

FLUIDIZED CALCIUM CARBONATE CRYSTALLIZATION IN ALKALINE LIQUIDS

by

Caroline Elizabeth Giacomini

B. Eng., McGill University, 2016

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(CHEMICAL AND BIOLOGICAL ENGINEERING)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

February 2019

© Caroline Elizabeth Giacomini, 2019

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, a thesis/dissertation entitled:

Fluidized calcium carbonate crystallization in alkaline liquids

submitted by Caroline Elizabeth Giacomini in partial fulfillment of the requirements for

the degree of Master of Applied Science

in Chemical and Biological Engineering

Examining Committee:

Dr. Walter Mérida

Supervisor

Dr. Fariborz Taghipour

Supervisory Committee Member

Dr. Yankai Cao

Additional Examiner

Additional Supervisory Committee Members:

Dr. Xiaotao Bi

Supervisory Committee Member

Supervisory Committee Member

Abstract

The effects of pH, pellet loading, and available surface area on CaCO_3 pellet growth were measured in highly alkaline liquids. These experiments included three scales. (i) Data from the bench scale reactor were used to predict CaCO_3 pellet diameter in larger scale reactors. (ii) Beaker scale experiments revealed that high pellet loading is more critical to CaCO_3 pellet growth than available surface area. At equal amounts of available surface areas, different retentions were found for different pellet sizes. Elevated temperatures proved detrimental to growth and produced smaller fines. An inversion of mole fractions of CaCO_3 morphologies occurred at the equivalence point of pH 12.3. (iii) Lab-scale fluidized bed reactor, designed and constructed for this thesis, showed that CaCO_3 pellet size is key to calcium retention within a fluidized bed reactor.

Lay Summary

One way to solve the carbon dioxide emissions problem is to remove carbon dioxide directly from the air. Recent work at Carbon Engineering Ltd. in Squamish, British Columbia, is doing just this. Ambient air laden with normal carbon dioxide enters the reactor and air, cleaned of this carbon dioxide, exits their reactor. Carbon dioxide is captured onto limestone pellets and then released as a profitable side stream of pure carbon dioxide which drives the economic feasibility of this process. This thesis deepens our understanding of how captured carbon dioxide causes the limestone pellets to grow. The results of this thesis may be used to improve the capture of carbon dioxide from ambient air that we breathe.

Preface

This thesis was industrially prescribed by Carbon Engineering, Ltd. in collaboration with Dr. Mérida's research group. I wrote the codes (listed in Appendix A) that I used in Chapter 2. Measurements given in Chapter 2 were utilized by me to glean empirical constants, the major finding presented in Chapter 2. For Chapter 3, I determined initial experiments to run for pH, pellet diameter, and surface size and Dr. Thomas Holm led me to the loading experiments. I designed and built the fluidized bed reactor for Chapter 4. I performed all of the experiments for Chapters 3 and 4. The experiments for Chapter 3 are beaker scale reactions to ascertain scientific knowledge about the CaCO_3 crystallization process. Experiments in Chapter 4 expand our knowledge of the crystallization in an industrially relevant environment. All research data from Chapters 3 and 4 was analyzed by me.

The work presented in Chapter 2 has been published [Luisa Burhenne, Caroline Giacomini, Trevor Follett, Jane Ritchie, Jenny S.J. McCahill, and Walter Mérida. (2017) "Characterization of reactive CaCO_3 crystallization in a fluidized bed reactor as a central process of direct air capture" *Journal of Environmental Chemical Engineering*. Vol. 5, no. 6, pp. 5968–5977]. Based on Dr. Luisa Burhenne's measurements, I developed MATLAB code to generate the empirical constants for Equation (10) in this paper. I generated Figures 7 through 11 through the developed model and this paper was written by Dr. Luisa Burhenne. Trevor Follett participated in experimentation and data collection. Jane Ritchie provided scaling knowledge for the construction of the experimental apparatus. Dr. Jenny S.J. McCahill provided scientific knowledge for the experimental design. Dr. Walter Mérida developed this collaboration, acquired funding, and provided advice on the scope of this project.

A version of Chapter 3 has been published as a conference proceeding. [Caroline E. Giacomini, Thomas Holm, Luisa Burhenne, and Walter Mérida. (2018) “Alkaline crystallization of CaCO_3 in a direct air capture process.” *AIChE Annual Meeting Proceedings*, Paper No. 737h]. I conducted all the testing and wrote the original paper draft. I developed an experimental test plan from an initial experiment by Dr. Burhenne. The introduction and results sections were rewritten by Dr. Thomas Holm. Results were interpreted together by me and Dr. Holm. Dr. Walter Mérida developed this collaboration and acquired funding for this project.

Table of Contents

Abstract	iii
Lay Summary.....	iv
Preface	v
Table of Contents.....	vii
List of Tables.....	x
List of Figures	xi
List of Symbols.....	xv
List of Abbreviations	xviii
Acknowledgments.....	xix
Dedication.....	xx
Chapter 1: Introduction.....	1
1.1 Direct air capture system	2
1.2 Reactor.....	3
1.3 Crystallization of CaCO ₃	3
1.3.1 Crystallization equations	4
1.3.2 Temperature and pH	6
1.4 Research objectives	8
1.5 Thesis organization.....	9
Chapter 2: Modelling for scale-up	10
2.1 Experimental methods	10
2.2 Modelling methods.....	12
2.3 Purpose	13

2.4	Theoretical bed growth model.....	14
2.4.1	Pellet growth.....	15
2.4.2	Pellet size dependence	19
2.5	Calibration	20
2.5.1	Validation	21
2.5.2	Process analysis	23
Chapter 3: Investigating crystallization at beaker scale.....		26
3.1	Direct air capture crystallization	26
3.1.1	Experimental procedure.....	27
3.1.2	Results and discussion.....	30
3.1.2.1	Ambient temperature	30
3.1.2.2	Elevated temperatures	33
3.2	Varied pH crystallization.....	39
3.2.1	Experimental procedure.....	39
3.2.2	Data processing method	41
3.2.3	Results and discussion.....	41
Chapter 4: Lab-scale reactor construction and operation		46
4.1	Construction	46
4.2	Experimental.....	51
4.2.1	Reactants.....	51
4.2.2	Operation	52
4.2.3	Experimental matrix	54
4.3	Results and Discussion	55
4.4	Industrial relevance	61

Chapter 5: Conclusion	62
5.1 Applications.....	63
5.2 Limitations.....	64
5.3 Future directions	64
Bibliography.....	65
Appendices	70
Appendix A : Codes	70
A.1 Minimizer	70
A.2 Pelletizer	71
Appendix B : Generate 2017 Conference Poster.....	76
Appendix C : Experimental procedures	77
C.1 Equivalence points for carbonate titration.....	77
C.2 Reactor flow conversion.....	78
C.3 Reactor operation.....	78
C.4 Sieve sizes	79

List of Tables

Table 2.1: Baseline operating conditions for the PPR and BPR, adapted from [6].	21
Table 3.1: Seed is the average size fed; mid-size is grown about halfway and makes up the predominant size range in the BPR; and mature pellets are fully grown and ready for removal..	27
Table 4.1: Hourly measurements from reactor run R6. Initial solids: 4500.15 g at mature size (see Table 3.1). Calcium retention for this trial was 35.0%.	53
Table 4.2: Experiments run in the LPR.	55
Appendix Table C.1: Conversion of flowmeter readings to superficial velocity	78
Appendix Table C.2: Initial, final, and average solution pH for experiments conducted in Subsection 3.2.....	78
Appendix Table C.3: Order of stacked sieve meshes, and the size of opening found in each.	79

List of Figures

Figure 1.1: Overall direct air capture process chemistry. Reprinted with permission from Elsevier [6].	3
Figure 1.2: Influence of temperature on the mole fraction of CaCO_3 morphologies. 1: vaterite, 2: aragonite, and 3: calcite (reprinted from Chen and Xiang [19] with permission from Elsevier).	7
Figure 1.3: Equilibrium mole fraction of carbonate versus pH [21].	8
Figure 2.1: Bench-scale pellet reactor (BPR) setup (left) and fluidized bed reactor (right). Reprinted with permission from Elsevier [6].	11
Figure 2.2: CaCO_3 pellet diameter, L_i , (dots, left axis) and calcium retention, R_{BPR} , (dashed line, right axis) in the benchtop pellet reactor. Flow velocity: 60 m h^{-1} , calcium loading: 3.0 mol h^{-1} , and seed diameter range $0.18 \leq L_i \leq 0.50 \text{ mm}$	16
Figure 2.3: Optimization of calculated particle size curves (dashed lines) compared to measured particle sizes (dots) at FV: 60 m h^{-1} , calcium loading: 3.0 mol h^{-1} and seed diameter range $0.18 \leq L_i \leq 0.50 \text{ mm}$	18
Figure 2.4: Calculated and measured particle sizes along the BPR height after 72 hours of operation at two calcium loadings, 1.6 and 3.0 mol h^{-1} , as well as pellet size data from the PPR with the same flow velocity and 3.0 mol h^{-1} calcium loading [36].	22
Figure 2.5: Modelled pellet surface area per unit volume (left) and porosity (right) over time at five different BPR bed heights at a flow velocity of 60 m h^{-1} , calcium loading of 3.0 mol h^{-1} , and seed diameter range $0.18 \leq L_i \leq 0.50 \text{ mm}$	24
Figure 3.1: SEM images of mid-size pellets (a) and their surface (b).	28
Figure 3.2: Crystallization reaction in progress for 50 g sample of mature pellets.	29

Figure 3.3: Experiments at 20°C: a) mid-size pellets at different mass loadings of 25, 50, and 100 grams, b) constant mass loading with varied pellet size, and c) constant surface area with varied pellet size. Retention herein is R_{beaker}	32
Figure 3.4: Retention for all trials shown in Figure 3.3 as well as best conditions experimental set. All shown with respect to surface area as calculated by BET isotherm measurements for the pellet size ranges. Retention herein is R_{beaker}	33
Figure 3.5: Percent of mass found on pellets over total mass collected, retention, after reaction for trials at different temperatures for mid-sized pellets. Retention herein is R_{beaker}	35
Figure 3.6: CaCO_3 fines grown at a) 20°C, b) 40°C, c) 60°C, and d) 80°C.....	36
Figure 3.7: Pellet surfaces after reaction at a) 20°C, b) 40°C, c) 60°C, and d) 80°C.....	37
Figure 3.8: XRD results for (a) pellets, and (b) fines at different temperatures. Reference spectra for calcite (pink), vaterite (green), aragonite (orange), and $\text{Ca}(\text{OH})_2$ (blue) are shown at the bottom.....	38
Figure 3.9: XRD Rietveld refinement mole fractions for relative prevalence of crystalline morphologies for $6.5 \leq \text{pH} \leq 14.5$	42
Figure 3.10: Equivalence point pH for OH^- to H_2O , CO_3^{2-} to HCO_3^- , and HCO_3^- to H_2CO_3 determined from 18 pH experimental titrations performed to with Oakton pHTestr 30. Data set is representative sample of pH versus volume added for a 1.0 M KOH and 0.5 M K_2CO_3 solution.	43
Figure 3.11: Experimental pH change of solution during 10 minute crystallization.	44
Figure 3.12: XRD Rietveld refinement mole fractions for relative prevalence of crystalline morphologies at the final pH of the reaction for the reactions starting at $6.5 \leq \text{pH} \leq 14.5$, on pH 0.5 intervals (see Figure 3.9).	45

