flue gas from the calciner (Table 9-8) than for any of the spectral lines identified in the carbonator flue gas (Table 9-8 and Table 9-9).

S had two additional spectral lines detected in the carbonator that weren't detected in the calciner, S 147.399 and S 180.731. The highest values were recorded during the beginning of the test period, where intensities of more than 1800 cps were detected. The count rate intensities then dropped steadily, achieving a mean value of ~450 cps towards the later stages of the test.

Readings for a number of elements showed either particularly high count rate intensities at a certain point in the test (Al 309.271, Ni 221.648, Sc 335.373 and Si 288.158), or considerably low count rate intensities at a certain point in the test (Al 396.152, S 142.503, S 182.034, P 177.495, P 178.287, S 147.399, S 180.731 and Sc 355.855).

The results from the ICP-OES analysis for the calciner-carbonator reactors identified the potential presence of several metals in the flue gases. In the carbonator, high count rates were recorded for Na, Ni, Sb and Si in particular, as shown in Table 9-8 and Table 9-9. Na had high count rates seen for spectral line Na 588.995, with count rate values often in excess of 100,000 cps; the peak count rate for this was 207,477 cps. Elevated count rates of up to 4250 cps were also recorded for a second Na spectral line (Na 589.592). Ni had peak count rate intensities of up to ~30,000 cps at spectral line Ni 221.648, whilst the presence of antimony was detected by the high count rates of ~27,000 cps at emission spectrum Sb 252.852. Si had peak count rates of ~45,000 cps, as seen for the emission spectra Si 251.612 and Si 288.158. Other elements that are considered likely to have also been present within the flue gas emissions include Ag, Al, Br, Ca, Cr, Fe, K, P, Sc and Ti, although the count rates for these elements were much lower (generally less than 3000 cps), suggesting presence at a lower concentration. Other than calcium, which had peak count rate intensities of approximately ~2100 cps, the other metal contaminants identified in the initial limestone were not considered to be present in the flue gas emissions. Of these elements, Mg, Fe and Sr, only Fe may have been

contained within the gases, as a maximum count rate for this of ~900 cps was recorded at spectral line Fe 373.486 [237].

For the calciner, high count rates were recorded for several elements, including Al, Ca, Na, S and Si, as presented in Table 9-8. Si had the highest peak count rate at 364,844 cps for spectral line Si 251.612. This spectral line was also elevated in the carbonator data, as previously mentioned. Na, at spectral line Na 588.995, was also found at high intensities, with count rates peaking at over 280,000 cps. High maximum count rates were also identified for other elements, including S, with 35,214 cps at spectral line S 142.506 and 18,937 cps for S 182.034; Ca had 26,119 cps for spectral line Ca 315.887; and Al had 13,275 cps at spectral line Al 396.271. Elevated count rates at other emission spectra of some other elements were also detected, including Ag 328.068, Al 309.271, Cr 205.552 and Na 588.995. The main impurities identified in the original limestone sample in the highest concentrations, Mg, Fe and Sr, could not be detected with any degree of certainty, suggesting that these elements were either not present in the gas-phase or were below the detection limit of the instrument [237].

It is apparent from ICP-OES elemental analysis of gas samples that naturally-occurring elemental impurities in limestone impact the composition of the calcium looping cycle flue gases. A wider range of impurities were identified in the carbonator flue gas when compared to the calciner flue gas, although those present in the calciner generally appeared to be at a higher concentration than those from the carbonator. This may be due to the higher temperatures present in the calciner, allowing those elements of lower volatility to partition to the gas phase. Predominant impurities identified from the ICP-OES analysis included Ni, Na, Sb and Si.

9.9 Thermodynamic Modelling - Sensitivity Analysis

A sensitivity analysis was carried out using MTDATA, in order to determine the effect of the presence of certain elements on the formation of compounds. The

analysis was carried out using the statistical method 'non-parametric Kruskal-Wallis ANOVA by ranks', using STATISTICA software (CSS Statistica/W, Release 5.0 with Industrial units, Statsoft UK). This method allows the comparison of two or more independent samples, and uses the sum of the difference between mean ranks of the samples, as the statistic. This then provides an indication of whether the absence of an element input to the model has an effect on the stability of a certain compound in the model output.

Due to extended calculation times required, a sensitivity analysis was carried out firstly for nine elements (Ba, Cd, Cr, K, Mg, Ni, Sr, Ti, Zn) and then for twenty-one trace elements (Li, Be, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Sr, Cd, Sb, Ba, Hg, Pb), in addition to the four 'base' elements (Ca, C, O, H) (always considered to be present from limestone and gas input), based on those which are considered to be most volatile, have the greatest negative impact on the environment and health, and which were present in the highest quantities in the limestone as identified by ICP-MS analysis, as outlined in Figure 6-6. MTDATA was run for all of 'base' elements and either the nine or twenty one elements present, and the data recorded. One element was then removed to see the effect on compound stability and formation. For the next run, this element was included, and the next trace element removed, and so on.

The results for carbonation and calcination respectively, are shown in Table 9-10 and Table 9-11 below. The results identify that for both carbonation and calcination, Mg has a strong link with the presence of many compounds, including CaCO_3 . In the case of the sensitivity analysis based on 9 elements, Mg appears to be the only element that has a link effect with the presence of compound formation in the model output. However, in the case of the sensitivity analysis based on 21 elements, a greater number of elements have a link with the presence of compounds formed under carbonation conditions, including Mg and Al, having a link with the greatest number of compounds. The reason for this may be that Ca and Mg are found in group 2 of the periodic table, and as one moves down group 2, the number of outer shells of each element increases, causing the reactivity of the group 2 elements to increase. Mg has

two outer shells, Ca has three outer shells, Sr has four, and Ba has five outer shells, meaning that Sr and Ba are generally more reactive than Ca and Mg. At higher temperatures however, the extra energy available means that in addition to Sr and Ba, Mg is also able to react and form compounds in place of CaCO_3 . The increased number of elements that have are linked with the presence of compounds under calcination conditions compared to carbonation conditions again may be due to the increased temperatures at which calcination is carried out, thus allowing the less volatile elements to react, due to an increased amount of thermal energy available for activation energies. It is also apparent that increasing the number of trace elements present in the model, increases the chemical interactions that are likely to take place. For example, when 21 trace elements are included in the model in addition to the four base elements, there are a greater number of compounds that are affected by the presence or absence of another trace element, compared to when only 9 elements are included in the model.

Table 9-10 MTDATA sensitivity analysis results for 9 elements.

		Compound presence significantly affected by absence of trace element in model		
		CaCO ₃	CaO	CH ₄
Trace element absent from carbonator model	Mg	/		
Trace element absent from calciner model	Mg		/	X

/ is removal of element from model increases compound presence; X is removal of element from model decreases compound presence.

Table 9-11 MTDATA sensitivity analysis results for 21 elements.

		Compound presence significantly affected by absence of trace element														
		CaCO ₃	LiCrO ₂	CaO	C	CH ₄ (g)	C ₂ H ₄ (g)	H ₂ (g)	Pb	Hg (g)	MnO	Ni	NiSb	SrO (g)	LiOH (g)	KOH (g)
Trace element absent from carbonator model	Mg	/		/												
	Ni															
	Al		/													
Trace element absent from calciner model	Mg			X	X	X	X	X	/		/	/	/			/
	Al				/							/		/		
	Sr				/											
	Pb					X										
	K						/									
	V						/									
	Se									/						
	Cr														/	
	Co								/							
	Ba								/							

/ is removal of element from model increases compound presence; X is removal of element from model decreases compound presence

9.9.1 Thermodynamic Modelling – Effect of Sorbent Mass

MTDATA estimates of the likely elemental partitioning including compound formation and associated phases, for increasing bed inventory are shown in Figure 9-26, Figure 9-27 and Figure 9-28. The bed inventories used in the model were 4.5 kg, to 6 kg, and 13 kg. The results identify that under carbonation conditions, the molar quantities of species in equilibrium with combustion gases and limestone, increase as bed inventory increases, and results appear consistent with experimental data for transition metals in particular (

Figure 9-3). Values for gaseous Cd concentrations increased from $8.0\text{E-}05$ for 4.5kg, to $6.0\text{e-}05$ for 6 kg, to $2.0\text{e-}04$ for 13kg, at 740°C . Similarly for Zn, molar gaseous emissions increased from $9.0\text{e-}04$ for 4.5kg, to $7.0\text{e-}4$ for 6 kg, to $2.0\text{e-}03$ for 13kg, at all temperatures. These trends shown from MTDATA outputs are consistent with the majority of the species present. Gaseous KOH concentrations however reaches its maximum value at 720°C for 4.5kg, before then declining in value, whereas for 6kg and 13kg, the temperature at which the maximum value is reached was 740°C and 760°C respectively. This shows the effect that increasing mass has on the thermodynamic equilibrium for a minority of species present.

Mg was identified as one of the primary impurities of limestone (Figure 6-6). Figure 9-27 identifies that increasing bed inventory increases the amount of solid MgO and MgCaO_2 at the relevant temperatures at which they are stable, but increasing bed inventory has no effect on the temperature at which both compounds are stable. Figure 9-28 however shows that in addition to bed inventory also increasing the mass of solid CaCO_3 and CaO present, for a bed inventory of 13 kg, the temperature at which the stability of CaCO_3 decreases and the stability of CaO increases, has risen to approximately 780°C compared a temperature of 760°C for sorbent masses of 4.5 kg and 6 kg. This temperature is much higher than the $600\text{--}650^{\circ}\text{C}$ at which maximum CO_2 capture

was achieved in the reactor with 13 kg bed inventory, and also higher than the widely reported optimum temperature of 650-700°C [107]. This effect should be due to partial pressure and not bed inventory, and outlines a limitation of MTDATA, in that it cannot take into account certain effects, including that of a pilot scale reactor whereby equilibrium conditions appear to be improved as a result of a temperature gradient across the bed [8].

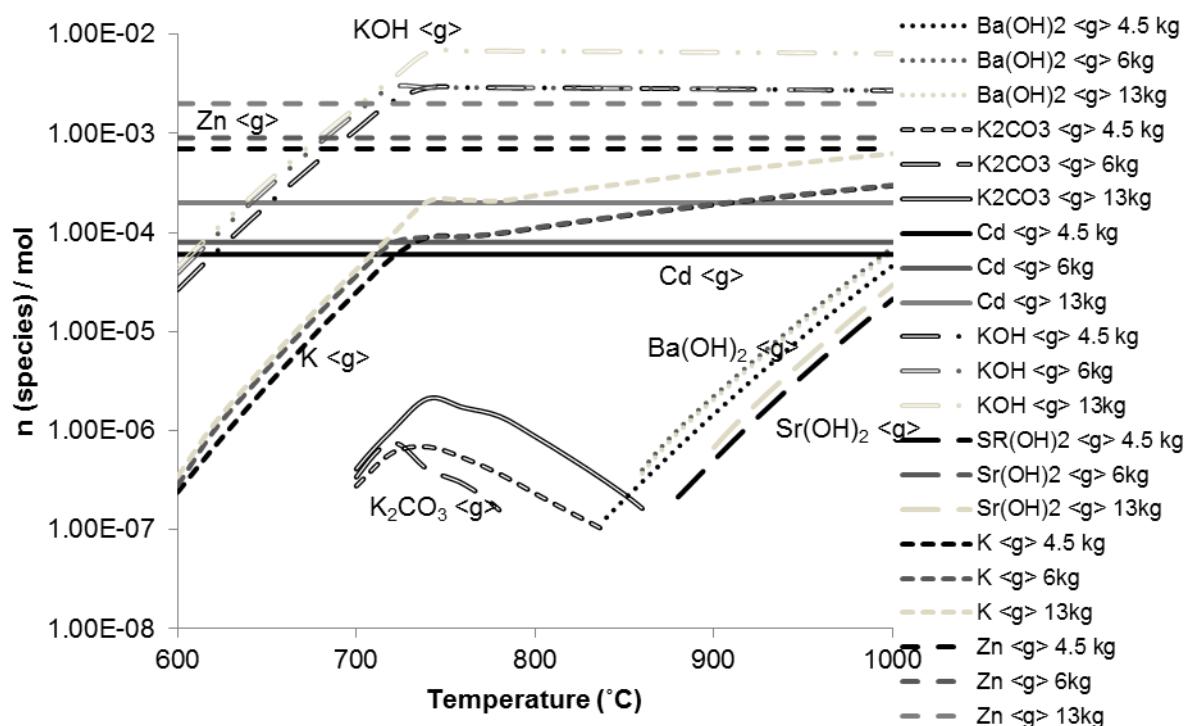


Figure 9-26 Calculated trace gaseous species (MTDATA) for 4.5 kg, 6 kg and 13 kg sorbent.

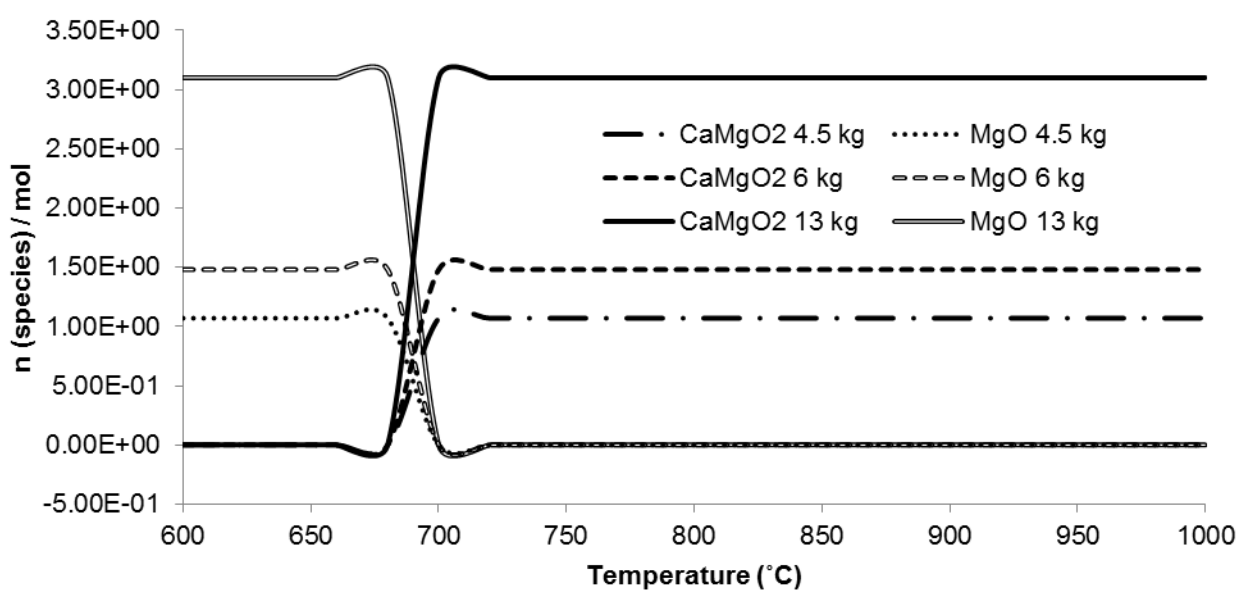


Figure 9-27 Calculated solid Mg-based species (MTDATA) for 4.5 kg, 6 kg and 13 kg bed inventory.

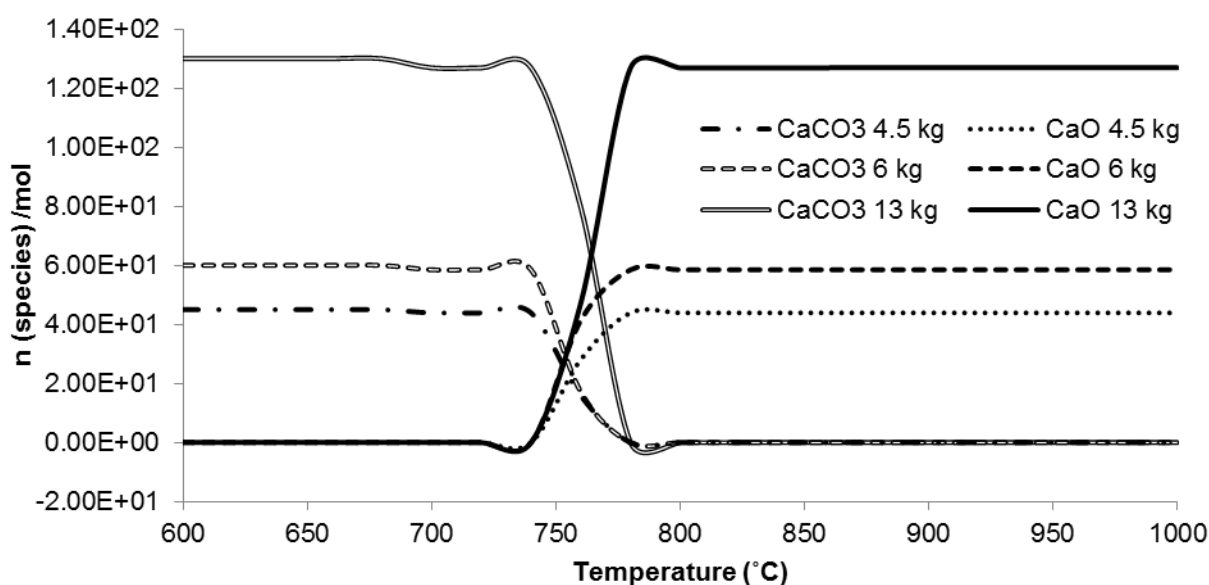


Figure 9-28 Calculated solid Ca-based species (MTDATA) for 4.5 kg, 6 kg and 13 kg bed inventory.

9.9.2 Thermodynamic Modelling – Effect of SO₂ concentration

It is apparent from the results of MTDATA thermodynamic equilibrium modelling that increasing SO₂ concentration during carbonation has an effect on the

species present at equilibrium. Figure 9-29 shows that the addition of SO_2 allows the formation of S-based compounds that would not otherwise form if SO_2 was not introduced. For example at 0 ppm SO_2 gaseous Ni and Zn are present, but at 1000 ppm and 2000 ppm SO_2 , ZnS is also formed, but only NiS is formed in place of Ni. Experimental data (Figure 9-15) identifies a minimum Ni concentration at 1000 ppm SO_2 concentration, but it would be expected that this would be found as Ni rather than NiS, given the oxidative conditions in the reactor, and the requirement of reducing conditions for H_2S , and in turn NiS formation. Increasing SO_2 concentration appears to have no effect on the stability of gaseous Cd or $\text{Ba}(\text{OH})_2$, although again experimental data (Figure 9-13) confirms a maximum Ba concentration at 1000 ppm SO_2 , although all experimental flue gas values for Ba are low at < 1 ppm. Modelling result show that SO_2 appears to have some influence on the stability of gaseous Zn and ZnS, whereby increasing SO_2 concentration appears to reduce the amount of gaseous Zn up until 780°C , above which temperature the amount of Zn reaches stability at -1.49 mol, regardless of the concentration of SO_2 present. Experimental data (Figure 9-13) however confirms decreasing Zn concentration with increasing SO_2 from 0 ppm to 2000 ppm SO_2 . Thermodynamic equilibrium data shows there is a small influence on the stability of gaseous K, with increasing SO_2 concentration slightly reducing the amount of gaseous K. For example, at 700°C and 0 ppm SO_2 , calculations show there to be -4.59 mol K, compared to -4.75 mol K with 2000 ppm SO_2 . This however is the opposite of what experimental data (Figure 9-13) suggests. Gaseous ZnS formation increases with SO_2 concentration, from -6.9 mol at 900°C for 1000 ppm SO_2 to -6.7 mol for 2000 ppm SO_2 . Again, the predicted formation of sulphides is unexpected given the O_2 concentration in the carbonator, and highlights the limitations of MTDATA compared to experimental data.

Figure 9-30 shows that at approximately 700°C and with 0 ppm SO_2 , the stability of solid MgO decreases compared to lower temperatures, whilst in its place the stability of solid MgCaO_2 increases to become the predominant Mg species. Increasing concentrations of SO_2 appear to increase the temperature at which the stability of MgO decreases and the stability of MgCaO_2 increases.

For example at 2000 ppm, the temperature at which MgO reaches its minimum and MgCaO₂ starts increasing is at approximately 740°C. Figure 9-31 shows that increasing SO₂ concentration has minimal effect on the stability of CaCO₃ which reaches a minimum at approximately 860°C, but SO₂ does have a small effect on the stability of CaO, with higher SO₂ concentrations increasing the temperature at which CaO is first formed, from 780°C with 0 ppm to 820°C with 2000 ppm SO₂. The model suggests that solid CaS is formed in the presence of SO₂, particularly under conditions typical of carbonation, and higher concentrations of which result in higher amounts of CaS formed.

The results show that thermodynamic modelling is a useful means of supporting experimental data with regards to gaseous element compositions and compounds, and elemental partitioning, over a range of temperature conditions relevant to Ca-based CO₂ capture. However, there may be several reasons for some discrepancies noted, primarily that MTDATA calculates the reactions at equilibrium, and assumes that the reactions go to completion, when in reality, this may not be the case. In addition, the model databases may not contain all of the compounds relevant to the required experimental conditions, and thermodynamic equilibrium data may not be available for all compounds at all required temperatures. Diffusion rates through sorbent pores are also an important factor in CO₂ capture efficiencies. Work carried out by Bhatia and Perlmutter (1981) [326] proposed the 'Random Pore Model' which describes kinetically-controlled fluid-solid reactions, taking into account factors including boundary layers and product layer diffusion. These influences are important when considering experimental reaction rates and in turn efficiencies, but unfortunately are not aspects that can be included when using thermodynamic equilibrium modelling to simulate reactions.

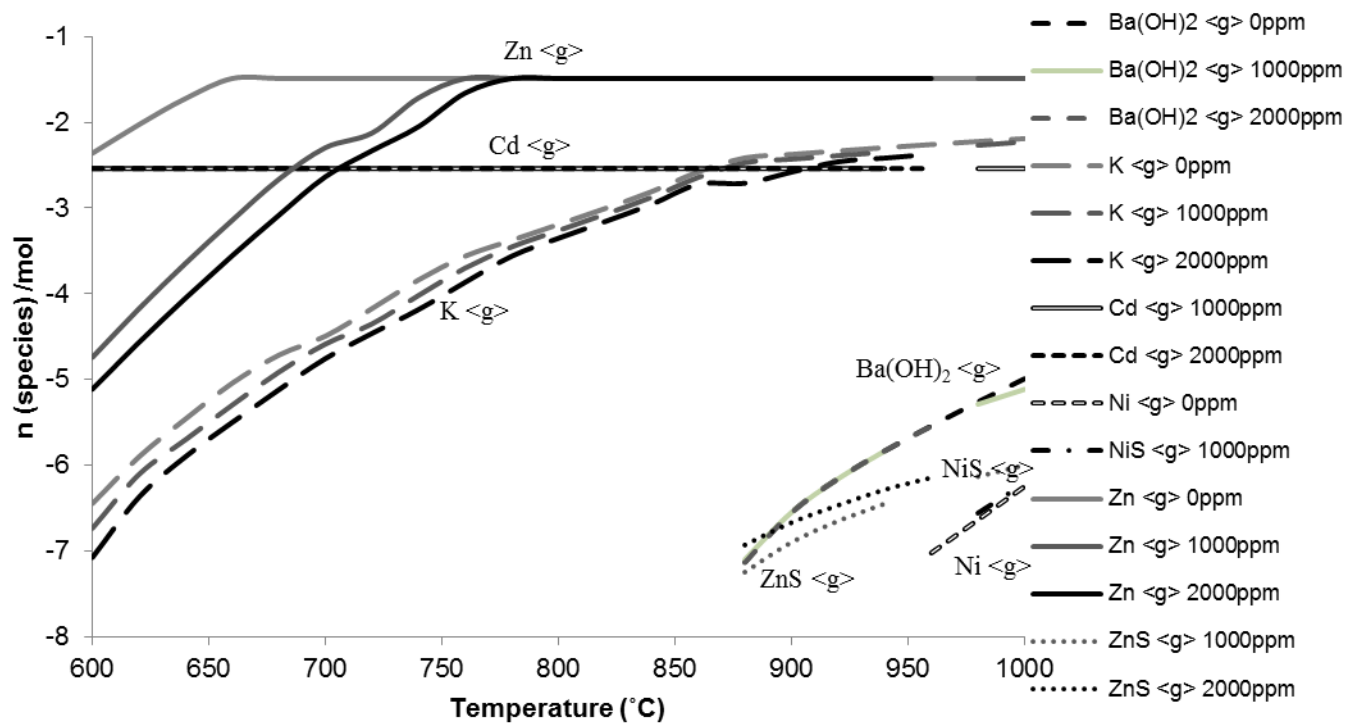


Figure 9-29 Calculated trace gaseous species (MTDATA) for 0 ppm, 1000 ppm and 2000 ppm SO₂.

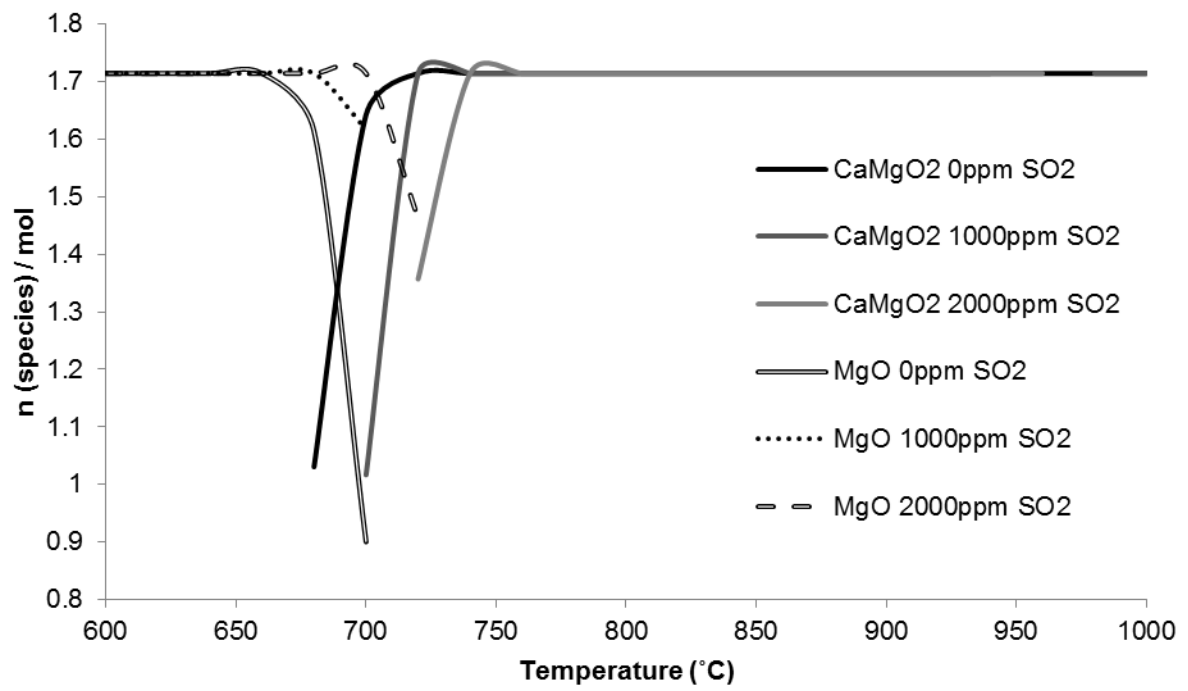


Figure 9-30 Calculated solid Mg-based species (MTDATA) for 0 ppm, 1000 ppm and 2000 ppm SO_2 .