Figure 4.1: Lab scale reactor at hour 2 of a mid-sized pellet trial.	49
Figure 4.2: Disengagement zone of LPR.	50
Figure 4.3: Bottom of LPR.	50
Figure 4.4: Settling tank of LPR while operating.....	50
Figure 4.5: Flowmeter and turbidity probe setups in LPR.	51
Figure 4.6: LPR inlet sampling port.	51
Figure 4.7: Reactor retentions, R_{LPR} , versus available initial surface area. Surface area determined using BET isotherm analysis (see Table 3.1) and initial pellet mass.	56
Figure 4.8: Average temperature deviation, settling tank minus DI water reservoir, hourly, for reaction duration in LPR.	57
Figure 4.9: Within one standard deviation (error bars), the fluidized bed height was held constant for all three pellet sizes tested. This was done by approximating bed porosity at 60 m/h and determining the mass of pellets to be added to control this fluidized height in the LPR.	58
Figure 4.10: Settling tank pH as calibrated to USA standard and measured with Oakton pHTestr 30 with two-minute measurement to allow reading stabilization. Measured hourly for reaction duration in LPR.	58
Figure 4.11: Mass fraction of pellets found in each sieve for R4, a representative size distribution change for a seed pellet size trial. R4 had a retention, R_{LPR} , of 58.3% (corresponding to a mass gain of 289.10 g) and a starting mass of 1200.21 g.....	59
Figure 4.12: Mass fraction of pellets found in each sieve for R9, a representative size distribution change for a mid-size pellet trial. R9 had a retention, R_{LPR} , of 59.8% (corresponding to a mass gain of 295.51 g) and a starting mass of 2500.72 g.....	60

Figure 4.13: Mass fraction of pellets found in each sieve for R3, a representative size distribution change for a mature pellet size trial. R3 had a retention, R_{LPR} , of 38.7% (corresponding to a mass gain of 203.10 g) and a starting mass of 4500.50 g.....60

Appendix Figure C.1: Titration of process solution sample post reaction run 10 for determining replenishing amounts for KOH and K_2CO_377

List of Symbols

Variable	Description	Units
$[\text{OH}^-]$	Concentration of hydroxide ions	mol/L
$\dot{V}_{slurry}$	Volumetric flowrate of slurry	m^3/min
$\Delta m_{\text{pellets}}$	Change in mass of pellets of CaCO_3	g
A	Reactor cross sectional area	m^2
A_s	Total pellet surface area	m^2
C	Crystallization rate	$\frac{\text{mol}}{\text{L min}}$
C_{w2}	Drag coefficient, Equation (2.2)	[-]
$[\text{Ca}^{2+}]$	Concentration of calcium ions	mol/L
$[\text{CO}_3^{2-}]$	Concentration of carbonate ions	mol/L
f_D^2	Activity factor for divalent ions [1]	[-]
F_d	Driving force of crystallization	$(\text{mol/L})^2$
F_w	Flow rate of process solution	m^3/s
g	Acceleration due to gravity	m/s^2
k_f	Mass transport coefficient, Equation (1.5)	$\frac{\text{L}}{\text{mol min m}^2}$
K_{sp}	Thermodynamic solubility product of CaCO_3 crystallization from ions	$(\text{mol/L})^2$
k_T	Crystallization rate constant for CaCO_3 at T	$\frac{\text{L}}{\text{mol min m}^2}$

k_{T20}	Crystallization rate constant for CaCO_3 at 20°C	$\frac{\text{L}}{\text{mol min m}^2}$
L_i	Mean pellet diameter, at i th port	m
$\log \theta$	Logarithm of constant, Equation (1.6)	$^\circ\text{C}^{-1}$
m_{fines}	Mass of fine particles of CaCO_3	g
$m_{\text{pellet},i}$	Mass of pellets in sample taken from height i in the BPR	g
$m_{\text{pellets,after}}$	Mass of pellets of CaCO_3 after reaction	g
$m_{\text{pellets,before}}$	Mass of pellets of CaCO_3 before reaction	g
$m_{\text{prospective}}$	Mass of solid CaCO_3 expected to be collected after reaction	G
MSE	Mean square error, Equation (2.7)	[-]
$\text{MW}_{\text{Ca(OH)}_2}$	Molecular weight Ca(OH)_2	g/mol
$\text{MW}_{\text{CaCO}_3}$	Molecular weight of CaCO_3	g/mol
n	Richardson-Zaki exponent [2]	[-]
$n_{\text{Ca(OH)}_2}$	Moles of Ca(OH)_2 fed	moles
p_i	Bed porosity	[-]
R	Retention	%
R_{beaker}	Retention of calcium on the pellets, Equation (3.1)	%
R_{BPR}	Retention of calcium on the pellets, Equation (2.10)	%
R_{FPR}	Retention of calcium on the pellets, Equation (4.1)	%
Re_0	Reynolds number, Equation (2.3)	[-]
SA_i	Specific surface area	m^2/m^3
T	Temperature	$^\circ\text{C}$

T_0	Temperature offset, Equation (1.6)	$^{\circ}\text{C}$
t_{run}	Duration of reactor run	min
$u_{0,i}$	Pellet terminal velocity, Equation (2.4)	m/s
V_i	Volume of control volume in BPR between heights i and $i + 1$	m^3
V_{sample}	Volume of sample taken from height i in the BPR	m^3
ρ_{bed}	Density measurement of a fluidized bed	kg/m^3
ρ_l	Mass density, liquid	kg/m^3
ρ_p	Mass density, pellet	kg/m^3
ρ_{slurry}	Density of slurry	g/mL
w	Weight fraction of $\text{Ca}(\text{OH})_2$ in the slurry	%
α	Empirical coefficient, Equation (2.2)	[-]
β	Empirical exponent, Equation (2.2)	[-]
θ	Bragg angle	$^{\circ}$
κ	Crystallization kinetic parameter	$\frac{\text{L}}{\text{mol min m}^2}$
ν	Kinematic viscosity	m^2/s

List of Abbreviations

ACS	American Chemical Society grade
BET	Brunauer–Emmett–Teller [3]
BPR	Bench-scale Pellet Reactor
CE	Carbon Engineering Ltd.
COD	Crystallography Open Database
DAC	Direct Air Capture
DI	Deionized water
FoM	Figure-of-Merit
FPT	Female pipe thread
GPM	Gallons per minute
LPR	Lab-scale Pellet Reactor
MPT	Male pipe thread
PPR	Pilot-scale Pellet Reactor
PVC	Polyvinylchloride
SEM	Scanning electron microscopy
VSP	Variable speed pump
XRD	X-ray diffraction

Acknowledgments

This is to acknowledge my research supervisors Professor Walter Mérida, Dr. Omar Herrera, Dr. Thomas Holm, and Dr. Luisa Burhenne of the University of British Columbia for their indispensable help. This is also to acknowledge my industrial research advisors Dr. Jenny McCahill and Dr. Kyle Kemp of Carbon Engineering Ltd. in Squamish, British Columbia. Many thanks to my committee members Professors Fariborz Taghipour and Xiaotao Bi. Thank you to Professor Yankai Cao for serving on my examining committee.

Doug Yuen, Graham Liebelt, Tobias Donaldson, and Serge Milaire of the Chemical and Biological Engineering Department machine shop have been exceedingly helpful to my reactor construction. Additionally, I acknowledge the Chemical and Biological Engineering Department safety officer Miles Garcia and storekeeper Richard Ryoo.

This work was supported by Carbon Engineering Ltd., Mitacs, and the National Sciences and Engineering Research Council of Canada (NSERC).

I thank Jesús Díaz Real, Patrick Elsässer, Ruben Govindarajan, and Ezgi Kisa for making long days in the lab more enjoyable.

Special thanks are owed to my parents. My mother for her tireless help in helping me move around the continent to pursue my degrees. My father who always keeps me encouraged

Dedication

To the waters of British Columbia for rejuvenation.

To the nature here for keeping me grounded.

To the friends who've helped along the way.

To the clubs I joined for balancing me.

Chapter 1: Introduction

Water softening in fluidized beds, and the flow regime occurring within its crystallization process, is analogous to the regime of the pelletizer used in the direct air capture process developed by Carbon Engineering Ltd. This calcium carbonate crystallization process is well-studied [4].

Water softening removes calcium from water via the introduction of carbonate. On an industrial scale, water is softened in a fluidized bed pellet reactor. Fluidized bed reactors are used for multiphase reactions where the fluid velocity is sufficient to suspend particles, and cause them to behave as a fluid [5], [6]¹. While many studies exist on the flow patterns in fluidized beds, these patterns are herein neglected as the reactor type is used as a tool rather than the subject of study. Under the conditions needed for direct air capture, crystallization is not an optimized process. Within the realm of adjustable variables for this process, this thesis explores what can be done to adjust the form of crystal nucleation that occurs. By *nucleation* we mean precipitation of a new phase from solution. Nucleation can occur as either primary or secondary. By *primary* nucleation we mean nucleation that occurs without an existing solid surface. *Secondary* nucleation is where nucleation of new crystals occurs onto an existing solid surface.

¹ Errata: "Richard-Zaki" should be "Richardson-Zaki" throughout; the left side of Eq. (4) should be squared.

1.1 Direct air capture system

Rising CO₂ levels in our atmosphere have led to the need for reducing emissions, however for the CO₂ that has already been released, new removal methods have been developed including direct air capture. By *direct air capture*, we mean the removal of CO₂ from the atmosphere, rather than from an emission source. Carbon Engineering, Ltd., in Squamish, British Columbia has patented an air capture process that uses an air contactor with highly ionic liquid to capture CO₂ as aqueous CO₃²⁻ ions [7]. These ions then react with calcium from calcium hydroxide (Ca(OH)₂) to form solid calcium carbonate (CaCO₃). This reaction results in the growth of CaCO₃ on pre-seeded pellets in the reactor. Once pellets reach mature size, they are conveyed to a calciner where they are heated to release gaseous CO₂, H₂O vapour, and CaO solid.

The purpose of direct air capture is to produce a stream of pure CO₂ that can be used as a reactant for other chemical processes. Uses include carbonation of soft drinks, production of dry ice, fire extinction, or green house growth acceleration. Some research is being done on converting CO₂ into low carbon fuels [8][9]. Early in 2018, the production of jet fuel was demonstrated successfully at Carbon Engineering [10].

The direct air capture system gives rise to our crystallization conditions constraints of high pH (between 14.0 and 14.6) and flowrates of inlet and outlet streams.

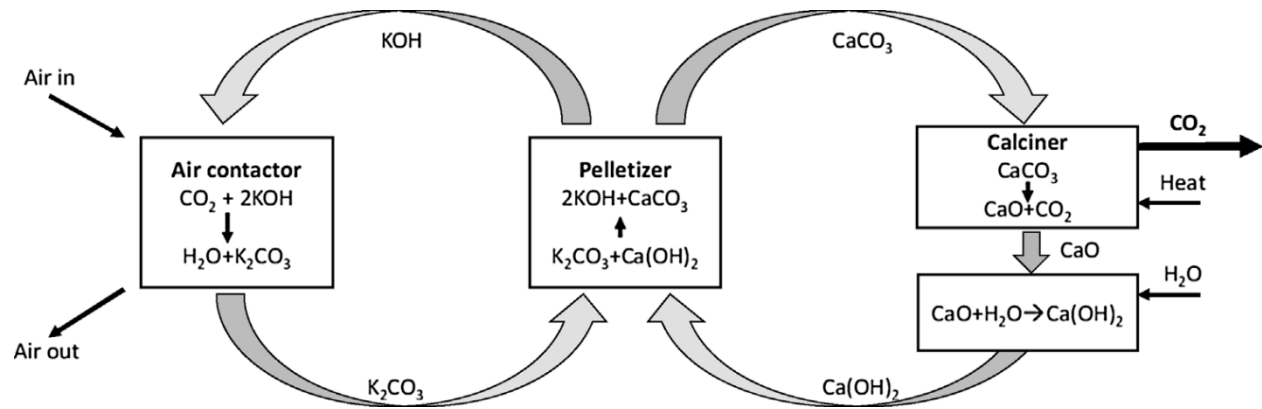


Figure 1.1: Overall direct air capture process chemistry. Reprinted with permission from Elsevier [6].

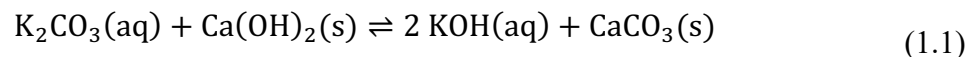
1.2 Reactor

Fluidized bed reactors allow a liquid-solid reaction to occur continuously. Continuous pellet motion prevents clumping that could damage the reactor. This clumping would interfere with calciner efficiency.