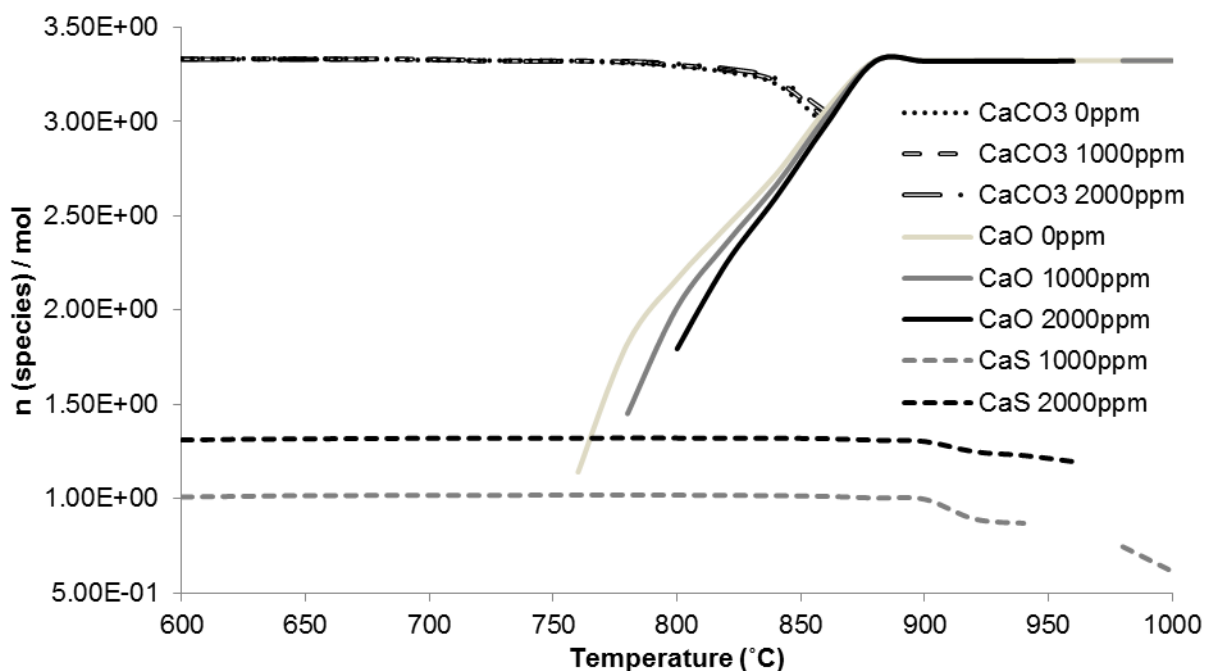


Figure 9-31 Calculated solid Ca-based species (MTDATA) for 0 ppm, 1000 ppm and 2000 ppm SO₂.

9.10 Conclusion

Solid, liquid and gaseous samples have been collected from the CO₂ capture reactor and analysed for elemental concentration. Concentrations appear to be influenced by bed inventory, with a number of species, particularly those of low volatility and transition metals, increasing in concentration as bed inventory increased. Effects of steam on elemental concentrations are apparent, although it is not clear whether increases in concentration, particularly for Fe, Ni, Mn and Cr are due the corrosive effect of steam on the 310 stainless steel reactor and its components, or due to changes in sorbent morphology as a result of additional steam. Increasing SO₂ concentration also appeared to have an effect on gaseous elemental emissions, although the effect appeared to differ depending upon the element concerned, with some increasing in concentration, and others decreasing in concentration as SO₂ concentration increased, suggesting the chemistry of the system is complex. The mass balances

confirmed that when compared to the concentration of elements in the sorbent, the concentrations partitioning to the gaseous phase are very low.

Data has been compared with that of best available technique emissions limits from a lime kiln and cement works identifying that from this study using a maximum of 13 kg bed inventory, all elemental emissions for which there are standards, were within the required limits. However, it is acknowledged that at industrial scale, much larger quantities of sorbent will be used, with potential for higher elemental emissions. In a potential scenario where the UK's future fossil-fuel derived energy may be predominantly natural gas based with inherent Ca-based CO₂ capture [39], limestone is likely to represent the primary source of elemental emissions, and these results suggest that with large quantities of the sorbent used, monitoring and filtering systems may be required. Maximum elemental concentrations in sorbent identified in this study have been compared with those typical of concentrations in cement. A number of elements in the sorbent exceed those concentrations typical of cement, most of which have beneficial effects in terms of improving cement properties, but Ni appears to be of most concern due to its potential environmental and health effects.

Thermodynamic modelling has been undertaken to verify the likely trace element speciation and partitioning under CO₂ capture conditions, results of which have proved useful in supporting the experimental work, although it is apparent that the process has a number of limitations when compared to the data derived experimentally.

This work has made a contribution to knowledge with regard to providing both experimental and modelling data on elemental partitioning to the solid sorbent and flue gas phases with respect to the calcium looping cycle process. This work has made progress in determining the potential for spent sorbent from the calcium looping cycle to subsequently be used within the cement industry, thus potentially reducing CO₂ emissions from both the power and cement industries. This work therefore meets Objectives 3a, 3b and 3c.

10 DISCUSSION

This chapter discusses the findings of the work undertaken for this thesis and the relevance for the industrial implementation of the calcium looping cycle, in accordance with the three PhD Aims provided in Chapter 1. Where relevant, the discussion has been separated in that applicable specifically to pilot scale research, and that applicable to industry.

10.1 Efficiency and Engineering Scale Up of the Calcium Looping Cycle

The tests run as part of this work have demonstrated that a good level of CO₂ capture close to 80 % was achieved in the pilot scale reactor when run as a continuous looping cycle. A number of factors have already been identified to account for the lower capture value when compared to the results available in the literature for other pilot scale reactors, including the Ca looping ratio and residence time, as discussed in Chapter 8. Little information is available in the literature on issues related to scale up of the calcium looping cycle, and those that are, as reviewed in Chapter 3, are noted to include insufficient residence time, control of solids circulation rate, and solids transfer, and that these were for the most part overcome with reactor modifications. Similar problems have also been encountered in this study, but since they are unlikely to have been identified at the bench scale, the lack of available information in the literature is unsurprising.

10.1.1 Pilot Scale Research

With regards to the scale-up of the process, one of the key issues identified throughout this work is the reliability of the calciner's oxy-fired burner, attributed in part to pressure differentials in the reactor and plenum, and gas supply system variations, particularly for CO₂ gas. Although this is unlikely to be an problem in industry due to the on-going availability of maintenance, and the lack of a requirement for cylinder gases, this may prove somewhat of a hindrance in further pilot scale testing. Although not all pilot scale reactors make use of burners, it should be noted that they are considered to be one of the most

realistic methods for introducing syngas into reactors, along with the introduction of a CO₂/N₂ cylinder-derived gas. The addition of heated elements had a positive effect on CO₂ capture %, but trace heating around loop seals would also be of benefit in ensuring that the temperature was sufficiently high above 420°C to prevent Ca(OH)₂ formation.

10.1.2 Industry

Lower carbonator temperatures of approximately 600-650 °C have been identified as being beneficial at the pilot scale due to the temperature gradient across a fluidised bed, and this has been confirmed in this study. This however has not been identified as being an important critical parameter in bench scale testing with carbonator temperatures at bench scale generally recommended to be in the region of 650-700°C, thus highlighting the importance of technology scale up prior to industry implementation. This may also allow energy savings to be made within industry by reducing the heat requirements, although one key benefit of the calcium looping cycle over alternative methods of CO₂ capture is the improved efficiency of the process due to the high temperatures involved, excesses of which could be used for steam and in turn electricity generation.

The importance of sufficiently high temperatures above 420°C in transfer lines between the reactors, has been highlighted in this study by the negative attributes of Ca(OH)₂ formation. Industrial use of the calcium looping cycle would need to ensure sufficient provision is in place for adequate temperatures to be maintained.

10.2 Potential for Sorbent to be Used at the Industrial Scale

Investigations into attrition provided unexpected results in that increasing bed inventory reduced attrition, and further work may be required to determine the reasons for agglomeration, which is likely to have caused the increased particle size. Blockage of the lower loop seal standpipe may have resulted in reduced transfer of solids from the calciner, and therefore enhanced agglomeration and sintering of solids, particularly at the high temperatures experienced in the calciner. The addition of the air shaker was used to create a vibration across

the loop seal to encourage solids transfer, and resulted in improved conditions but did not completely solve this problem. It may be that an improved loop seal design with a larger volume, and employing an increased number of nozzles for improved fluidisation and thus transfer, as well as loop seal trace heating to prevent Ca(OH)_2 formation at lower temperatures, would benefit the process in the reactor.

During batch tests, the addition of steam supplementary to that produced by the burner, acted to improve CO_2 capture capacity in the reactor, and is in accordance with the majority of work available in the literature (Chapter 3). Although this is deemed a positive in respect of pilot scale research and enhancing the CO_2 capture capacity of the sorbent, with regards to industry, the use of additional steam would not be considered efficient, due to the high parasitic energy requirements and in turn costs associated with steam production, which would reduce the efficiency of the process. However, the results provide important information, in that the inherent presence of steam in industrial flue gas is likely to have a beneficial effect on the capture capacity of the sorbent, thus enhancing the potential of limestone-derived sorbent to be used at the industrial scale.

Increasing SO_2 concentration in batch and continuous mode tests had a negative effect on % CO_2 capture, and is in collaboration with findings of other work, as described in Chapter 8. A flue gas SO_2 concentration of 2000 ppm is considered reasonably high and is typical of that from Chinese coal power stations, whilst coal-derived flue gas in the UK is more likely to have a flue gas SO_2 concentration of approximately 1000 ppm or less when derived from a typical low sulphur coal. The reduced capture capacity as a result of 1000 ppm SO_2 is apparent when compared to 0 ppm SO_2 , achieving approximately 70 % and 75 % capture for 1000 and 0 ppm SO_2 respectively. However a much lower capture capacity is achieved with 2000 ppm at approximately 50 % capture. This implies that the calcium looping cycle may be beneficial particularly for CO_2 capture from low sulphur coals, given the reasonably small difference in % capture between 0 and 1000 ppm SO_2 .

Further, it is considered that the inherent presence of steam from burner use had a positive effect in maintaining capture capacity for the test duration for all SO₂ concentrations. This is considered important for the technology, in that the need for fresh sorbent addition during tests may be reduced, thereby reducing costs in terms of buying sorbent and also reduced costs associated with parasitic energy required for initial heating of fresh sorbent as it enters the calciner. Although some fresh sorbent will always be required, the amount added to maintain adequate levels of capture may be reduced.

10.3 Elemental Partitioning and Potential for Sorbent to be Used Within the Cement Industry

One of the major advantages of the calcium looping cycle over other methods of CO₂ capture is the potential for spent CaO sorbent to be used within the cement industry, which in turn would reduce CO₂ emissions from the cement manufacturing, as well as the power generation process.

The sorbent elemental concentrations found in this study are generally considered low. However, concentrations of several elements were found at higher levels than that typical of cement. For the most part the elements concerned are considered likely to improve cement properties, although elevated concentrations of Ni in particular are considered cause for concern, due to the adverse environmental and health impacts that may be caused by excessive Ni concentrations in cement dust, and also because Ni is known to replace Ca and therefore increasing the free lime in the kiln, which in turn reduces its burnability [11]. Again, the limited bed inventories used in these tests are small compared to the masses of sorbent which will be required for industry. This implies that sorbent elemental concentrations as a result of partitioning will likely increase at the industrial scale, which may impact on cement properties. It is therefore considered that there is a high potential for spent sorbent to be used, but concentrations of the majority of elements, including Ca, Mg, Al, Fe, Cr, Ni, Pb, V, Mn and Zn are likely to be higher than those typical of cement, and therefore mitigation measures may be required to

ameliorate high dust levels, and therefore elemental levels of spent sorbent-containing cement, to reduce risk to health and the environment.

The work carried out as part of this thesis has identified that gaseous emissions from the calcium looping cycle are generally low, the highest value achieved in this study being 2.2 ppm, with reactor component degradation considered to be a factor in both gaseous emissions, and also elemental content of the sorbent sample from the addition of corroded reactor particles. Although quantification of separate emissions from limestone and the reactor has not been possible, visual observations of reactor degradation, and chemical analysis of both the limestone and the reactor, suggests that the presence of particular elements are from the limestone (Ca, Mg, Al), whilst others are from the reactor itself (Fe, Cr, Mn, Co). This in turn suggests that reactor material may be an important factor in scale up of the technology, in aiming to reduce both degradation which can prove costly, and sorbent elemental concentration. From the literature available, reactor degradation specific to the calcium looping cycle and related factors such as steam addition, have not to date been reported in the literature as an issue in the running of other pilot scale reactors, but this may be because there appear to be no studies investigating sorbent elemental concentrations which led to this finding.

Despite the fact that the reactor is made from 310 stainless steel which is designed for high temperature, continuous testing, the conditions to which it and its components were exposed appear to have resulted in significant degradation of the alloy. The use of a protective overlay material may prolong the life of other such pilot scale reactors, preventing degradation and thus sorbent contamination, allowing more cost-effective materials to be used for research purposes. This is however an issue considered relevant only to research, and is unlikely to be of concern in industry, due to the existing high temperature, corrosive nature of power station processes and therefore the higher grades of steel already used, along with refractory linings, meaning that the reactor is unlikely to be exposed to corrosive conditions. In addition, the oil and gas industry has experience with conditions similar to those of the calcium looping

cycle, in particular the use of high temperature fluidised beds. However, the use of probes, flow meters, thermocouples, valves and other such components in industry which would be exposed to carbonation/calcinations conditions represents a potential opportunity for degradation and in turn sorbent contamination. Although reactor and component degradation processes are outside the remit of this thesis, such factors should be considered in future investigations of sorbent contamination and the potential for spent sorbent to be used in the cement industry (see section 10.3). In addition, this may also be important in determining when industrial reactors should be replaced, as although the end of a reactors life may not have been reached, corrosion may result in higher concentrations of particular elements in the sorbent. Nevertheless, stainless steel remains an important material for industrial processes.

In a future situation whereby UK government policy proposes increased use of natural gas-fired power stations over coal [39], employing calcium based CO₂ capture will mean that the limestone based sorbent will be the main source of both particulates and elemental emissions. The limestone derived gaseous emissions from this study were considered low and in many cases negligible. However, the bed inventories used in these tests in a 25 kW reactor are relatively small compared to the masses of sorbent which will be required for industry in a typical 50 MW plant. Based on the effect of bed inventory work described in Chapter 9.2, this implies that gaseous element emissions as a result of partitioning will likely increase at the industrial scale. The use of existing filter and scrubber systems should however act to reduce gaseous emissions from power generation sites, particularly after nucleation of volatile species, allowing sites to remain within environmental emissions regulations.

11 CONTRIBUTIONS TO KNOWLEDGE AND FURTHER WORK

The achievement of the PhD objectives in order to fulfil the aims of the PhD, as outlined in section 1.1, has provided calcium looping cycle-related information that was not previously available in the literature. The contributions to knowledge are provided below, as is the further work required identified from this PhD work. Limitations identified during the course of the work are provided as Appendix G.

11.1 Contributions

Thesis objectives 1a and 1b have been achieved through the design and operation of a full-scale cold model of the 25 kW_{th} pilot scale reactor, outlined in chapters 5, 6 and 7. This work enabled the determination of optimum operating conditions for the hot reactor, including the identification of ideal superficial gas velocities for the carbonator, calciner, and loop seals, in a bid to optimise solids entrainment and solids flux, whilst at the same time minimising gas bypassing between reactors, and therefore maximising process efficiency. A number of modifications were made to the cold model in order to improve solids circulation, benefits of which have been verified through reactor pressure measurements. Calculations have been made to estimate how much the reduction in particle size distribution as a result of attrition will reduce minimum fluidisation velocity values. This implies that feeding of fresh sorbent will be required to maintain capture capacity.

CO₂ capture tests run in continuous mode in the hot reactor have resulted in a maximum CO₂ capture % achieved in the reactor of close to 80 %. This figure has been increased throughout the testing period, through reactor and process modifications in order to improve the capture %. Modifications made included the addition of air shakers to encourage solids transfer, and therefore the calcium looping ratio, between reactors. Heated elements were added to increase the temperature of air going into the lower loop seal, in a bid to

improve the % capture. A limit on residence time was apparent however due to the building's height restriction.

Thesis objectives 2a and 2b have been achieved through the operation of Cranfield's pilot scale reactor, results and analysis of which are provided in chapter 8. Analysis of sorbent morphology has been carried out, showing that that increasing bed inventory appeared to reduce attrition, attributed to agglomeration effects. Increasing additional steam concentration had a beneficial effect on CO₂ capture, confirmed by SEM and BET analysis showing improved porosity with increasing steam concentration. Effects of SO₂ have also been investigated at the pilot scale in both batch and continuous experiments, and it was found, in accordance with the literature, that SO₂ has a detrimental effect on CO₂ capture. This is supported by PSD, BET, EDS and SEM analysis of sorbent samples subsequent to testing, showing decreased porosity. However, the high steam content in the reactor from the combustion of fuel from the use of the burner appears to have a positive effect in reducing decay in sorbent activity, and therefore maintaining the CO₂ capture % achieved by the sorbent. Results have been compared with other pilot scale and bench scale reactor results, with differences in results accounted for, and confirmation that in particular a lower carbonator temperature is beneficial at pilot scale.

Thesis objectives 3a, 3b and 3c have been achieved and associated findings are presented in chapter 9. Gaseous elemental emissions in the flue gas from the process have been analysed using both a sampling train system and ICP-MS, and also on-line continuous monitoring using ICP-OES. High concentrations of certain elements were recorded, including Fe, Cr, Mg, Al and Mn, and supported with thermodynamic equilibrium calculations data, but gaseous emissions were found to be within regulations for a lime kiln/cement works based on the 13 kg bed inventory used. Concentrations were influenced by bed inventory, with a number of low volatility, transition metal species increasing in concentration as bed inventory increased. Additional steam effects on concentration are apparent, although it is not clear whether increases in

concentration, particularly for Fe, Ni, Mn and Cr are due the corrosive effect of steam on reactor components, or due to changes in sorbent morphology as a result of additional steam. Increasing SO₂ concentration also appeared to have an effect on gaseous trace element emissions, although the effect appeared to differ depending upon the trace element concerned. It was noted that the bed inventories used in industry will be much larger than those used in this study, which may result in higher concentrations of certain elements, suggesting that monitoring and filtering systems may be required.

Elemental concentration in the sorbent was analysed using ICP-MS and it was found that for the most part, concentrations were not above those typical of average concentrations in cement. Those that were found in higher concentrations were generally considered beneficial for cement properties, although one of them, Ni is considered to have adverse effects. Based on this pilot scale study, it is considered that the use of spent sorbent in cement manufacturing is a viable option, although this would need to be confirmed at the industrial scale due to the limited bed inventory used.

A summary of the contributions to knowledge made as part of the work for this thesis are provided below, and have been classified into those relevant specifically to the reactor, and those relevant to the process technology:

11.1.1 Reactor

- Design and development of a full scale cold model specific to Cranfield's pilot scale reactor, from which optimum fluidising conditions were identified necessary to achieve maximum CO₂ capture conditions;
- Identification of the likely decrease in U_{mf} observed with increasing particle attrition;
- Operation and development of a pilot scale reactor in continuous mode, to obtain a good level of CO₂ capture close to 80 %, typical of other sources in the literature; and
- Confirmation that thermodynamic equilibrium calculation software is useful in supporting experimental analysis of elemental partitioning from limestone use in the calcium looping cycle, but has a number of

limitations, so that thermodynamic equilibrium calculation modelling data is not sufficient on its own in predicting elemental partitioning.

11.1.2 Technology

- The importance of maintaining a temperature in the loop seals of higher than 420°C has been identified, to prevent sorbent cooling and Ca(OH)_2 formation, and therefore maintain capture in the reactor;
- Identification of the requirement for a taller carbonator column to increase residence time, and therefore improve calcium looping ratio and % CO_2 capture in the reactor;
- Identification that elemental concentrations of carbonator flue gas are affected by bed inventory, steam concentration and SO_2 concentration;
- Confirmation that flue gas element concentrations for the tests carried out as part of this study using a maximum bed inventory of 13kg, are below the cement works/lime kiln best available technique (BAT) emissions limits for Hg, Cd, Tl and Group 3 elements. This implies that should spent sorbent from the calcium looping cycle be subsequently used for cement manufacture in a bid to reduce CO_2 emissions and minimise waste, then elemental emissions in flue gas should not be of concern provided adequate monitoring and filtering provision is in place.
- Verification that sorbent elemental concentrations appear to be influenced by bed inventory, with a number of species, particularly those of low volatility and transition metals, increasing in concentration as bed inventory increased.
- Identification that the effects of steam and SO_2 on elemental concentrations are apparent, although effects appear to differ depending upon the trace element concerned, with some increasing in concentration, and others decreasing in concentration as steam/ SO_2 concentration increased.

11.2 Implications of Findings

The findings made as part of this PhD will help towards further development of the calcium looping cycle for industrial implementation. Engineering challenges encountered and described in this work will help in future design of other pilot scale reactors, such as the requirement for a sufficiently high temperature across the loop seals to maintain efficiency and prevent Ca(OH)_2 formation. The beneficial effects of steam have been confirmed in the carbonator, including the potential importance of it in maintaining the capture activity of the sorbent through improved porosity even with 2000 ppm SO_2 . Although the adding of steam beyond that that is produced inherently by the use of burners would not be economic at the industrial scale, the positive effect observed may influence future pilot scale work to investigate this further. Confirmation at the pilot scale that spent sorbent is likely to be promising for use in the cement industry will eliminate the need for disposal of the spent sorbent, and will therefore improve the overall life cycle analysis and efficiency of the calcium looping cycle process.

11.3 Further Work

The work carried out for this PhD, while significantly contributing to knowledge regarding the engineering scale-up of the calcium looping process and elemental partitioning from limestone, has raised many more questions and revealed further gaps in the knowledge that may be addressed in future work. These knowledge gaps may be addressed by the following research directions, which have been classified into those relevant specifically to the reactor, and those relevant to the process technology:

11.3.1 Reactor

- Investigation into loop seal design and development of a more efficient loop seal to improve solids transfer between reactors, including implementation of view ports to allow additional analysis of solids transfer by loop seals;

- Investigation into gas distributor design and the trial use of bubble caps to prevent solids weeping, and nozzle blockage occurring. This would help to reduce burner failure and allow longer test runs;
- Investigation into burner design and trial of alternative burners to reduce burner failure rate;

11.3.2 Technology:

- Exploration of how varying CO₂ concentration between 4–16 % influences CO₂ capture capacity at the pilot scale;
- Investigation into the influence of additional steam during calcination and carbonation at the pilot scale in continuous looping mode;
- Experimental analysis of the effect of sorbent pre-calcination on capture capacity at the pilot scale;
- Exploration into potential sorbent interactions with reactor material, and subsequent consequences on the sorbent chemistry;
- Investigation into integration of the pilot scale calcium looping cycle with the water gas shift reaction, to simultaneously produce H₂ and capture CO₂ from fossil fuels in a method known as ‘sorption enhanced hydrogen production’;
- Experimental investigation of cement production from spent sorbent from the pilot scale calcium looping cycle, and chemical analysis of cement to verify elemental concentration; and
- Exploration of the health impacts and environmental risk due to concentrations of heavy metals and elements in cement dust arising from use of spent sorbent.

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Appendix A Journal and Conference Papers

The first page of each of the published and submitted journal papers, and accepted conference papers, produced during the work of this thesis are provided below.



Hydrodynamic characteristics of a pilot-scale cold model of a CO₂ capture fluidised bed reactor

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ABSTRACT

Global anthropogenic emissions of CO₂ are increasing, and it appears that carbon capture and storage (CCS) has the potential to mitigate CO₂ emissions, thereby reducing potential effects of global warming and climate change. The calcium looping cycle is a novel method of CO₂ capture, comprising the use of limestone (CaCO₃) as a CO₂ sorbent within a fluidised bed. An understanding of the hydrodynamics of such a system is important in order to optimise the efficiency of the CO₂ capture process. A full-scale 3D cold model of a 25 kW_{th} calcium-looping CO₂ capture reactor has been designed, constructed and operated in order to investigate the hydrodynamics of the hot system. The system comprises an entrained flow carbonator, and a bubbling fluidised bed calciner, with a lower and upper loop seal to allow control of solids transfer. Investigations into minimum fluidisation velocity, solids flux, gas bypassing between reactors, and pressure profiles of the system have been undertaken, the results of which are presented and discussed. Experimental minimum fluidisation velocity results compare well with the literature and theoretical values calculated from existing models. Gas bypassing results identify that predominant bypassing is from the loop seals to the calciner reactor, but modifications made to the cold model system as a result of the investigations show positive results in terms of reducing gas bypassing to a maximum of 5 %, and also improving the pressure profile of the system.

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1. Introduction

Global CO₂ emissions are increasing year on year, and it is widely accepted that anthropogenic emissions of which are contributing to climate change [1]. Carbon capture and storage is an emerging technology, which has the potential to prevent 33 % of global atmospheric CO₂ emissions by the year 2050 [2].

The calcium looping cycle is a novel method of CO₂ capture, comprising the use of CaO derived from limestone, as a CO₂ sorbent within a fluidised bed, and has been the subject of significant interest within the research community over recent years. Limestone is considered to be cost effective, efficient and abundant, thereby making CO₂ capture via the calcium looping cycle an attractive option for CO₂ capture from industrial point sources [3–5]. The calcium looping cycle process comprises the separation of CO₂ from flue gases by passing the CO₂-containing flue gas through a fluidised bed of lime (CaO) in a reactor known as a carbonator, whereby CaO reacts with and captures the CO₂ to form CaCO₃. The gas which exits the reactor is CO₂-free, and the CaCO₃ is then transferred to a second reactor,

known as the calciner, where due to an increase in temperature, the CaCO₃ decomposes, releasing CO₂ for compression, transport and storage. CaO is reformed and is then transferred back to the carbonator for further cycles of CO₂ capture (Fig. 1).