In the pelletizer, particle diameters range from 100 to 800 μm . Product particles being conveyed to the calciner range in diameter from 800 to 1400 μm . At this size, they can be removed from the pelletizer and conveyed continuously.

1.3 Crystallization of CaCO_3

The focus of this thesis is the study of the pellets themselves. Calcium carbonate can form crystals in a variety of structures including aragonite, vaterite, and calcite [11]. The stoichiometry for this exothermic reaction is:



whose heat of reaction, in the forward direction, is -12.3 kJ/mol [12].

The aragonite structure is an orthorhombic crystal with crystal class dipyramidal. The vaterite structure is a hexagonal with crystal class dihexagonal dipyramidal. The calcite structure is a trigonal with crystal class hexagonal scalenohedral. Crystallization occurs in two forms: primary and secondary nucleation. *Primary nucleation* is the precipitation of a crystal nuclei where the phase being created is not present until its formation. *Secondary nucleation* is nuclei forming on an already existing crystal structure, or crystal growth.

1.3.1 Crystallization equations

Crystallization of CaCO_3 from alkaline solution is relevant for a process capturing CO_2 directly from air. Recently, this process was found to be economically feasible at a cost of less than \$100/ton CO_2 [8]. Figure 1.1 shows the overall industrial process with its central pelletizer, a fluidized bed reactor that precipitates dissolved carbonate as $\text{CaCO}_3(\text{s})$. Precipitation can occur either (i) on the solid CaCO_3 pellets or (ii) spontaneously in solution, where spontaneously nucleated particles, significantly smaller than the pellets, are called *fines*. The precipitation on pellets, *growth*, is the desired outcome. To quantify the growth occurring the term retention is introduced. *Retention* is the change in pellet mass divided by the ideal scenario end mass and is expressed as a percentage:

$$R = \frac{\Delta m_{\text{pellets}}}{m_{\text{prospective}}} \quad (1.2)$$

where $\Delta m_{\text{pellets}}$ is the change in mass of pellets over reaction duration and $m_{\text{prospective}}$ is the perfect ideal mass of CaCO_3 that could be recovered. Retention is differently calculated in each of the proceeding chapters based on whether, and how, mass is recovered from each reactor type.

Both forms of precipitation, production of fines and growth, have the same driving force, the supersaturation, F_d , defined by [13]:

$$F_d = [\text{Ca}^{2+}][\text{CO}_3^{2-}] - \frac{K_{sp}}{f_D^2} \quad (1.3)$$

where, $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the concentrations of calcium and carbonate in solution, K_{sp} is the thermodynamic solubility product, and f_D is the activity factor for divalent ions [1].

Crystallization of CaCO_3 has been studied in the water softening industry, where addition of dissolved carbonate is used to reduce the calcium content of water by precipitation on CaCO_3 pellets [1][14][11][15][16]. Tai et al. [14] found that increased temperature, supersaturation, and pH accelerate spontaneous nucleation and decelerate pellet growth. Where the effect of surface area was studied, seed pellets with diameters between 0.6 and 4 μm were used, and whereas the total available surface area significantly impacted calcium removal, pellet size showed no impact [15]. For industrial water softening, the optimum pellet seed size is 250 μm [17]. Also, Ševčík et al. [11] used beaker experiments to show that increasing the probability of contacting a solid particle, via higher stirring velocities, increases pellet growth.

The crystal growth on solid pellets was successfully modelled by van Schagen et al. [18] and the crystallization rate is given by:

$$C = \kappa A_s \left([\text{Ca}^{2+}][\text{CO}_3^{2-}] - \frac{K_{sp}}{f_D^2} \right) \quad (1.4)$$

where, κ is the crystallization kinetic parameter, and A_s , the pellet surface area. The reaction was described as two-stage, where the first is the ion transport to the solid surface and the second, the

crystallization on the pellets. Depending on the local conditions in the reaction vessel, the pellet growth is limited by either mass transport, kinetics, or both.

The crystallization kinetic parameter is given by [4]:

$$\kappa = \frac{k_T k_f}{k_T + k_f} \quad (1.5)$$

where k_f describes mass transport of ions to particle surfaces. Whereas k_f depends on flow pattern and temperature, k_T depends only on temperature and describes the crystallization step. For trials at ambient temperature, we use the k_f value for the water softening process given in van Schagen et al. [18]. The k_T term is given by [18]:

$$k_T = \theta^{T-T_0} k_{T20} \quad (1.6)$$

where T is temperature in Celsius and k_{T20} is the crystallization rate constant for CaCO_3 at 20°C .

The values for the temperature offset parameter, $k_{T20} = 1.53$, $T_0 = 20^\circ\text{C}$, and the empirical constant $\theta = 1.053$ are from [1]. From this section we hypothesize that the conditions expected to be favorable for pellet growth are large total surface area, low temperature, high stirring rate, low supersaturation, and low pH.

1.3.2 Temperature and pH

Over a range of temperatures, the crystal morphology has been shown to vary [11]. Aragonite and vaterite have both been found to have a prevalence inversion at 65°C [19] as shown in Figure 1.2. Increasing temperature reduces the mean crystal diameter, regardless of morphology [20]. Ma et al. [20] also hypothesized a codependence of morphology on pH and temperature. Higher pH can also produce smaller diameter crystals (see Fig. 3 of [20]).

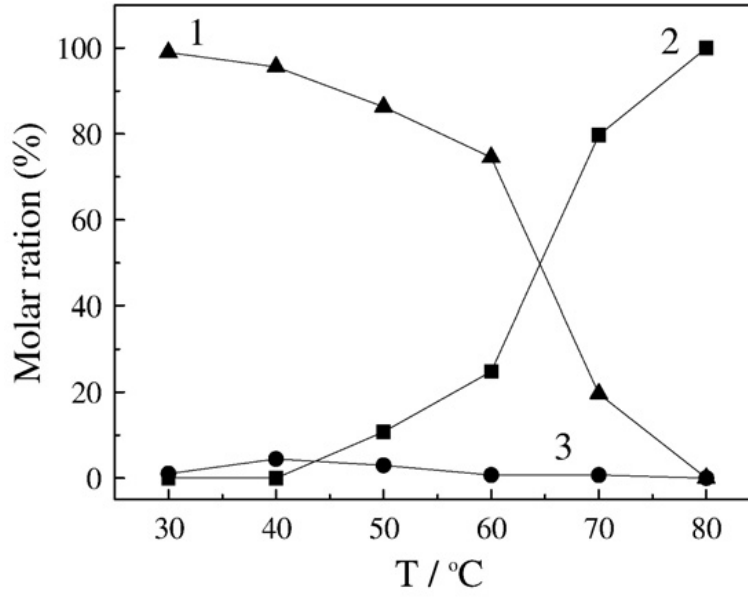


Figure 1.2: Influence of temperature on the mole fraction of CaCO₃ morphologies. 1: vaterite, 2: aragonite, and 3: calcite (reprinted from Chen and Xiang [19] with permission from Elsevier).

In a carbonate solution, the present ions are pH dependent (as seen in Figure 1.3). The process solution used in the direct air capture system is a solution of hydroxide and carbonate, so the precise location of the inversions shown in Figure 1.3 will be shifted in our experiments. The inversions of ions are important for determining chemical composition of our solution via titration (see Appendix C).

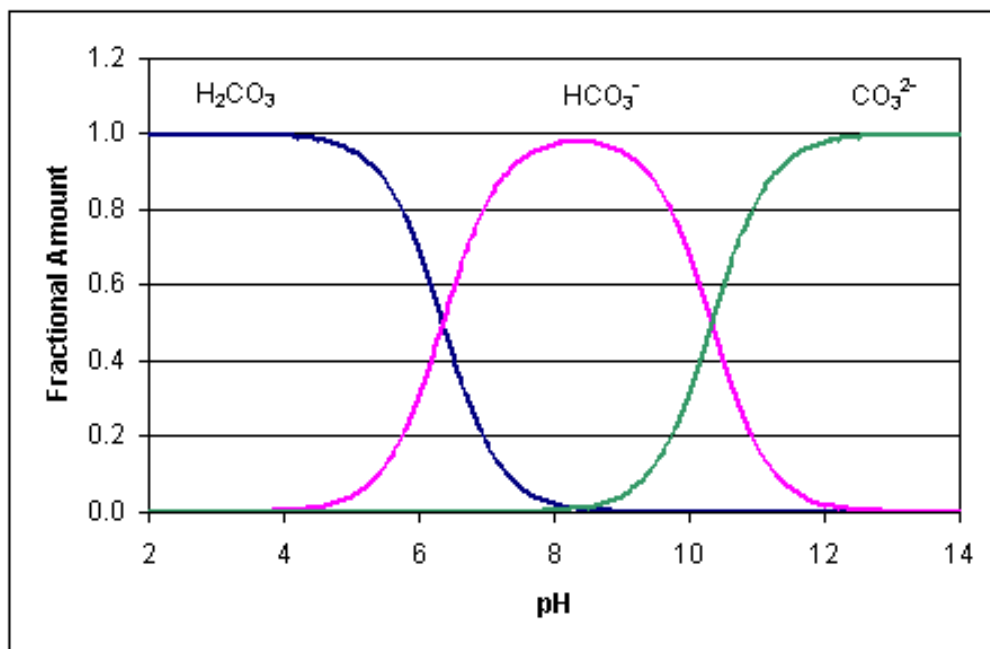


Figure 1.3: Equilibrium mole fraction of carbonate versus pH [21].

1.4 Research objectives

The objectives of this thesis are industrially prescribed and seek to provide knowledge on the topic of crystallization in alkaline environments by (i) confirmation of the use of a bench scale system to test parameters for Carbon Engineering's pilot scale system, (ii) identification of the effect temperature has on crystallization in a highly ionic environment used in a direct air capture reactor, (iii) determination of CaCO_3 crystalline morphology over a greater pH range than previously known, (iv) design and construction of a reactor to run batch trials of multiple pellet sizes, and (v) determination of the pellet size producing the most rapid growth.

1.5 Thesis organization

The thesis is composed of five chapters: the introduction (Chapter 1); three main chapters describing the works completed and results obtained (Chapters 2, 3, and 4); and a final concluding chapter (Chapter 5).

Chapter 2 describes our ability to model the pilot system with results from smaller reactors to demonstrate their mathematical similarity in pellet growth dynamics. Chapter 3 evaluates crystal growth dependence on loading, size, temperature, and pH, and Chapter 4 outlines the fluidized bed reactor design and construction and the tests performed.

Chapter 2: Modelling for scale-up

Earlier work completed by Dr. Luisa Burhenne as part of her post-doctoral fellowship within the research group included constructing and running a bench-scale pellet reactor (BPR) model of the fluidized bed pellet reactor described in Chapter 1 (chemically represented, centrally, in Figure 1.1). With the data obtained from experimentation with this BPR, an adaptation to an equation used in a water softening reactor to predict growth for fluidized bed particles was proposed. Using the MATLAB code developed in this thesis (in Appendix A) with the data collected by Dr. Burhenne, two empirical constants were found and confirmed to be reliable with data from the pilot-scale pellet reactor (PPR) operated by Carbon Engineering Ltd. [6]. The modelling work, completed by Burhenne et al. [6], is presented in this chapter. This work was also in part presented in the poster in Appendix B.

2.1 Experimental methods

Week-long trials were run on the BPR, Figure 2.1, that included daily sampling at five heights along the reactor. Trials were run at a superficial velocity matching the PPR with varied calcium loading. Samples were taken daily, from which bed density and pellet diameter were measured, and then averaged for each sample height. Bed density was found by a mass and volume measurement, pellets are then removed from the sample and their diameters were found using sieving with a series of meshes. *Bed density* is the measure of mass per unit volume within the reactor. Bed density, ρ_{bed} , is related to bed porosity, p_i , by the following:

$$p_i = \frac{\rho_p - \rho_{bed}}{\rho_p - \rho_l} \quad (2.1)$$

where ρ_l is the density of the liquid (1 M KOH and 0.5 M K₂CO₃) in the reactor (1100 kg/m³) and ρ_p is the density of the pellets (CaCO₃) in the reactor (2711 kg/m³). *Bed porosity* is the void, or non-solid, space within the bed, empirically calculated in Equation (2.5).

The fluidized bed was divided into five control volumes, V₁ to V₅, corresponding to the volumes between six sampling ports (SP) 11, 9, 7, 5, 3, and 1 (Figure 2.1, right side) each of reactor height 0.1, 1.1, 2.1, 3.1, 4.1, and 5.1 m, respectively.

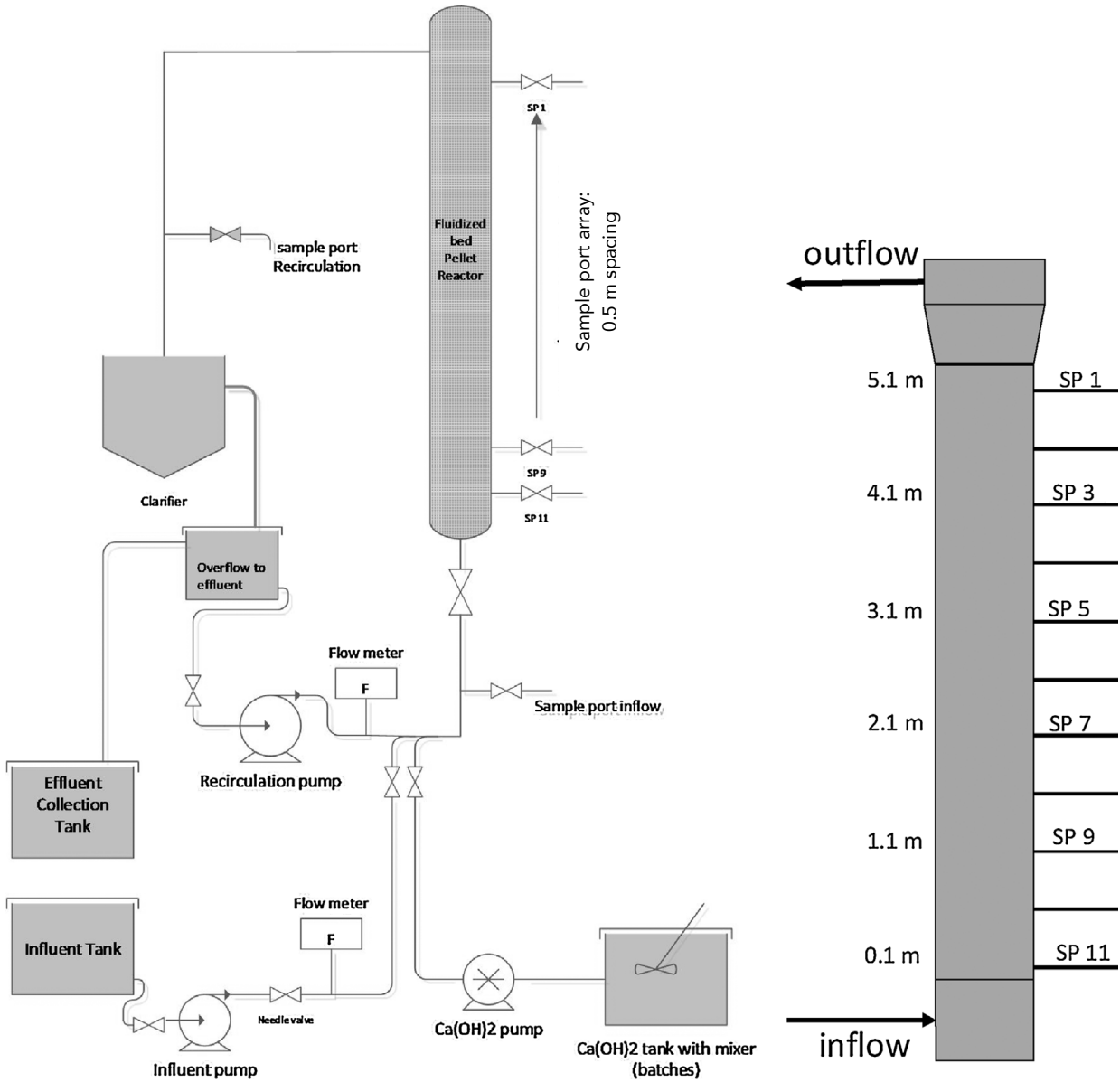


Figure 2.1 Bench-scale pellet reactor (BPR) setup (left) and fluidized bed reactor (right). Reprinted with permission from Elsevier [6].

2.2 Modelling methods

A bed growth model was written in MATLAB R2015b (Appendix A) for the pelletized calcium process using equations (i) Richardson-Zaki [18], (ii) Newton-Stokes [22], and (iii) Mean square error (MSE) [23] used within a nonlinear least squares algorithm for iterative optimization.

2.3 Purpose

The aim of this model is to characterize the fluidized bed with limited data, as well as give insight into the change in porosity and total pellet surface area of the bed for a given particle growth rate. The model input is limited to what can practically be measured within the full-scale, PPR, system during operation. The bed growth rate model was validated using measurements from the BPR as well as the PPR.

To help us predict pellet diameter in a fluidized bed reactor from a measurement of bed density, we introduce the empirical expression for a dimensionless drag coefficient for a sphere within a fluidized environment [4][18][24]:

$$C_{w2} = \frac{24}{\text{Re}_0} \left(1 + \alpha \text{Re}_0^\beta \right) \quad (2.2)$$

in which α and β are dimensionless empirical constants. Ergun and Richardson-Zaki approaches give these empirical constants for round, smooth, and uniform particles [23]. For diverse particles in an unbounded environment, as found in this process, these empirical parameters can be adjusted to account for non-exact flows [25]. Re_0 is the Reynolds number for flow around a pellet:

$$\text{Re}_0 = \frac{u_{0,i} L_i}{\nu} \quad (2.3)$$

where, at height i , the pellet terminal velocity is $u_{0,i}$, the pellet diameter L_i , and where ν is the kinematic viscosity. $u_{0,i}$ can be calculated using the Newton-Stokes equation (Equation (6.1-7) of [22] or [26]):

$$u_{0,i}^2 = \frac{4}{3} \frac{L_i (\rho_p - \rho_l) g}{C_{w2} \rho_l} \quad (2.4)$$

where g is the acceleration due to gravity, and where ρ_p and ρ_l are the densities of the CaCO_3 pellets and the process liquid, respectively. Thus, L_i is the weighted mean diameter at height i .

2.4 Theoretical bed growth model

Correlation analysis was performed between the particle size and bed density data from the BPR tests and the theoretical values of L_i , were determined from the bed growth model, for given operation conditions. The bed growth in each control volume is defined as the change in CaCO_3 pellet mass over time, which is given by the (i) pellet growth and (ii) change in average bed porosity. Both of these values were calculated following the Richardson-Zaki approach, as described by van Schagen et al. [18], in which the daily bed growth in each control volume is evaluated from the change in bed porosity. The bed porosity in each control volume is given by:

$$p_i = \left(\frac{F_w}{A u_{0,i}} \right)^{1/n} \quad (2.5)$$

where F_w is the liquid flowrate and A , the reactor cross-sectional area. The dimensionless exponent, n , is given by the empirical Richardson-Zaki relation [2][27][18][28][29]:

$$n = \begin{cases} 4.6, & \text{Re}_0 < 0.2 \\ 4.4 \text{Re}_0^{-0.03}, & 0.2 \leq \text{Re}_0 < 1 \\ 4.4 \text{Re}_0^{-0.1}, & 1 \leq \text{Re}_0 < 500 \\ 2.4, & \text{Re}_0 \geq 500 \end{cases} \quad (2.6)$$

A nonlinear least squares algorithm was used to fit Equations (2.2) through (2.4) to get the identifying parameters C_{w2} , Re_0 , α , and β which minimize the mean square error (MSE):

$$MSE = \frac{1}{N} \sum_{i=1}^N \left(\frac{L_{i,model} - L_{i,meas}}{L_{i,meas}} \right)^2 \quad (2.7)$$

where N is the product of the number of ports (six in our BPR) and the number of measurement intervals (six for our BPR measurements) plus one. MSE thus depends upon the mean measured pellet diameter, $L_{i,meas}$, and the one calculated from Equation (2.4), $L_{i,model}$:

$$L_i = \frac{3 u_{0,i}^2 C_{w2} \rho_l}{4(\rho_p - \rho_l)g} \quad (2.8)$$

For our initial guess, parameters found in literature were used $\alpha = 0.79$ and $\beta = 0.87$ [18]. The minimum value of the MSE, corresponding to the optimal set of parameters, is thus the goodness of fit.

Once α , and β were identified for each set of data, the specific surface area, SA_i , in each control volume, V_i , was calculated using [18]:

$$SA_i = \frac{6(1 - p_i)}{L_i} \quad (2.9)$$

Model validation was performed using data from the pilot scale pellet reactor as well as from the BPR.

2.4.1 Pellet growth

The average pellet growth rate was determined in the BPR at a flow velocity, F_w/A , of 60 m h^{-1} , a calcium loading rate of 3.0 mol h^{-1} , and a seed size range of $0.18 \leq L_i \leq 0.50 \text{ mm}$. The particle growth rate was studied over a period of 144 hours by taking representative samples of each control volume every 24 hours at sampling ports (SP) 11, 9, 7, 5, and 3.

Retention for the BPR is calculated without pellet mass being measured but with the bed density being measured and extrapolation of a pellet mass from that. BPR retention is given as:

$$R_{BPR} = \frac{\sum_{i=1}^5 \left(\frac{m_{\text{pellet},i}}{V_{\text{sample}}} V_i \right)}{m_{\text{prospective}}} \quad (2.10)$$

where V_{sample} is the volume of the sample taken at height i , hourly, $m_{\text{pellet},i}$ is the mass of pellets found in that same sample. V_i is the reactor volume between height i and $i + 1$.

Prospective mass of CaCO_3 , $m_{\text{prospective}}$, is the mass of CaCO_3 if 100% conversion of fed calcium occurred.

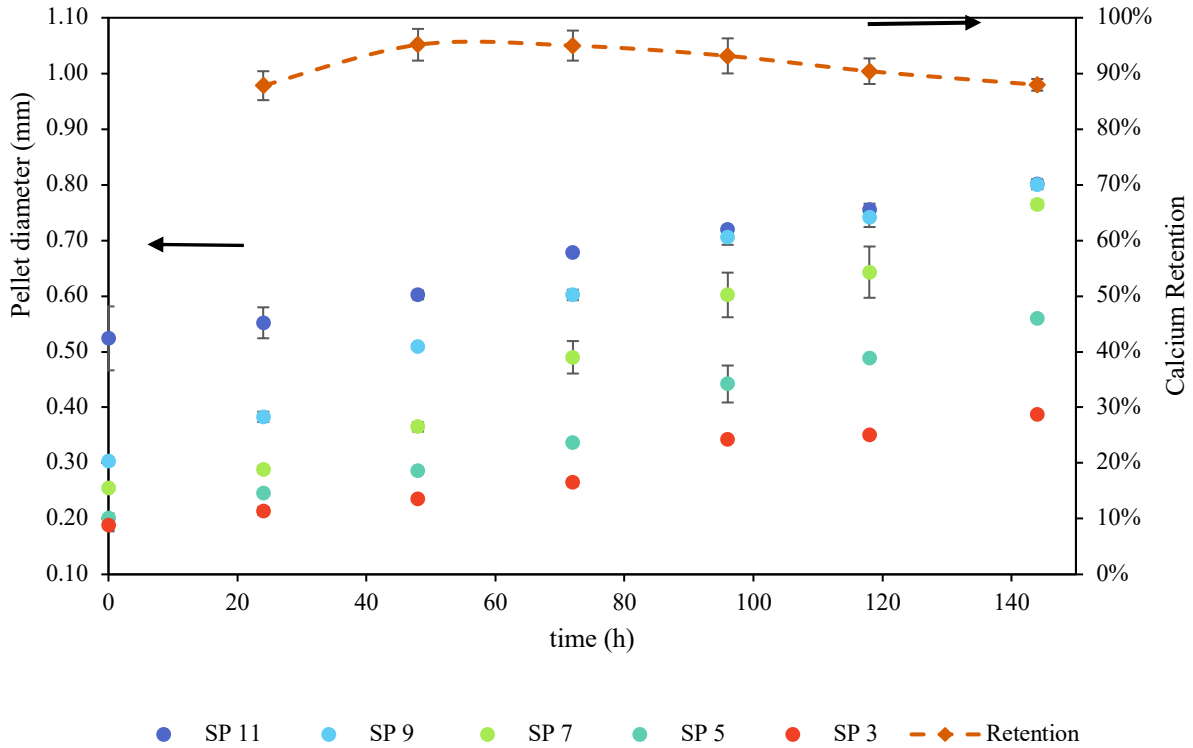


Figure 2.2: CaCO_3 pellet diameter, L_i , (dots, left axis) and calcium retention, R_{BPR} , (dashed line, right axis) in the benchtop pellet reactor. Flow velocity: 60 m h^{-1} , calcium loading: 3.0 mol h^{-1} , and seed diameter range $0.18 \leq L_i \leq 0.50 \text{ mm}$ [6].