The carbonation reaction is exothermic ($\Delta H_r^\circ = -178$ kJ/mol), whilst the calcination reaction is endothermic ($\Delta H_r^\circ = +178$ kJ/mol). The reactors are separate, meaning that there is no gaseous exchange between the two, ensuring the efficiency of the process is optimised.

Due to the continuous processes on-going within a fluidised bed, it is important to have an understanding of the hydrodynamics of such a system, in order to optimise the CO₂ capture process. This includes information regarding the pressure characteristics of the system in order to gain an understanding of solids transfer throughout the system, as well as information on minimum fluidisation velocities in order to ensure that sufficient gas flows are present to entrain solids. Knowledge on the solids transfer flux of a system is required to gain further understanding of rates at which solids are moving around the reactors and to ensure sufficient heat is transferred for reactions to occur. Further, an understanding of any gas bypassing that may be occurring is required, in order to optimise the efficiency of the capture process.

Based on test results from Cranfield's 25 kW_{th} pilot-scale post-combustion capture reactor, a number of important issues have been

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Figure A-1 Published journal paper Cotton *et al.*, 2013

Novel Optimized Process for Utilization of CaO-Based Sorbent for Capturing CO₂ and SO₂ Sequentially

Hongwei Chen,[†] Zhenghui Zhao,[†] Xinzhang Huang,[‡] Kumar Patchigolla,[§] Alissa Cotton,[§] and John Oakey^{*,§}

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ABSTRACT: Calcium oxide (CaO) based sorbents, used for CO₂ capture in calcination/carbonation cycles, reduce in activity with increasing numbers of cycles, thus reducing the economic benefits of this capture process, generating a significant amount of spent sorbent and raising the potential for pollution from its disposal. This paper presents research into the use of this spent sorbent for the prior capture of sulfur oxides (SO₂), as required when the cycle is used with coal-derived flue gases. Using a thermogravimetric analyzer (TGA), the sulfation behaviors of two limestones from Hebei Province (named LA and LB) were examined after different numbers of calcination/carbonation cycles. The results show that the sulfation conversions for spent sorbent of the LA and LB after 40 cycles were, respectively, about 4% and 14% less than that of the original sorbent, indicating that spent sorbents from CO₂ capture cycles remain active for SO₂ retention. As the number of cycles increased, there was a difference in the sulfation conversions between LA and LB, probably due to the difference in pore structure development for the two limestones as the sulfation reaction progressed. The surface morphology and pore structure of sorbents after different numbers of cycles were examined by scanning electron microscopy (SEM) and nitrogen adsorption/desorption spectroscopy. It was found that the pore size distributions show two peaks in all cases, and as the number of cycles increased, the larger pores fuse together while the number of small pores was not markedly diminished, which is not consistent with the existing sintering model. The observed sintered pore structure provides greater product growing space for reactions to occur in the pore inner surface, which benefits sulfation more than carbonation due to their different product molar volumes, helping to explain why cycled sorbent samples remain active in sulfation.

1. INTRODUCTION

CO₂ emissions, as the main greenhouse gas of concern, are believed to be causing increasingly serious environmental problems, due to global warming effects. As an effective postcombustion technology for capturing CO₂, the cyclic, calcination/carbonation reaction using a CaO-based sorbent has gained increasing focus for its cost effectiveness and flexibility in application to existing power plants.^{1–3} However, sorbent activity decays with increasing cycles due to sintering⁴ and sulfation,⁵ which produce significant amounts of spent sorbent.⁶ The spent sorbent is potentially hazardous to the environment due to the presence of unreacted CaO, which can react exothermically when in contact with water to produce Ca(OH)₂, which is alkaline and has potential to cause damage to living things.^{7,8} The need for the disposal of the spent sorbent may reduce the economic value of the whole process. Considering that SO₂ is also produced from fossil fuel combustion, and can also be captured by the same sorbent, a combination of the two CO₂ and SO₂ capture processes would enhance resource utilization and reduce costs.

Several research studies have shown CaO-based sorbent capturing SO₂ and CO₂ simultaneously, and the results predict that while SO₂ impedes sorbent carbonation, resulting in rapid decay in sorbent activity,^{9–11} CO₂ had a beneficial effect on sulfation behavior.¹² This has led to the consideration being given to a new process for utilization of CaO-based sorbents in

fluidized bed (FB) systems by separation of the two processes, namely, capturing SO₂ and CO₂ sequentially with a solid CaO-based sorbent. The reaction mechanisms are given in eqs 1 and 2, and the process flow diagram is shown in Figure 1. The flue

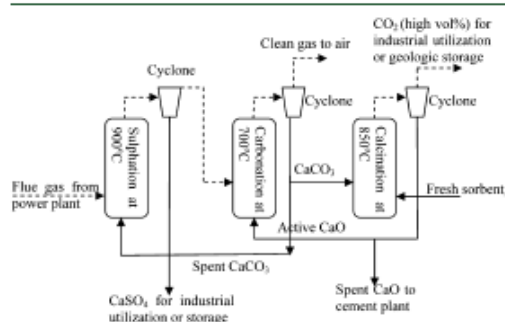


Figure 1. System process of CaO-based sorbent cyclic CO₂ capture preceded by SO₂ retention.

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Minor and Trace Element Emissions from Post-Combustion CO₂ Capture from Coal: Experimental and Equilibrium Calculations

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Abstract

Gaseous trace element emissions from pilot scale (25 kW_{th}), post combustion CO₂ capture using a Ca-based sorbent, have been investigated, due to the presence of naturally occurring trace element species found in limestone, that have the potential to be released to the environment under carbonation and calcination conditions. ICP-MS analysis of Longcliffe SP52 limestone was undertaken to identify other species present, and the effect of sorbent mass and SO₂ concentration on carbonator gaseous trace element emissions was investigated, using a bubbler sampling system. Samples were analysed using ICP-MS, which concluded that sorbent mass and SO₂ concentration in the carbonator had an effect on the concentrations of gaseous trace elements sampled. Thermodynamic modelling of the carbonation and calcination process was also undertaken, based on molar quantities of trace elements identified from ICP-MS analysis of limestone, which provided useful information with regards to trace element stability and partitioning under realistic CO₂ capture conditions.

Key Words: Trace elements, Emissions, CO₂ capture, Thermodynamic modelling

1. Introduction

Carbon capture and storage (CCS) is an emerging technology which has the potential to mitigate further effects of global warming, and in turn, climate change, through the capture, compression, transport, and subsequent subsurface storage of CO₂ emissions from single point sources, particularly power stations. The use of limestone as a CO₂ sorbent in fluidised bed carbon capture systems from coal, is gaining interest due to the high prevalence, low cost, and potential for high CO₂ sorption efficiency of the limestone-derived sorbent. However, limestone is a naturally-occurring material, and thereby often contains other species in the form of trace elements. The high temperature conditions under which carbonation and calcination occur, present opportunities for trace elements to be released to the environment, thereby representing a potential source of environmental contamination, in addition to that produced from coal combustion. A large amount of research has been carried out on the use of limestone in the calcium looping cycle as a method of CO₂ capture, but it is apparent that minimal work to date has investigated the potential pollutants that may be produced by the calcium looping cycle as a result of limestone impurities.

Figure A- 3 Accepted journal paper

Quantification of trace element emissions from low-carbon emission energy sources: I. Ca-looping cycle for post-combustion CO₂ capture and II. Fixed bed, air blown down-draft gasifier

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Abstract

The integrated technologies of gasification and the calcium looping cycle represent the opportunity to produce H₂ as an energy carrier with inherent CO₂ capture, thus producing a near-zero or negative emission fuel. Gasification of waste-derived fuel including demolition wood and low density plastic is gaining in interest due to the potential to minimise waste to landfill, whilst also representing a carbon-neutral energy source. However, potential trace element emissions from the gasification of such fuels require investigation to ensure compliance with targets under the EU Ambient Air Quality Directive 2008 and the UK Air Quality Standards Regulations 2010. Likewise, contaminants present in limestone have the potential to be released to the environment under the operating regimes required for carbonation and calcination in the calcium looping cycle for CO₂ capture. Solid samples (offline), liquid (offline) and gaseous (offline/online and in-situ mobile ICP-OES) products from a pilot scale fixed bed, air-blown down-draft gasifier and from a pilot scale CO₂ capture reactor comprising of the calcium looping cycle, have been collected and analysed in a bid to gain further understanding of the likely trace element partitioning in both processes. Results identified that a number of trace element contaminants present in the original CO₂ sorbent and gasifier fuel samples were also present in the flue gas from both the CO₂ capture and gasification processes, implying that integration of the technologies may result in enhanced contamination in the final gaseous product. The main outputs of this study assist in analysing plant requirements, for example gas cleaning, and identifying the environmental emissions and residual disposal.

Key Words: Chemical analysis; Downstream processing; Energy; Environment; Low carbon technologies; Trace element

1. Introduction

Increasing global awareness of anthropogenic-induced climate change and subsequent global warming from single point energy sources has led to increased research into low-carbon emission energy technologies. Fossil fuel usage in non-Organisation for Economic Cooperation and Development (OECD) countries including China, India and Brazil has increased and is predicted to do so for the coming decades [1]. As a result, carbon capture and storage (CCS) using limestone as a CO₂ sorbent has been growing in interest initially due to its potential use in capturing CO₂ emissions from coal combustion or gasification, but there is also the

Figure A- 4 Submitted journal paper

GHGT-11

Overview of, and experimental methodology for, sorption enhanced hydrogen production

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Abstract

The worldwide abundance and relative low cost of coal, and its increasing use in gasification for syngas production for synthetic fuel and chemical manufacturing, presents ample opportunity for H₂ production with inherent CO₂ capture, through the use of limestone-derived CO₂ sorbent. The combining of the water gas shift reaction and carbonation reaction in a single reactor has potential to increase process efficiency and reduce costs of the process, when compared to conventional H₂ production. This paper presents a brief overview of the wider research to date and outlines proposed experimental work to further investigate effects of temperature and feed gas composition, as well as potential trace elements emissions from the process, in a bench-scale, bubbling fluidized bed reactor.

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Selection and/or peer-review under responsibility of GHGT

Keywords: Sorption enhanced hydrogen production, CO₂ capture, coal, limestone

1. Introduction

Sorption enhanced hydrogen production (SEHP) is gaining in interest due to its potential for production of a clean energy carrier in the form of hydrogen, from solid fossil fuels including coal. The use of coal as an energy source is increasing worldwide, and in 2011 was responsible for 42% of global energy production [1]. Many of the world's coal reserves are located in developing countries including China and India, where growing economies along with high global population growth, are increasing demand for energy production. As a result, the demand for coal gasification is also increasing, due to the use of the coal-derived syngas comprising H₂ and CO, in coal-based synthetic fuel and chemical production, including in the manufacture of ammonia, urea and methanol. There is also the potential for product H₂ to be used in solid oxide fuel cells (SOFC) in a drive towards a 'hydrogen economy' to

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Appendix B % CO₂ Capture Calculation

% CO₂ Capture:

$$\%C = \frac{V_{\text{CO}_2 \text{ in}} - V_{\text{CO}_2 \text{ out}}}{V_{\text{CO}_2 \text{ in}}} * 100$$

Where % C is % CO₂ capture; V_{CO₂in} is total known volume of CO₂ introduced into carbonator; and V_{CO₂out} is total volume of CO₂ exiting carbonator, measured at carbonator orifice plate and analyser.

V_{CO₂in} = CO₂ from CH₄ combustion in air-fired burner + CO₂ in secondary air + secondary CO₂ + CO₂ in lower loop seal fluidising air.

V_{CO₂out} = (% CO₂ at carbonator gas analyser / 100) * flow through carbonator exhaust measured from pressure differential at orifice plate.

Table APNDX 1 % CO₂ Capture Calculations

Time	Carb T7	Carb Orifice Pressure	CO2 Carb	O2 Carb	Carbonator Orifice Flow	Carb Orifice flow	Carbonator CH4	Carb CH4	CO2 moles	Air in	Air in	Air in CO2	Air in CO2	Total Lower Loop Seal air flow	Loop seals CO2	Loop seals CO2
Seconds	°C	PaΔ	%	%	L/min	moles/min	l/min	moles/min	n	l/min	moles/min	l/min	moles/min	l/min	moles/min	l/min
13117	129.06	147.2	8.2	12.6	209.7589192	6.362323036	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4
13118	129.14	147	8.2	12.6	209.6163715	6.356734503	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4
13119	129.22	147.3	8.2	12.6	209.8301567	6.361952042	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4
13120	129.28	147.6	8.2	12.6	210.0437244	6.367477463	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4
13121	129.4	147.8	8.2	12.6	210.1859822	6.369889875	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4
13122	129.48	147.8	8.2	12.6	210.1859822	6.368623747	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4
13123	129.56	148.2	8.2	12.6	210.4702095	6.375968482	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4
13124	129.61	148.3	8.2	12.6	210.5412064	6.377327159	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4
13125	129.67	148.3	8.2	12.6	210.5412064	6.376376903	16	0.714285714	0.6659452	130	5.41080496	5.2	0.216432	10	0.416215766	0.4

2nd Air	2nd Air	2nd Air CO2	2nd Air CO2	2nd CO2	2nd CO2	TOTAL CO2 intro	Total CO2 exit	CO2 captured
l/min	moles/min	l/min	moles/min	l/min	moles/min	moles/min 20C	moles/min 20C	% (from moles/min)
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.521710489	72.60877425
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.521252229	72.63283413
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.521680067	72.61037146
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.522133152	72.58658329
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.52233097	72.57619731
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.522227147	72.58164827
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.522829416	72.55002755
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.522940827	72.54417814
200	8.3243153	8	0.332972613	15	0.624323649	1.904662806	0.522862906	72.5482692

Appendix C Example PSD Analysis Results

Table APNDX 2 Example PSD Analysis Results

Sample name		Result Between User Sizes (Sizes in um)																								
	um	0.95	1.10	1.26	1.45	1.66	1.91	2.19	2.51	2.88	3.31	3.80	4.37	5.01	5.75	6.61	7.59	8.71	10.00	11.48	13.18	15.14	17.38	19.95	22.91	26.30
Sample 51	%	0.04	0.13	0.24	0.36	0.50	0.64	0.79	0.94	1.08	1.20	1.30	1.38	1.41	1.41	1.37	1.29	1.18	1.06	0.92	0.79	0.70	0.66	0.70	0.84	1.12
Sample 51	%	0.05	0.14	0.25	0.37	0.51	0.65	0.79	0.92	1.05	1.16	1.24	1.30	1.33	1.33	1.30	1.23	1.14	1.02	0.90	0.78	0.69	0.64	0.67	0.80	1.06
Sample 51	%	0.05	0.15	0.26	0.38	0.51	0.65	0.78	0.91	1.03	1.13	1.22	1.27	1.30	1.30	1.27	1.20	1.11	1.00	0.89	0.77	0.68	0.64	0.67	0.80	1.06
Sample 51 - Ave	%	0.04	0.14	0.25	0.37	0.50	0.65	0.79	0.93	1.05	1.16	1.25	1.32	1.35	1.35	1.31	1.24	1.14	1.03	0.90	0.78	0.69	0.65	0.68	0.81	1.08
	um	39.81	45.71	52.48	60.26	69.18	79.43	91.20	104.71	120.23	138.04	158.49	181.97	208.93	239.88	275.42	316.23	363.08	416.87	478.63						
Sample 51	%	2.76	3.52	4.30	5.06	5.71	6.21	6.50	6.56	6.37	5.96	5.36	4.64	3.84	3.05	2.26	1.48	0.69	0.05	0.00						
Sample 51	%	2.71	3.51	4.35	5.17	5.89	6.44	6.77	6.83	6.61	6.14	5.47	4.68	3.82	2.98	2.13	1.30	0.39	0.01	0.00						
Sample 51	%	2.69	3.48	4.32	5.14	5.87	6.42	6.75	6.82	6.61	6.16	5.50	4.72	3.87	3.04	2.20	1.38	0.51	0.03	0.00						
Sample 51 - Ave	%	2.72	3.50	4.32	5.12	5.82	6.36	6.67	6.73	6.53	6.09	5.44	4.68	3.84	3.03	2.20	1.38	0.53	0.03	0.00						

Appendix D Example BJH Analysis Results

Table APNDX 3 Example BJH Analysis Results

TriStar 3000 V6.08 A	Unit 1 Port 2	Serial #: 1001	Page 1
Sample:	Ali_41		
Operator:	ZS		
Warm Free Space:	8.4962 cm ³ Measured	Cold Free Space:	26.1839 cm ³ Measured
Equilibration Interval:	5 s	Low Pressure Dose:	None
Sample Density:	1.000 g/cm ³	Automatic Degas:	No

BJH Adsorption dV/dD Pore Volume

Pore Diameter (nm)	Pore Volume (cm ³ /g·nm)
157.5523	3.13E-05
115.2611	5.19E-05
85.26198	7.63E-05
46.63703	0.00012
29.13627	0.000195
21.78333	0.000254
17.54309	0.000286
14.64642	0.000333
12.4104	0.000369
10.82867	0.00041
9.055494	0.000463
7.493785	0.000512
6.368488	0.000568
5.514932	0.000637
4.843818	0.000727
4.298273	0.000807
3.843073	0.000878
3.45667	0.000886
3.120357	0.000829
2.824775	0.000795
2.550695	0.000697
2.30143	0.000583
2.150036	0.000581
2.056182	0.000552

Appendix E EPA Method 29 Sampling Train

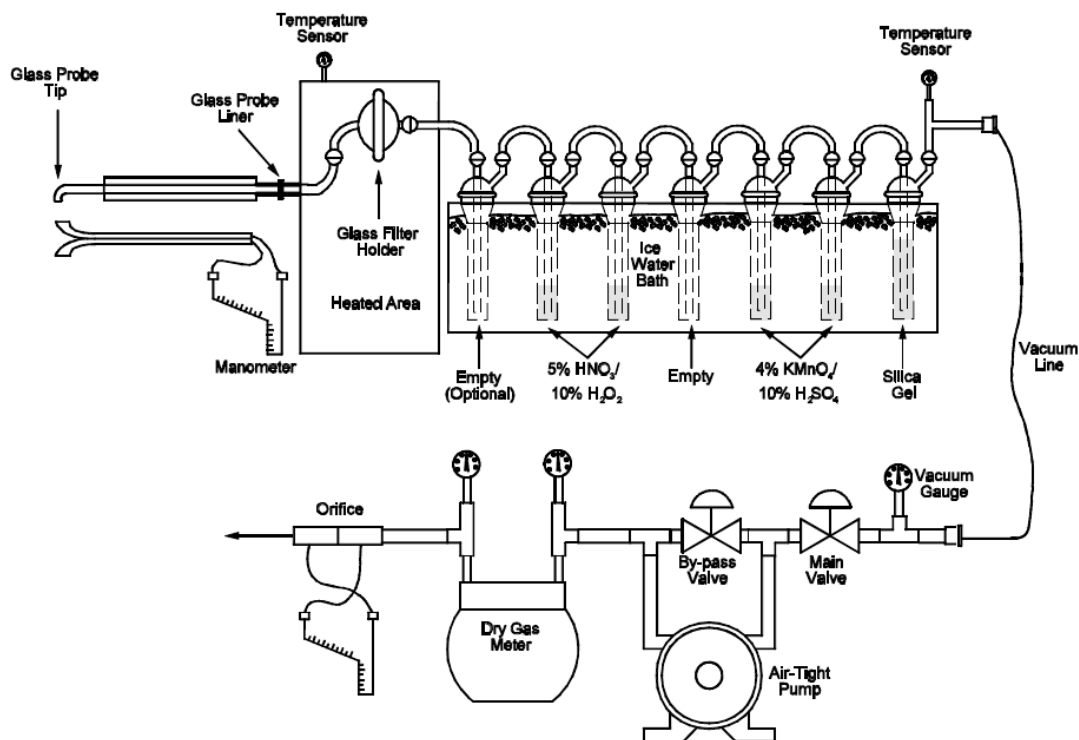


Figure A-6 EPA Method 29 Sampling train adapted to investigate metals concentration in the carbonator flue gas.

Appendix F Principal Component Analysis

Results of the principal component analysis (PCA) are provided in this appendix, and shows correlation between the data.

F.1 Effect of Bed Inventory

F.1.1 Major Elements – Solid Phase

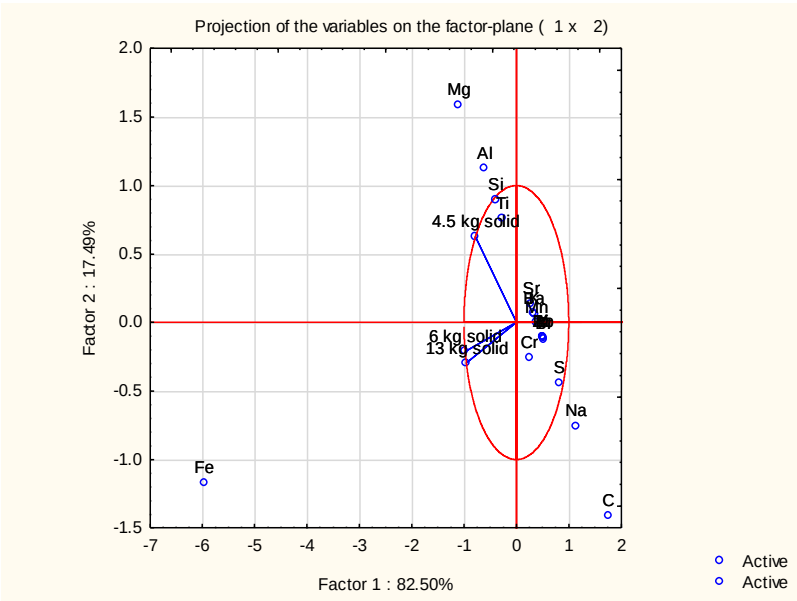


Figure A- 7 PCA Effect of bed inventory: Major elements – Solid Phase

F.1.2 Major Elements – Gas Phase

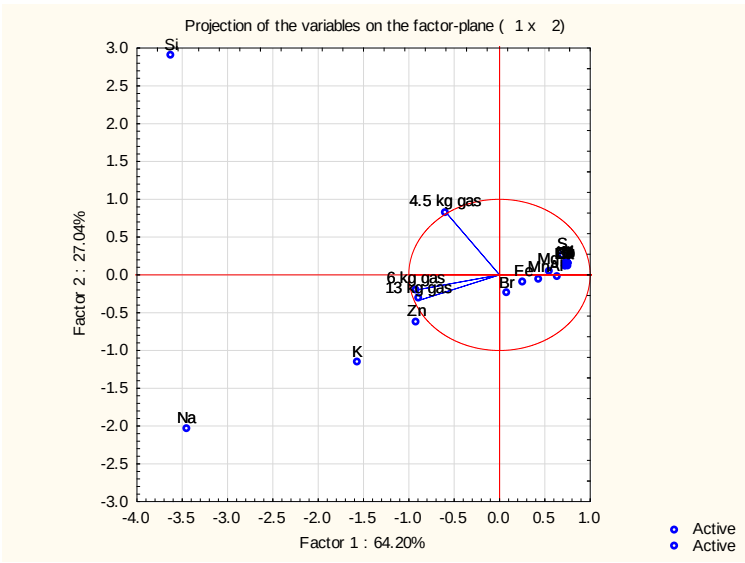


Figure A- 8 PCA Effect of bed inventory: Major Elements – Gas Phase

F.1.3 Minor Elements – Solid Phase

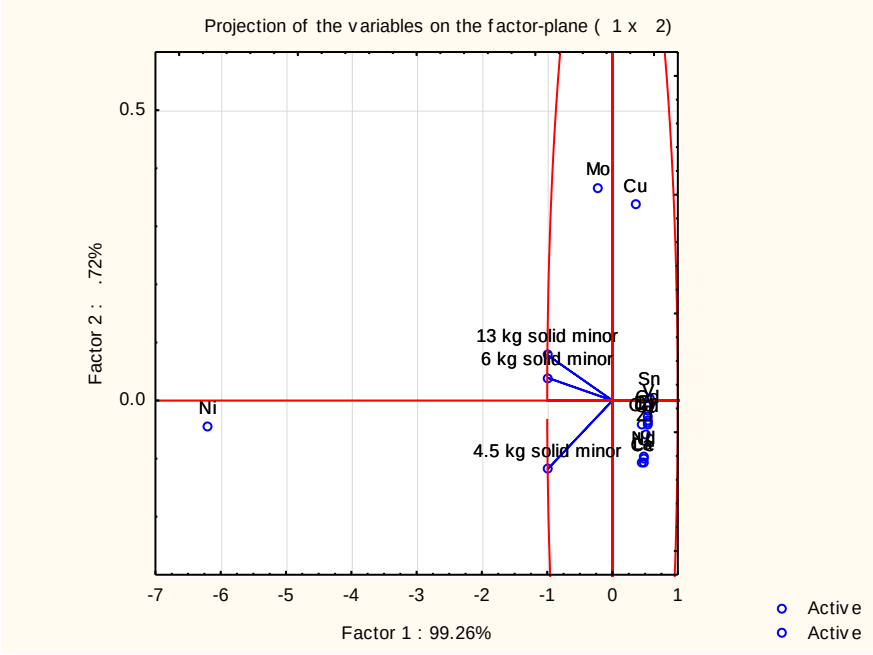


Figure A- 9 PCA Effect of bed inventory: Minor Elements – Solid Phase

F.1.4 Trace Elements – Solid Phase

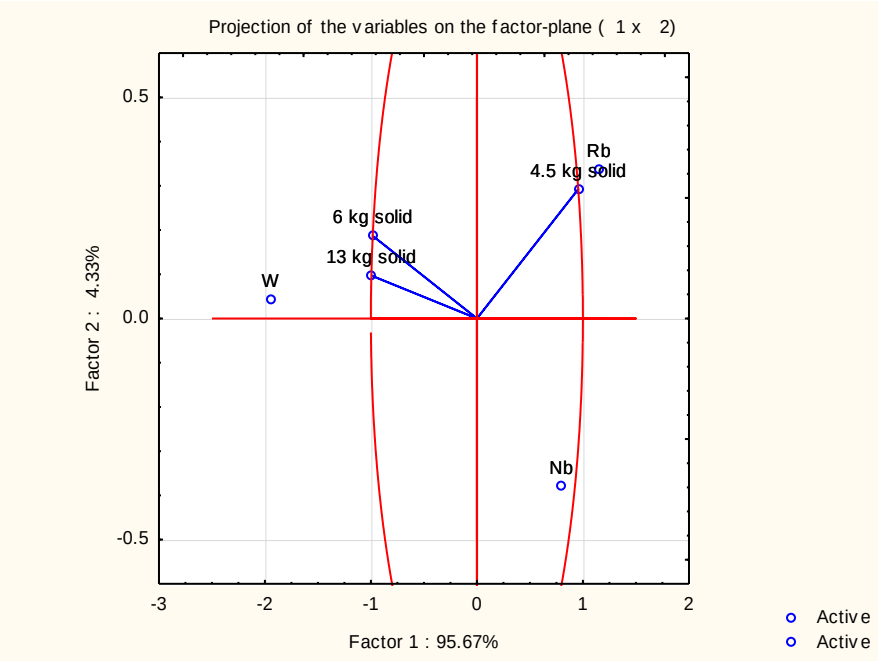


Figure A- 10 PCA Effect of bed inventory: Trace Elements – Solid Phase

F.2 Effect of Steam (Batch test)