The mean pellet diameter at each height, L_i , was plotted over time (Figure 2.2). During the first 72 hours of each test, the solids in each control volume showed linear growth, the fastest of which was observed at heights 0.1 and 1.1 m (SP 11 and SP 9). This was attributed to higher calcium carbonate precipitation rate, driven by the higher upstream concentration of calcium hydroxide (lime slurry injection being upstream of the reactor bed). Van der Weijden et al. [30] studied the influence of total available calcium on the calcite growth rate. They found that this calcite growth rate increased with increasing calcium concentration, due to increased interfacial supersaturation. Interestingly, the growth rate 0.1 m from the bottom of the reactor (SP 11) decreased once pellet diameter reached 0.68 mm, after 72 hours. However, the growth rate observed at 1.1 m (SP 9) maintained the initial linear growth rate until an average diameter, L_{SP9} , of 0.72 mm was reached, after 96 hours. Thereafter, the growth rate at SP 9 decreased to the same growth rate as observed at SP 11. This result contrasts with findings in literature where higher growth rates were observed with increasing crystal size [14], [31]–[33]. However, our work has been conducted under significantly higher ionic concentrations than such literature, and hence, the previous findings might not be directly applicable to our study.

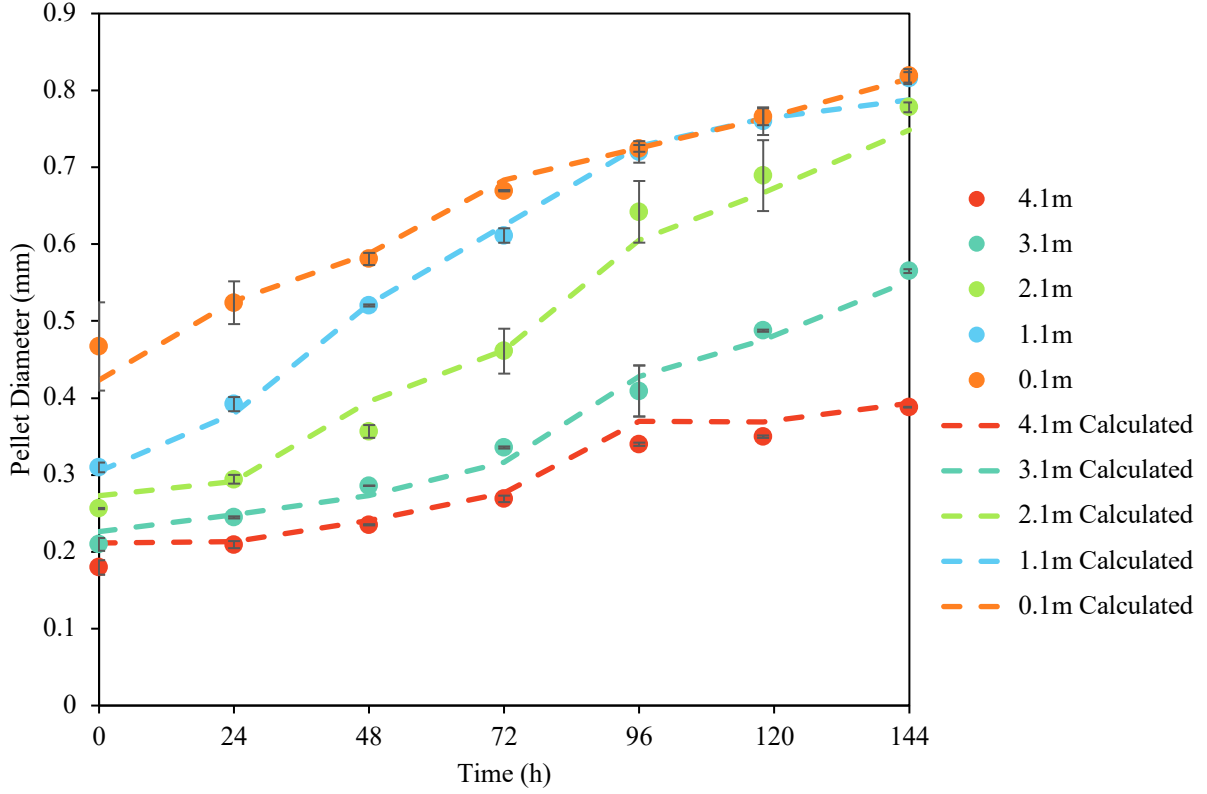


Figure 2.3: Optimization of calculated particle size curves (dashed lines) compared to measured particle sizes (dots) at FV: 60 m h⁻¹, calcium loading: 3.0 mol h⁻¹ and seed diameter range $0.18 \leq L_i \leq 0.50$ mm.

One explanation for the slower growth, after reaching a pellet diameter of about 0.7 mm, is the lower surface to volume ratio for larger pellets, discussed in Subsection 2.5.2. Also, the smoother surface of the larger pellets may also contribute to the observed reduction in surface reaction rate [34]. The impact of pellet surface area on the surface reaction rate and on pellet growth will be further investigated in Chapter 3.

The faster growth observed for pellets at reactor heights 2.1 to 4.1 m was attributed to upstream pellets expanding into downstream control volumes. For example, a jump in pellet size from 0.46 to 0.64 mm was observed at SP 7 between hours 96 and 120.

The average pellet growth rate, in m/s, at reactor heights of 0.1 m (SP 11) and 1.1 m (SP 9) as well as the total calcium retention over time reaches a maximum between 48 and 72 hours (see Fig. 6 of [6]). At the onset of this test campaign, the growth at the reactor bottom accelerated significantly from $8.1 \times 10^{-10} \text{ m s}^{-1}$ at 24 h to $11 \times 10^{-10} \text{ m s}^{-1}$ at 48 h and remained constant up to 72 h. Following this, growth decelerated to a minimum of $4.9 \times 10^{-10} \text{ m s}^{-1}$ at 144 h. The growth rates determined under these conditions are approximately 10 times those of calcite seeds of comparable size (0.46 – 0.92 mm) [35]. Tai et al. [35] also found that for fluidization velocities between 85 and 280 m h^{-1} , velocity had no impact on the crystal growth rate. However, Tai et al. [35] did find that the crystal growth rate is strongly affected by local supersaturation, seed size, ionic strength, and pH. For instance, they found that the crystal growth accelerates with increasing pH up to the isoelectric point of approximately pH 10.5 (see Figure 1.3), and with increasing ionic strength up to $0.0185 \text{ kmol m}^{-3}$. Our study was performed at even higher ionic strength (and thus higher pH) which shifts the ionic equilibrium towards CO_3^{2-} . A higher CO_3^{2-} content means a higher supersaturation of CaCO_3 . Therefore, the faster growth observed in this study may be attributed to higher process solution concentration. To prove this, the effect of other reaction conditions (e.g., seed size, measured surface areas, and temperature) on the pellet growth rate will be investigated in Chapters 3 and 4.

2.4.2 Pellet size dependence

Threlfall and Coles [36] stated that different crystal sizes have different propensities for growth. Tai et al. [32], [35] found that the secondary CaCO_3 crystal nucleation rate decreases with an increase in particle size, due to a decrease in interfacial supersaturation. Hence, smaller particles can lead to higher calcium retention on the pellet surface. Our findings seem to follow this trend

in the first 48 h. After 48 h, we observed less calcium retention with an increase in average particle size. This decrease in calcium retention corresponds to the decelerated growth after 72 h. This retention decrease may be attributed to increased abrasion at the reactor bottom due to bed densification. We hypothesize that there is an ideal surface to volume ratio that maximizes the pellet growth and minimizes fines production in the active region of the bed leading to higher retention. However, further studies are necessary to test this hypothesis and to identify the impact of seed size on process performance.

2.5 Calibration

The theoretical fluidized bed composition was described using a Richardson-Zaki approach which is known to be effective in predicting bed expansion characteristics [37]. In a first step, the model was calibrated using data from the BPR to identify the model parameters that are specific to Carbon Engineering's pelletized calcium process. Model parameters, namely α and β in Equation (2.2), that are constant for one fluidization velocity, were calculated using the measured pellet size and bed density, per the equations in Section 2.3. These parameter values were optimized by minimizing the MSE defined by Equation (2.7). As our initial guess, α and β values from literature were used [18]. MSE minimization yielded values of α and β to be 0.1515 and 1.0035, respectively, which results in the following new expression for the drag coefficient at a flow velocity of 60 m h⁻¹ under baseline operation conditions:

$$C_{w2} = \frac{24}{Re_0} (1 + 0.1515 Re_0^{1.0035}) \quad (2.11)$$

By *baseline operation conditions*, we mean the conditions defined in the third column of Table 2.1. For mean particle sizes between 0.2 and 0.84 mm, the drag coefficients were found to range

between 13.5 and 4.5, respectively, and terminal velocities, between 0.017 and 0.059 m s⁻¹.

Equation (2.11) is a main result of this thesis.

Table 2.1: Baseline operating conditions for the PPR and BPR, adapted from [6].

Parameter	Units	PPR/BPR baseline validation tests	BPR growth rate tests
Flow velocity	m/h	60	60
Calcium loading rate	mol/h	3	1.6, 3.0
Bed material size	mm	0.65-0.84	0.15-0.5
Test duration	h	24	144

The optimized correlation curve for the pellet diameter over time at five different bed heights is shown in Figure 2.3. The overall MSE between the measured and the calculated curves is less than 0.051 and the coefficient of determination, R^2 , has an overall value of 0.9932. The largest deviation observed is at the beginning of the test and most probably due to the uncertainty in the bed density measurement. This uncertainty is attributed to the uneven flow observed at the reactor bottom, which makes it challenging to measure bed density reliably, and particularly, for slurries of small particles.

2.5.1 Validation

The theoretical bed growth model was validated against data from the PPR, as well as from additional testing using the BPR. Validation at pilot scale was performed by calculating the pellet diameter along the reactor height using the measured bed density at baseline operating conditions. The calculated pellet diameter was compared to the measured weighted mean pellet diameter at the same height. Figure 2.4 shows the calculated particle size profile along the reactor height. The pellet size decreases slowly starting at a height of around 3 m up to a height

of 9 m from the reactor bottom. Below 3 m, the pellet size hardly changes. Figure 2.4 also shows that this particle size profile mirrors the trend observed in the BPR (compare green and blue curves for BPR with teal curve for PPR). Figure 2.4 is a main result of this thesis.

The MSE values for the PPR were found to be 0.06, 0.04, 0.01, and 0.11 for reactor heights of 1.95, 4.68, 5.46, and 7.80 m, respectively. The deviation (rightmost of teal curve on Figure 2.4) at the PPR bottom is most probably a result of the error in the bed density measurement in that region as outlined before for the BPR (see subhead of Section 2.5). Non-simultaneous density and pellet size measurements in the PPR may also lead to discrepancy. Considering these sources of error, the model gives a good estimate of the bed profile.