F.2.1 Major Elements – Solid Phase

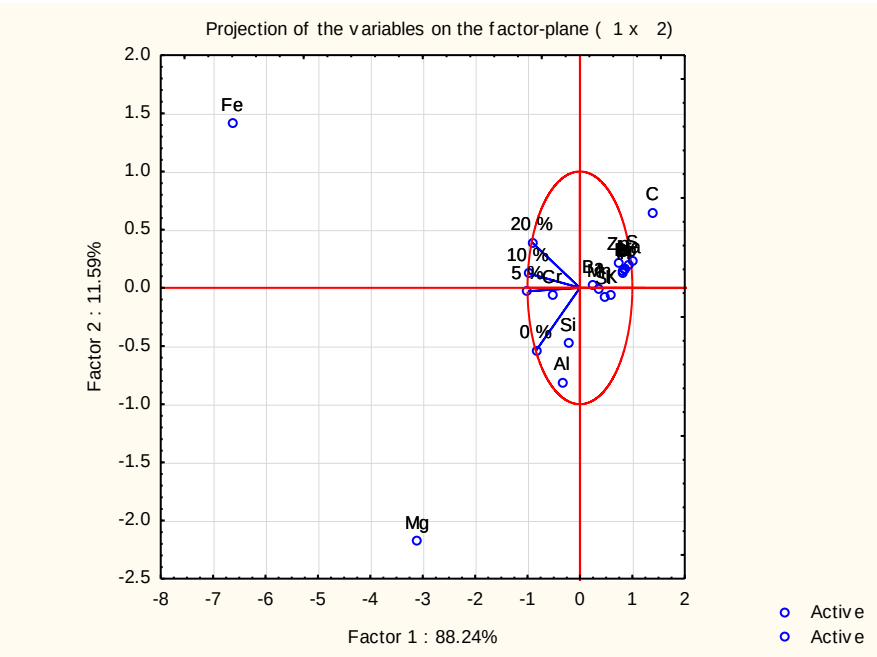


Figure A- 11 PCA Effect of additional steam: Major Elements – Solid Phase

F.2.2 Major Elements – Gas Phase

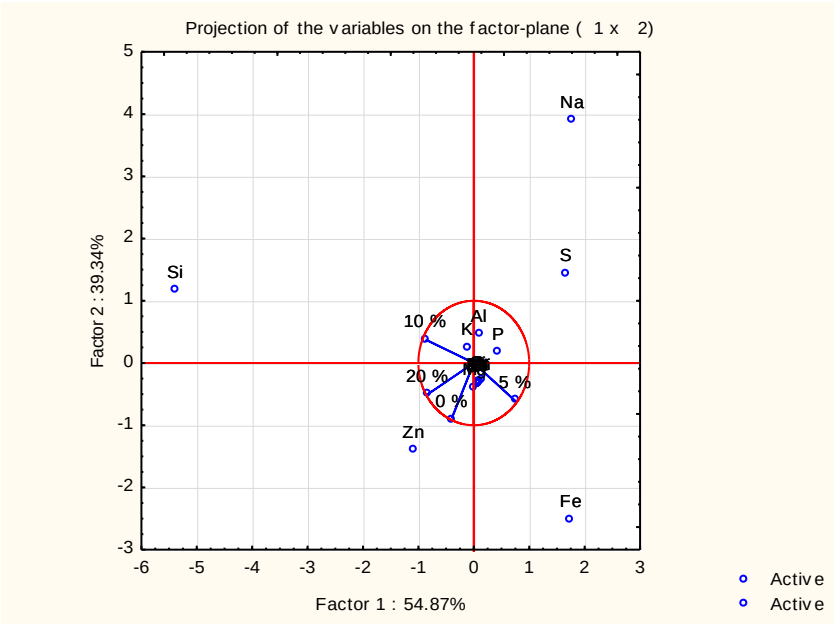


Figure A- 12 PCA Effect of additional steam: Major Elements: Gas Phase

F.2.3 Minor Elements – Solid Phase

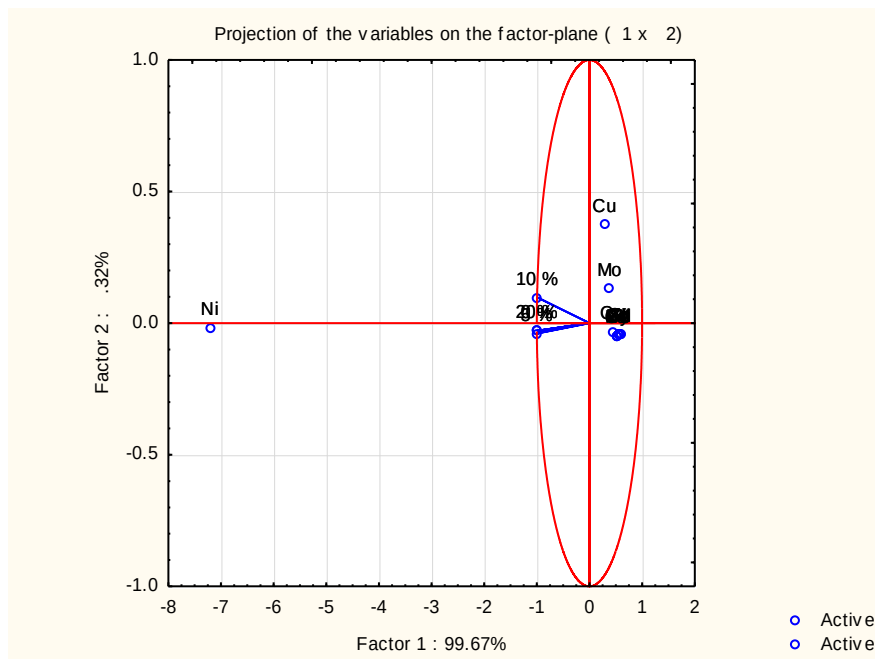


Figure A- 13 PCA Effect of additional steam: Minor Elements – Solid Phase

F.2.4 Trace Elements – Solid Phase

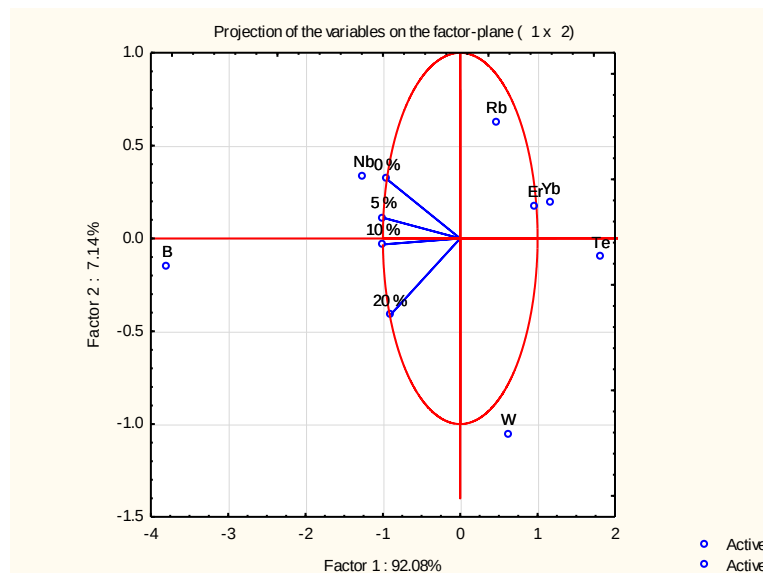


Figure A- 14 PCA Effect of additional steam: Trace Elements – Solid Phase

F.3 Effect of SO₂ (Batch tests)