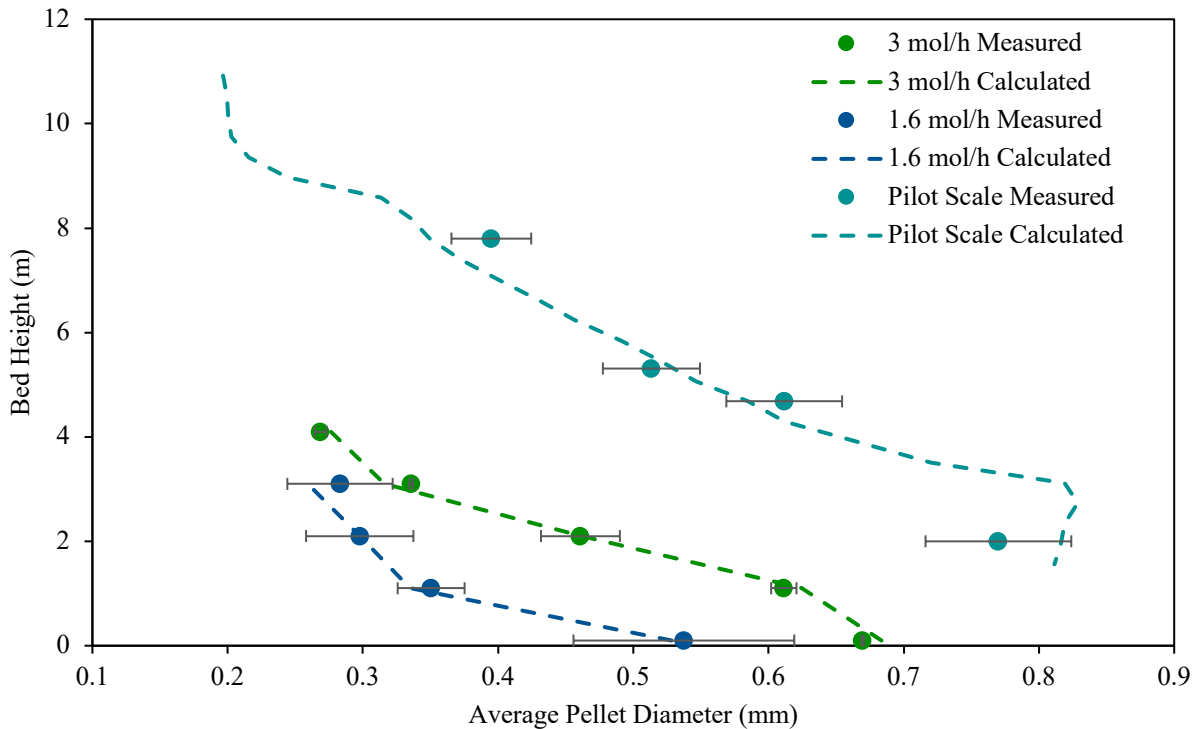


Figure 2.4: Calculated and measured particle sizes along the BPR height after 72 hours of operation at two calcium loadings, 1.6 and 3.0 mol h⁻¹, as well as pellet size data from the PPR with the same flow velocity and 3.0 mol h⁻¹ calcium loading [38].

The calculated bed profile in the BPR at a calcium loading rate of 1.6 mol h^{-1} was also used to validate the model. This fit can also be seen in Figure 2.4. The slower pellet growth observed can be attributed to the lower amount of calcium available at this lower calcium loading rate. The slow growth at the reactor bottom will be further investigated with respect to pellet loading and surface area in Chapter 3.

The MSE between measured and calculated values ranged from 6×10^{-4} at the beginning of the test to 9×10^{-8} at 72 h of operation. The higher MSE at the beginning is before the reactor had reached steady state. Thereafter, the model gives a good estimate of the bed profile beyond the first sampling port since steady state is reached.

2.5.2 Process analysis

The parameters α and β , identified previously (Equation (2.11)), were used to calculate the respective porosity and total pellet surface area over time at each reactor height at baseline operation conditions. As Figure 2.5(b) illustrates, the bed porosity in the reactor decreases over time. The calculated total bed surface area over time revealed that the surface area at the very bottom of the reactor (0.1 m) slowly decreases over time. The decrease in total bed surface area is attributed to the particle growth, resulting in less surface area to volume. Additionally, pellets are being pushed upwards into the next control volume due the total pellet growth and the lack of pellet discharge in the BPR. The pellet surface areas at 1.1 m and 2.1 m were found to increase over the first 48 h or 72 h, respectively, up to a maximum of $2900 \text{ m}^2 \text{ per m}^3$ of reactor volume. Thereafter, the surface area decreases to $2500 \text{ m}^2/\text{m}^3$. The surface area above 2.1 m increases

over time to about $2800 \text{ m}^2/\text{m}^3$, which we attribute to pellets being pushed upwards from the lower control volumes.

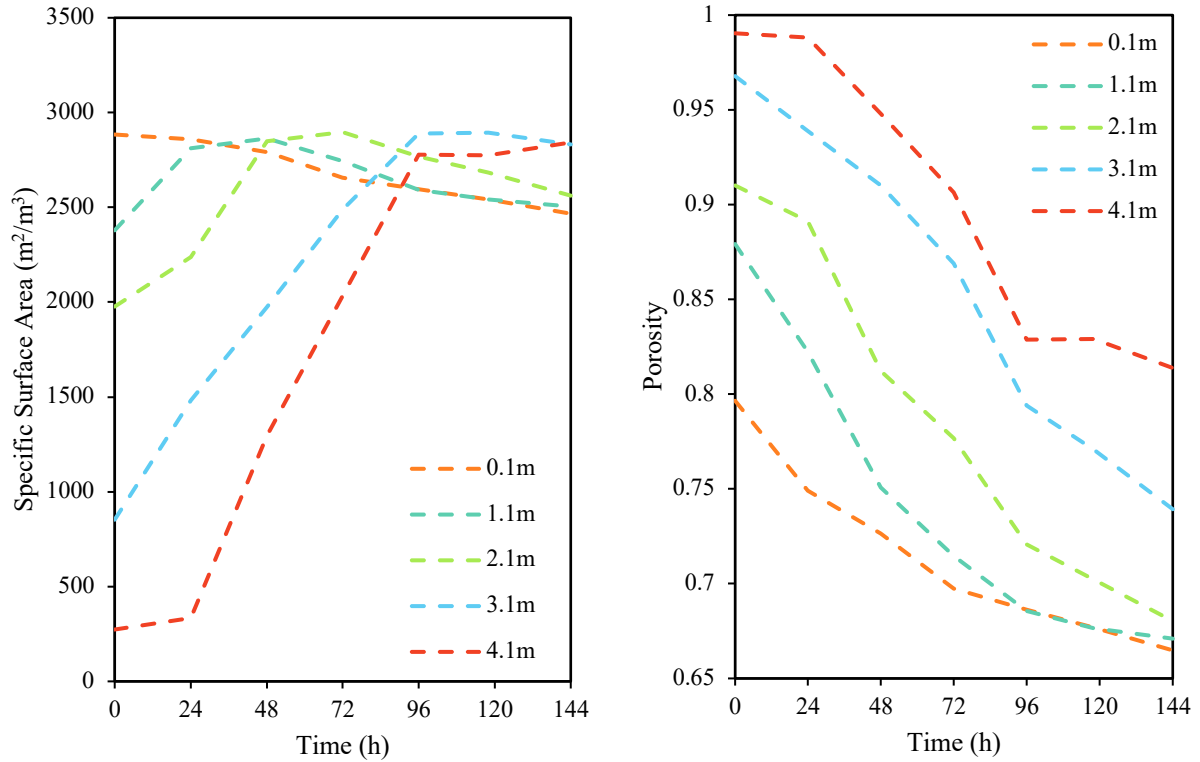


Figure 2.5: Modelled pellet surface area per unit volume (left) and porosity (right) over time at five different BPR bed heights at a flow velocity of 60 m h^{-1} , calcium loading of 3.0 mol h^{-1} , and seed diameter range $0.18 \leq L_t \leq 0.50 \text{ mm}$.

The trends observed in the total pellet surface area in the bottom 2.1 m of the reactor mirrors the pellet growth rate as well as the retention behaviour over time. Various researchers have attributed crystal growth and reactor performance to available surface area, stating that particle growth accelerates with increasing available pellet surface area [18], [35]. Therefore, it can be concluded, if spherical, smooth pellets are assumed, that the available pellet surface area at the

bed bottom impacts the overall reactor performance significantly. The following chapter will investigate the reality of this assumption.

The resultant drag coefficient given by Equation (2.11) will allow for scale to be investigated provided superficial velocity is held constant. Superficial velocity changes mixing significantly within this fluidized bed and is thus the critical parameter to be held constant in scaled investigations. This is to say; Reynolds number of the bed is allowed to vary in favour of maintaining Reynolds number for flow around pellets (Equation (2.3)) as a constant.

Chapter 3: Investigating crystallization at beaker scale

The work from this chapter can mostly be found in Giacomini et al. [39]. Crystallization of $\text{CaCO}_3(\text{s})$ from solution in an alkaline environment was studied as a function of temperature, CaCO_3 pellet loading, and CaCO_3 pellet size. Occurrence of crystallization as spontaneous nucleation or growth on pellets are both possible where the latter is desired. Growth is quantified as retention. The crystallization on pellets was found to be mass transport controlled, while spontaneous nucleation was found to be kinetically controlled (see Equation (1.5)). The highest reported retention, 73%, was found at the conditions where mass transport was favoured by high pellet loading and small pellet diameter, and where kinetics were hindered by low temperature. When alkalinity was varied, the following clear trend in morphologies was observed. Above a pH of 12.2, calcite was the most prominent. At a pH of 12.2, calcite and vaterite morphologies crossed in prevalence (see Figure 3.9) and below a pH of 12, down to 6.5, vaterite was most prominent.

3.1 Direct air capture crystallization

This reaction, being studied for direct air capture, is operated at high pH (between 14-14.6), high carbonate concentration, and at high supersaturation since calcium is fed as solid $\text{Ca}(\text{OH})_2$ particles. In addition, the pellets are large, more than 150 μm in diameter [6]. All these factors are expected to increase fines production. However, high retention, of approximately 85%, has been demonstrated with high loading of CaCO_3 pellets, even at high supersaturations [8][6]. Therefore, it is interesting to study pellet growth in a controlled environment to deepen our understanding of how the experimental parameters influence retention. Additionally, to place this reaction in context of earlier works performed at pH values of no more than 10 [10][12][17], the

study of crystal morphology dependence on solution pH was investigated through unseeded crystallization.

In this work, CaCO_3 pellet growth was performed in beaker experiments controlled for pellet size, mass loading, total pellet surface area, and temperature to understand their effects on the overall retention. Unseeded CaCO_3 pellet growth was also studied for $6.5 \leq \text{pH} \leq 14.5$.

3.1.1 Experimental procedure

The reaction medium comprises three components: process solution, seed pellets, and lime slurry. The process solution used in these beaker experiments is a 1.0 M KOH (Sigma Aldrich, 99%, 45wt% solution) and 0.5 M K_2CO_3 (Sigma Aldrich, 99%, reagent grade) solution using deionized water (18 M Ω -cm). The seed pellets consist of CaCO_3 and are sieved to yield a uniform pellet size (see Table 3.1) and washed with deionized water to ensure all fine CaCO_3 powder is removed (see Figure 3.1). Sieving is done using a Fritsch Analysette 3 PRO to shake approximately 150-200 g of pellets at an amplitude of 1.0 mm for 30 minutes. The lime slurry consists of a 2.0 M KOH solution that has 20wt% of $\text{Ca}(\text{OH})_2$ powder (Sigma Aldrich, 95+%, ACS).

Table 3.1: Seed is the average size fed; mid-size is grown about halfway and makes up the predominant size range in the BPR; and mature pellets are fully grown and ready for removal.

	Mesh	Diameter range [μm]	BET surface area [m^2/g]
Seed	60 - 50	250 – 300	39.7
Mid-size	45 - 40	355 - 425	27.6
Mature	25 - 14	700 - 1410	24.5

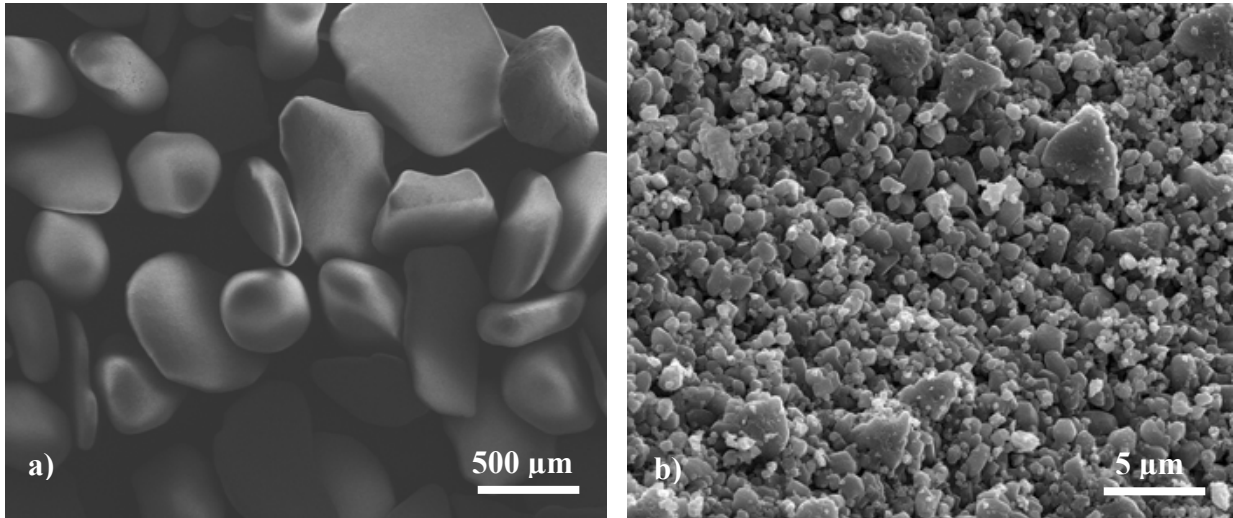


Figure 3.1: SEM images of mid-size pellets (a) and their surface (b).

First, 250 mL of process solution is added to a 500 mL Pyrex beaker. The beaker was stirred using an overhead mixer (JJ-1 Precise Strength Power Mixer) with a two-bladed stainless-steel impeller (see Figure 3.2). A measured mass of calcium carbonate pellets is added from one size group listed in Table 3.1. Stirring is constant and sufficiently fluidizes the sample for all pellet sizes and loadings.



Figure 3.2: Crystallization reaction in progress for 50 g sample of mature pellets.

An aliquot of approximately 6.0 g of lime slurry was added. The precise mass and volume of lime slurry is then recorded. After 30 minutes the beaker contents were poured through a wet sieving device consisting of a size 70 mesh (210 μ m) encased in PVC pipe. Effluent from the mesh was vacuum filtrated in a 9.0 cm Buchner funnel with a Type 1 filter paper from Whatman. The solids found on the filter paper are the fines. By looking at the mid-sized pellets using a Nova NanoSEM, Figure 3.1, the pellet irregular shape and porous surface was characterized. Surface area measurements and data for each size group are in Table 3.1.

The recovered pellets and fines are placed in separate glass petri dishes. These samples are dried overnight (at least 12 hours) at 105-110°C. Samples then cool to room temperature before their

mass gain is recorded. To account for relative humidity fluctuation, a control 50 g mid-size trial is run on all experiment days.

For temperature dependent trials, a Type K thermocouple feeding into National Instruments LabView 2017 software was added to the reaction beaker, and a Corning PC 420D heat plate was used as a heat source and temperature controller. The process solution was heated to the reaction temperature prior to pellet and slurry addition. Three trials were run for each set of conditions.

Results are reported as retention, R_{beaker} , calculated from:

$$R_{beaker} = \frac{m_{\text{pellets,after}} - m_{\text{pellets,before}}}{m_{\text{pellets,after}} + m_{\text{fines}}} \quad (3.1)$$

where $m_{\text{pellets,after}}$ and m_{fines} are the masses of pellets and fines after reaction, respectively, and $m_{\text{pellets,before}}$, the original mass of CaCO_3 pellets added.

After the reactions, process solution concentrations are analyzed via titration (see Appendix C) for their ion ratio, $[\text{OH}^-]:[\text{CO}_3^{2-}]$. SEM images were then taken of both the pellets and fines produced. Powder x-ray diffraction (XRD) was also performed on both using a Bruker D8 Advance with $10 \leq 2\theta \leq 90$, step size 0.1, and scan time of 0.3 s per step.

3.1.2 Results and discussion

3.1.2.1 Ambient temperature

For all ambient temperature conditions reported, a positive retention rate was observed and CaCO_3 was formed, both on pellets and as fines. In these experiments, process solution

concentration, amount of fed $\text{Ca}(\text{OH})_2$ particles, and stirring rate were constant. This means that the driving force of supersaturation, F_d , was constant. Therefore, this set of experiments evaluates the influence of mass transport.

For varied mass loading with a constant pellet size (mid-size), Figure 3.3(a), the retention varies from 52% at 25 g loading to 64% at 100 g loading. Higher loadings are expected to increase the surface area of CaCO_3 in the beaker and thus, elevate retention. This increased retention at higher loading was confirmed in our experimental data, but lower loadings did not seem to affect the retention at all. This suggests that factors other than loading, such as pellet size, are more important.

When the pellet size was varied at constant mass loading, Figure 3.3(b), the retention changed from 67% at seed size to 22% at mature size. The change of pellet from seed to mature thus increases the particle size and decreases the total surface area of CaCO_3 resulting in fewer particles. Both of these effects are expected to reduce the retention rate, and therefore explains the reduced retention trend observed in Figure 3.3(b). In an attempt to deconvolute the two effects, a third set of experiments was performed where the total surface area, confirmed through BET analysis, was held constant (at $1,215 \text{ m}^2$). Figure 3.3(c) shows that the pellet size has a large effect, and the retention reduces from 58% at seed size to 22% at mature size. The seed size pellets and mid-size pellet retentions are within one standard deviation of each other.

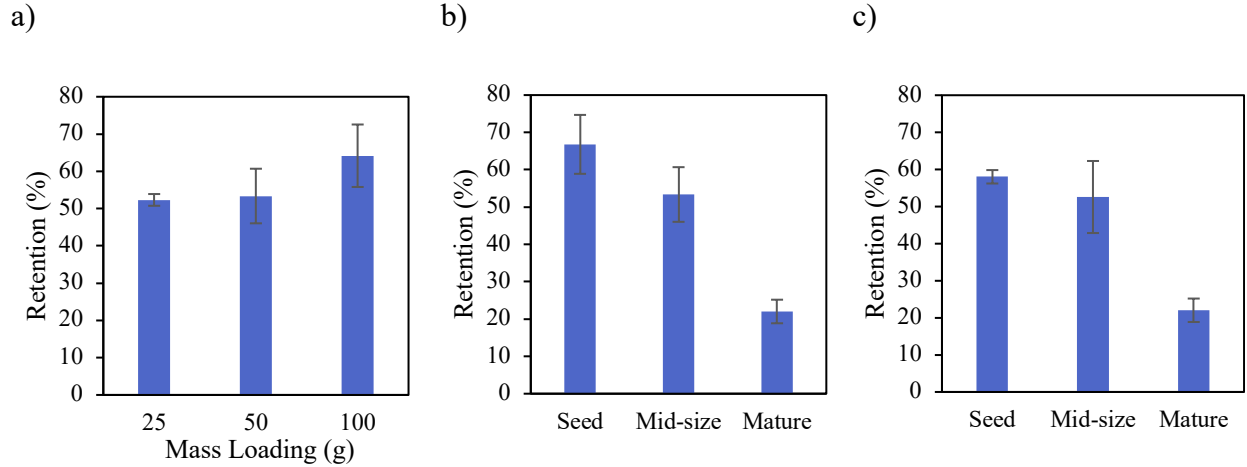


Figure 3.3: Experiments at 20°C: a) mid-size pellets at different mass loadings of 25, 50, and 100 grams, b) constant mass loading with varied pellet size, and c) constant surface area with varied pellet size. Retention herein is R_{beaker} .

To understand this reduced retention trend, and to separate the effect of pellet size and surface area, the retention rate was plotted in Figure 3.4 as a function of surface area for all results reported in Figure 3.3. Here, the trend in Figure 3.3(c) is confirmed where mature pellets give a low retention rate, while the seed and mid-size pellets yield comparable retention rates. This can be explained if the actual pellet size is considered (Table 3.1), where the seed and mid-size pellets diameter ranges are close, while the mature pellets have a diameter approximately 2.5-6 times the seed size and 1.75-4 times the mid-size pellets. From these results, we see that while Equation (1.4) can explain the overall reaction in some cases, care should be taken when interpreting the results solely with this equation. In particular, when Ca(OH)_2 is fed as solid particles, as is the case here, the actual driving force of supersaturation, F_d , is largely confined to the volume around the solid Ca(OH)_2 particles. Thus, to achieve high retention, one must ensure that solid CaCO_3 is present near the Ca(OH)_2 particles. From the results reported in Figure 3.3 and Figure 3.4, high mass loading and small pellet sizes is the best approach. To confirm this, an

additional experiment was performed using 100 g of seed pellets resulting in 73% retention. Figure 3.4 shows this datum as the rightmost triangle. Overall, this suggests that collisions, or near collisions, between the $\text{Ca}(\text{OH})_2$ particles and CaCO_3 pellets are key to high retention, and this gives an important guideline for how to achieve an even higher retention rate at the pH and concentration used in this work. This guideline is a main result of this thesis.

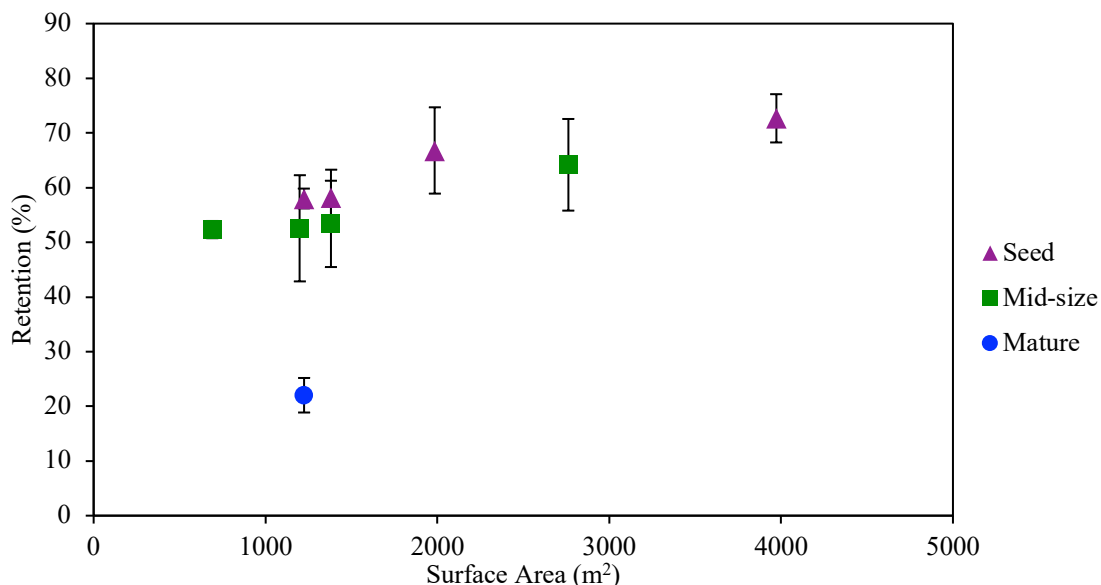


Figure 3.4: Retention for all trials shown in Figure 3.3 as well as best conditions experimental set. All shown with respect to surface area as calculated by BET isotherm measurements for the pellet size ranges. Retention herein is R_{beaker} .