F.3.1 Major Elements – Solid Phase

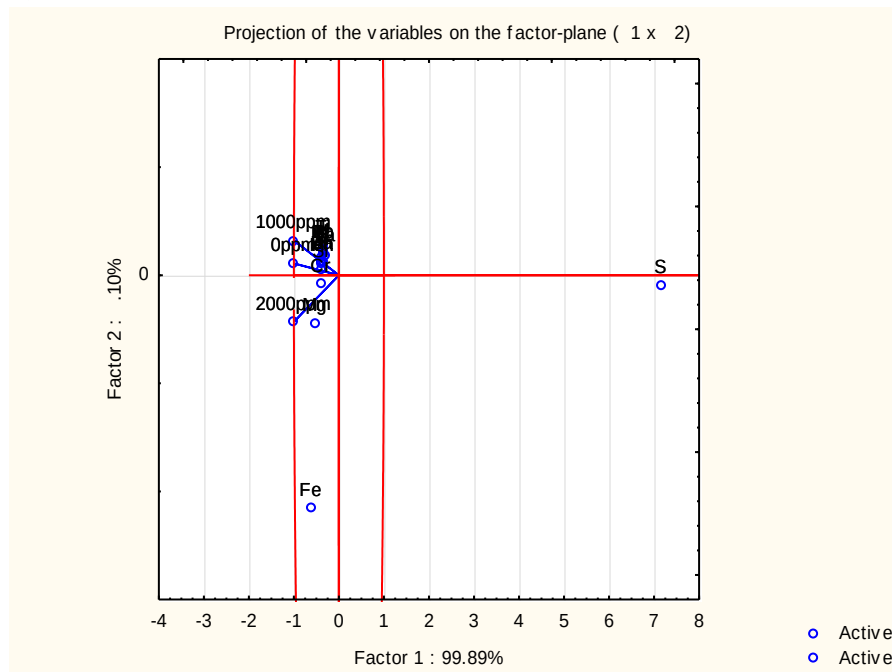


Figure A- 15 PCA Effect of SO₂ (batch test): Major Elements – Solid Phase

F.3.2 Major Elements – Gas Phase

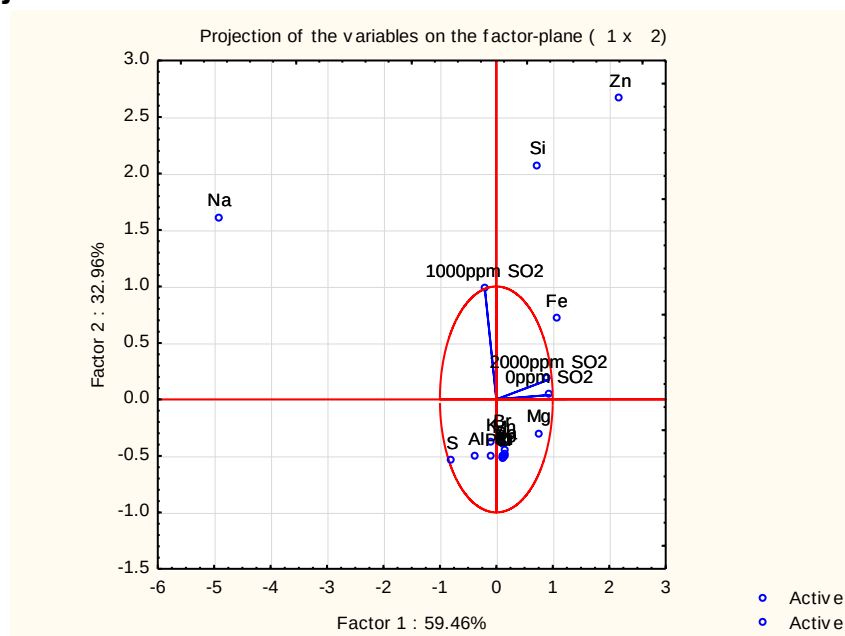


Figure A- 16 PCA Effect of SO₂ (batch test): Major Elements – Gas Phase

F.3.3 Minor Elements – Solid Phase

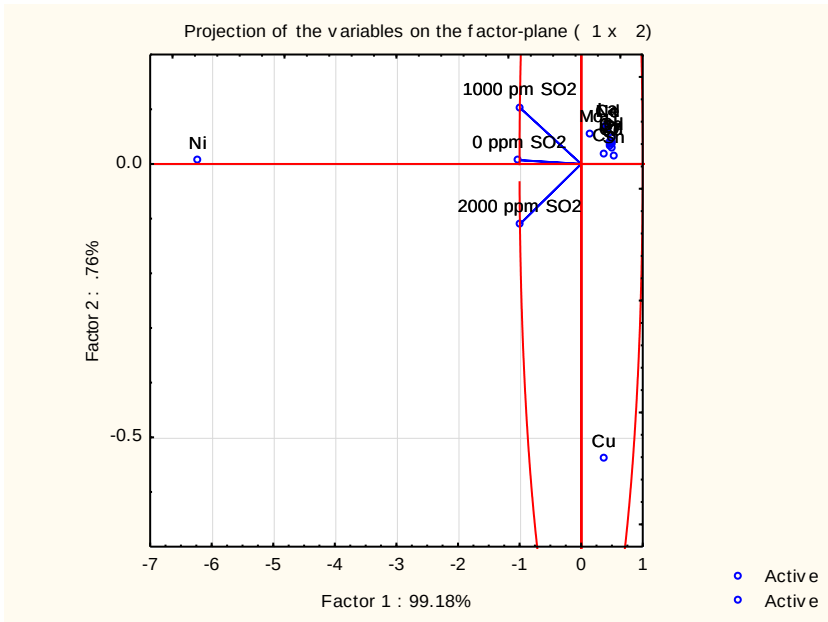


Figure A- 17 PCA Effect of SO₂ (batch test): Minor Elements – Solid Phase

F.3.4 Trace Elements – Solid Phase

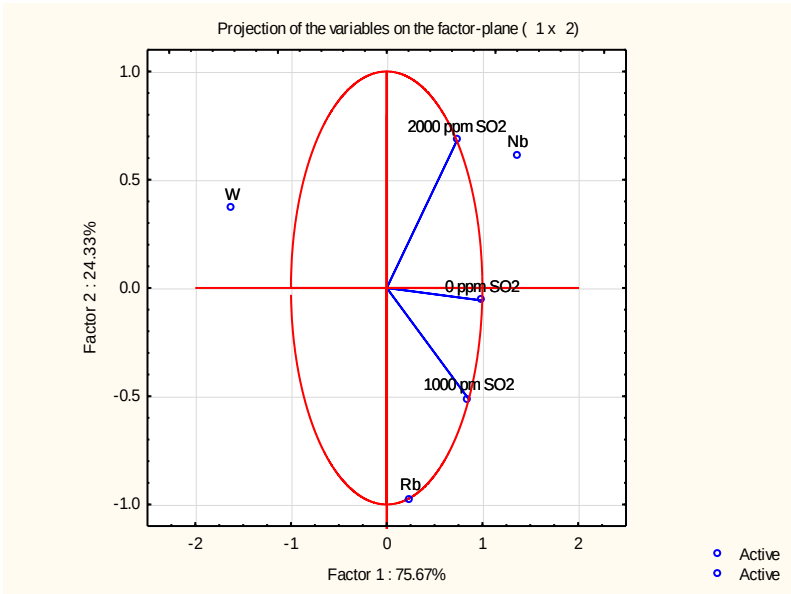


Figure A- 18 PCA Effect of SO₂ (batch test): Trace Elements – Solid Phase

F.4 Effect of SO₂ (continuous looping cycle)

F.4.1 Major Elements – Solid Phase

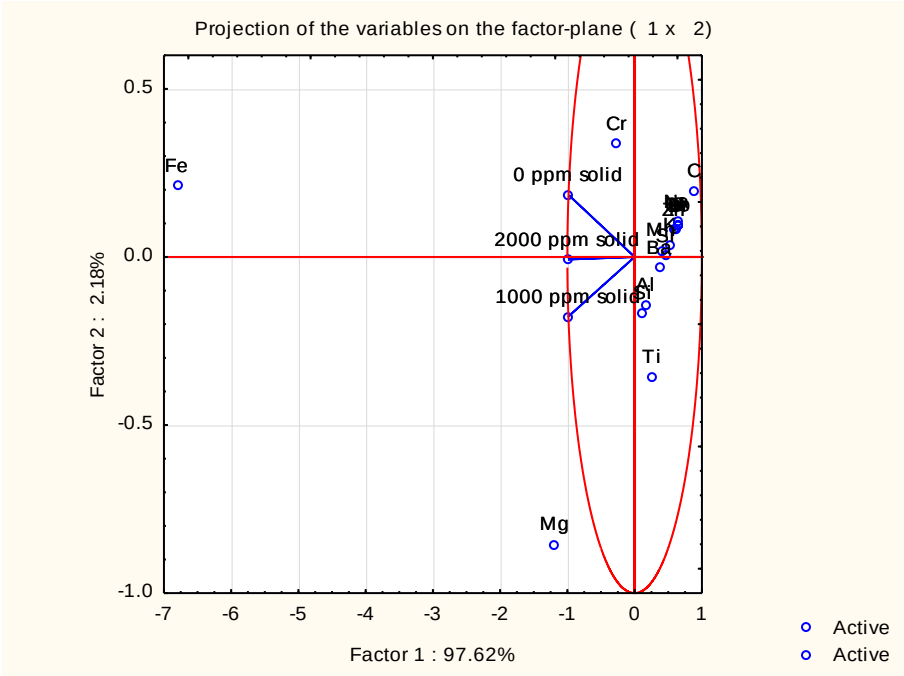


Figure A- 19 PCA Effect of SO₂ (looping): Major Elements – Solid Phase

F.4.2 Major Elements – Gas Phase

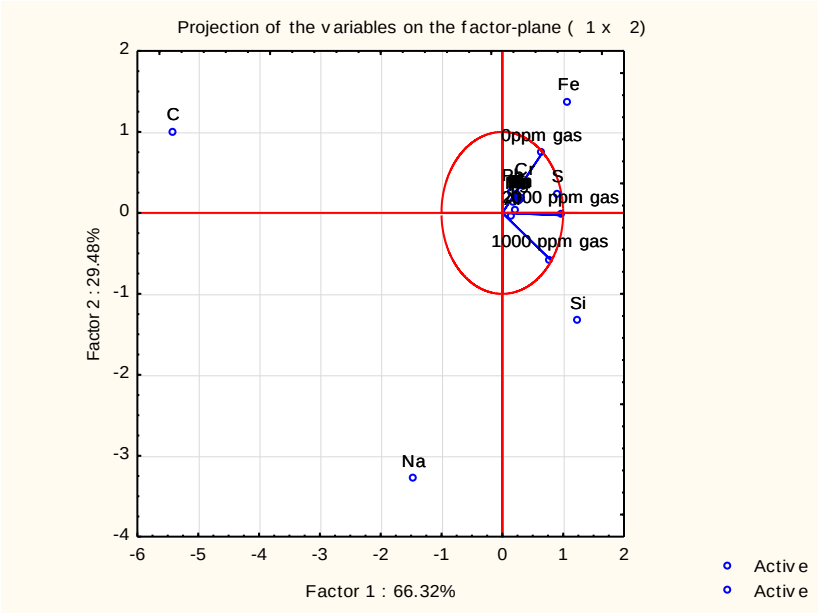


Figure A- 20 PCA Effect of SO₂ (looping): Major Elements – Gas Phase

F.4.3 Minor Elements – Solid Phase

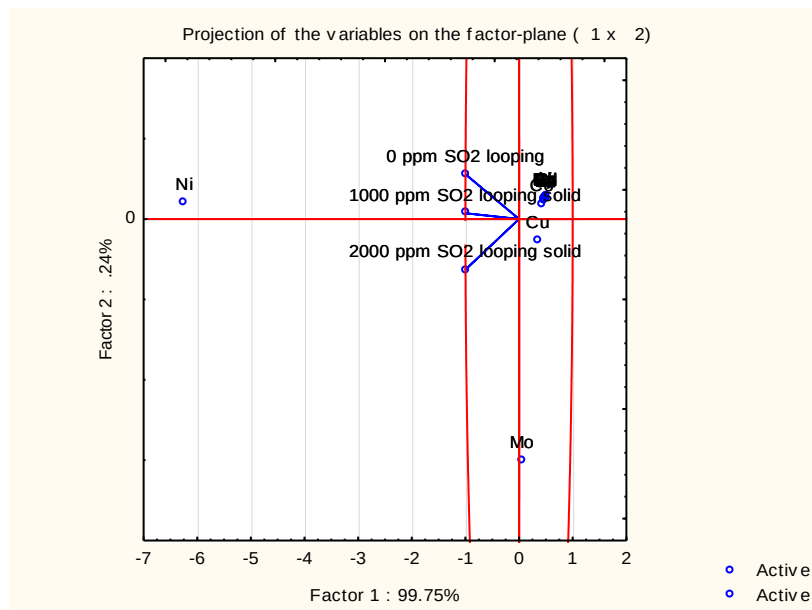


Figure A- 21 PCA Effect of SO₂ (looping): Minor Elements – Solid Phase

F.4.4 Trace Elements – Solid Phase

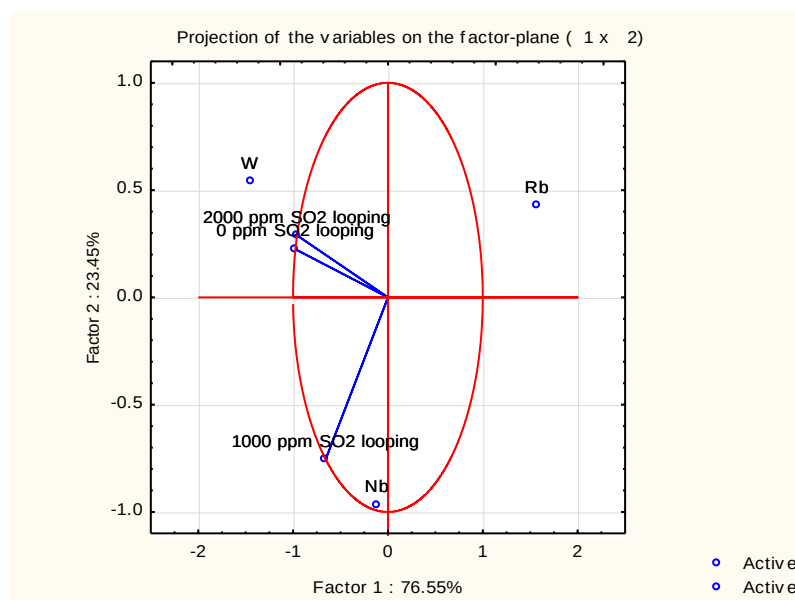


Figure A- 22 PCA Effect of SO₂ (looping): Trace Elements – Solid Phase

Appendix G Limitations of the Work

A number of limitations of the work were identified during the course of the PhD, and these are provided below.

One of the main limitations of the work was frequent burner failure, whereby the burner would either not light, or would switch off. A number of factors appeared to influence this, including the progressive emptying, and in turn freezing, of gas cylinders as the test went on. Other influences included an increased pressure across the calciner plenum, which could be caused by either blocked gas distributor nozzles, or by blockage in the exhaust. As a result, when the burner did fail, it would affect both gas concentrations and temperatures in the reactor during tests. Therefore these factors often limited the length of time for which tests would run at stable conditions.

In addition to this, due to the length of time it took to prepare the reactor for testing and for the reactor to heat up to the desired temperatures suitable for testing, often this meant that only two or three hours were available for tests to be run for. Due to health and safety regulations it was not possible to leave the reactor running unattended overnight for example, in order to increase the amount of time available for testing. This meant that the sorbent underwent a reduced number of cycles compared to tests in other pilot scale reactors, meaning that the sorbent morphology was not as affected as it may have been in longer tests.

Due to a lack of time and resources, results presented from additional steam tests were run as batch tests instead of looping tests, due to the issues encountered when testing with additional steam. These included exhaust and standpipe blockages as a result of $\text{Ca}(\text{OH})_2$ formation from low temperatures in across the lower loop seal and associated standpipes and also the exhaust. As mentioned, the 90° angle in the calciner exhaust also attributed to the particulate deposition from the flue gas, and thus blocking. A number of measures and amendments have been recommended from this, including removal of the 90 ° angle, additional of insulation along the length of the exhaust to prevent cooling, condensing and thus deposition, and the addition of

trace heating across the lower loop seal and its standpipes. Unfortunately the time taken to incorporate all of these measures and carry out tests was not available in the timeframe of this PhD, and future work would be required to validate the findings in looping tests. Despite this, the batch additional steam tests have provided useful information and have contributed in filling the knowledge gap. Further, the identified amendments will be useful in future design and testing of pilot scale reactors.

Further limitations related to the batch tests, and as mentioned in Section 9.3, was the requirement to pre-calcine the sorbent overnight in a furnace prior to testing, so that carbonation tests could then be carried out in the pilot scale reactor. Evidence in the literature regarding the outcome of this practise is not clear, with some studies suggesting pre-calcination can improve capture capacity [316] [160] [317] due to formation of a 'rigid interconnected CaO skeleton' [119], whilst others suggest that precalcination provides no improvement [319] [320]. Nonetheless, this was considered necessary in order to carry out batch tests.

Other limitations included the CO₂ gas analyser, which had a maximum concentration that it could measure of 10%, meaning that a concentration of 8 % more typical of both a natural gas-fired power station and also that from gas flaring, was used in the carbonator syngas, instead of the preferred 15 % typical of a coal-fired power station. This value is approximately half that of the 15 % used in some studies, whilst several other pilot scale studies also used a flue gas CO₂ concentration of 8 %, including in studies by Hughes *et al.*, 2009 [297] and Rodriguez *et al.*, 2011 [298].

The mass of limestone in the reactors was limited by the burner, as with a bed inventory of over approximately 13.5kg of limestone in the calciner, the burner would not light. As mentioned, bed inventory is important in influencing the calcium looping ratio to optimise % capture, and in investigating element partitioning. However, the use of 13 kg is a noteworthy increase in bed inventory compared to the much lower bed inventories used in bench scale testing.

Thermodynamic equilibrium modelling was undertaken for a select number of elements due to prolonged process calculation times experienced for large numbers of elements. The elements selected were based on those that were present in the initial limestone sample in the highest concentrations, and also those that are considered to present the greatest risk to human health and the environment.