3.1.2.2 Elevated temperatures

Elevated temperature is expected to modify the crystallization kinetics [1]. With mass transport variables held constant, increased crystallization rate is expected to increase spontaneous nucleation [14]. In earlier work [11][20], at high temperatures, different CaCO_3 morphologies were reported and thus temperature can change the precipitation mechanism both for

spontaneous nucleation and pellet growth. For example, the aragonite morphology has a needle-like structure that can increase retention, even at higher temperatures, by assuring a large surface area of CaCO_3 . This aragonite morphology was reported at temperatures above 50°C [20].

In Figure 3.5, the retention rate at four temperatures is reported for mid-size pellets. Here, we see that the higher temperature reduces retention from 53% at 20°C to -1.8% at 80°C . The negative retention at 80°C was within one standard deviation of no retention, and was thus, due to experimental uncertainty. To test for pellet dissolution, a control of fluidized pellets in process solution at 80°C , without slurry, was run for 30 minutes. Since the pellets did not lose mass, this confirmed the absence of pellet dissolution.

If the limiting mechanism for pellet growth is physical proximity of CaCO_3 pellets to $\text{Ca}(\text{OH})_2$ particles, an increase in temperature is expected to mainly influence the spontaneous nucleation rate. An increased spontaneous nucleation rate is expected to produce fines that are both more numerous and smaller than would slower spontaneous nucleation. To investigate this, SEM imaging was done on the fines at the various temperatures. Figure 3.6 shows that the size of the fines decreases with increasing temperature.

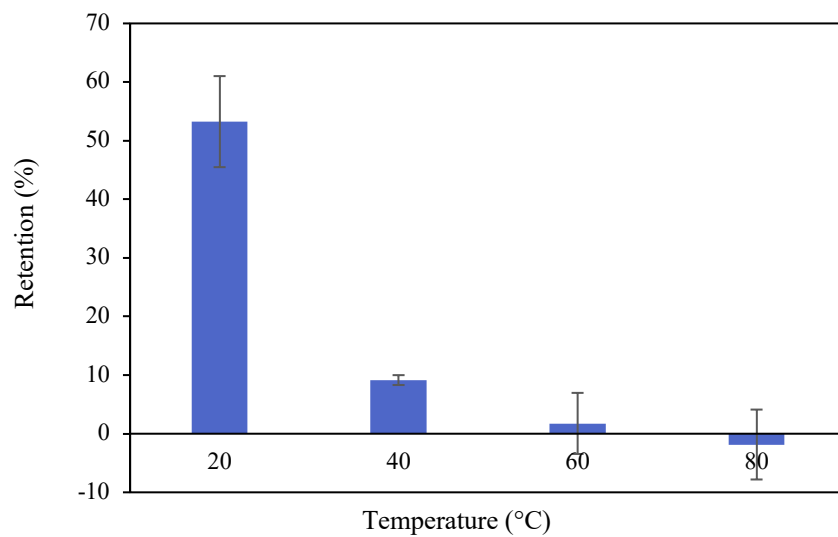
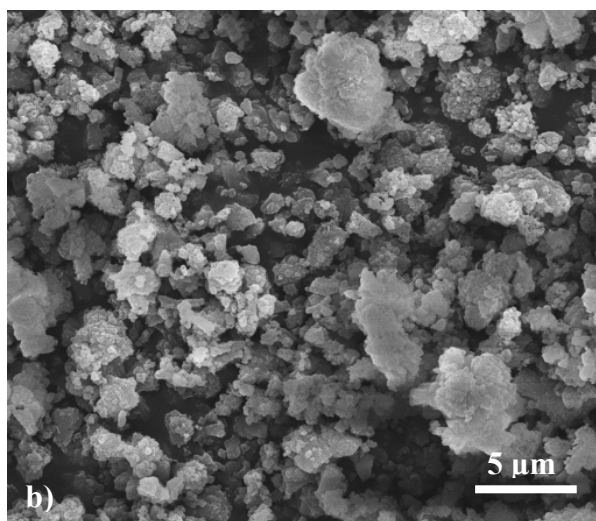
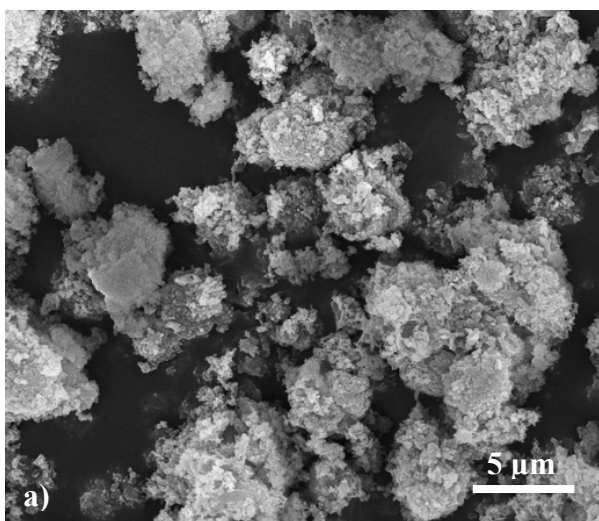


Figure 3.5: Percent of mass found on pellets over total mass collected, retention, after reaction for trials at different temperatures for mid-sized pellets. Retention herein is R_{beaker} .



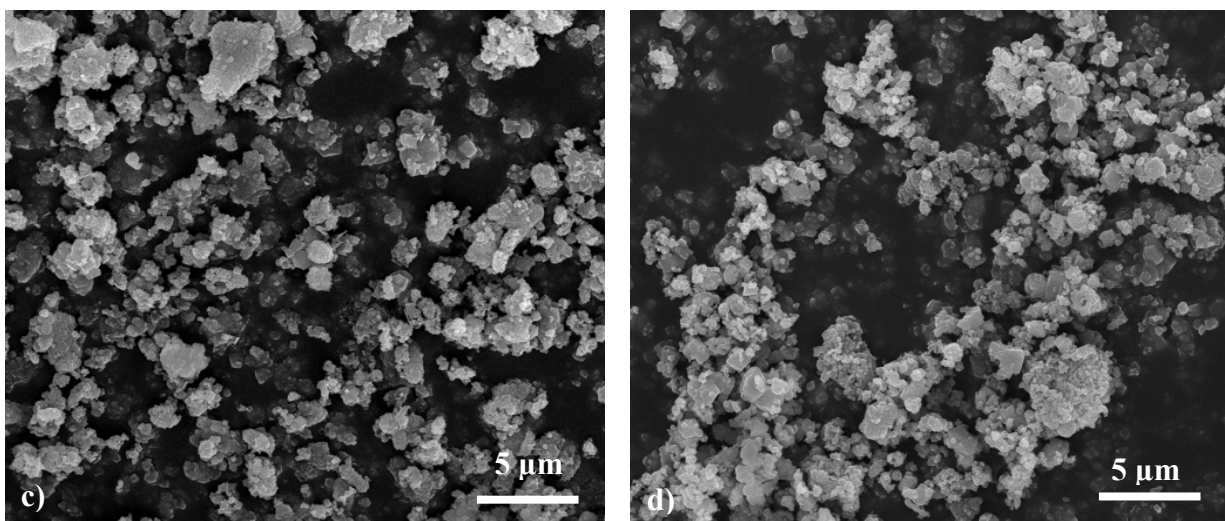
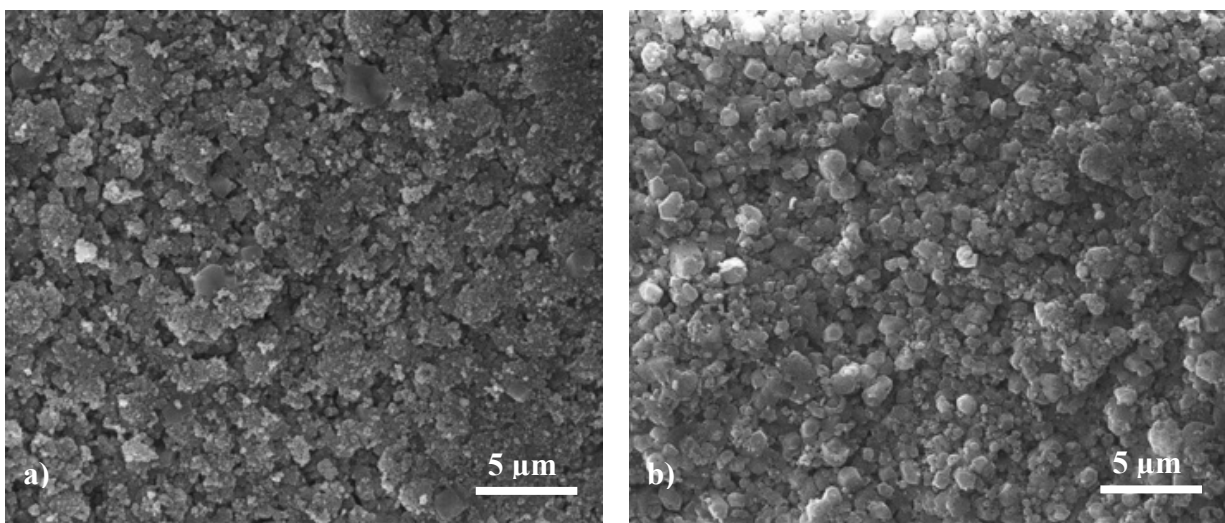


Figure 3.6: CaCO₃ fines grown at a) 20°C, b) 40°C, c) 60°C, and d) 80°C.

SEM imaging was also done on the pellets after growth. Figure 3.7 show no clear trend, which is expected since the amount of CaCO₃ deposited on a single pellet is relatively small compared to the overall pellet size (mass gain at 50% retention is 0.80 g or only 1.6% of total mass for a loading of 50 g). A longer term experiment might thus give different results and possibly different CaCO₃ morphologies.



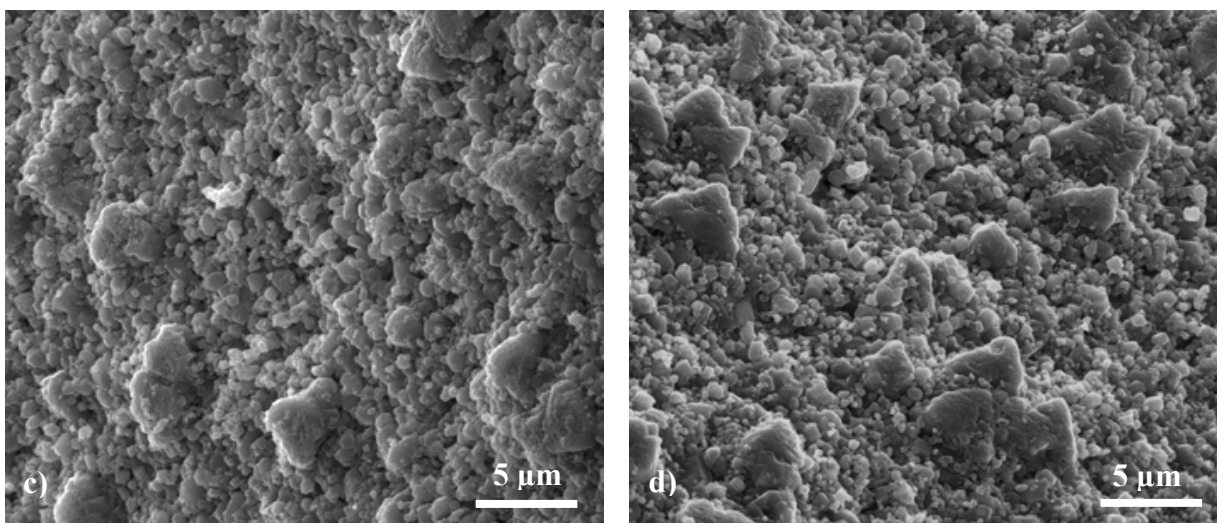


Figure 3.7: Pellet surfaces after reaction at a) 20°C, b) 40°C, c) 60°C, and d) 80°C.

The different CaCO_3 morphologies result in different particle shapes, so these may be visible in SEM images of CaCO_3 in Figure 3.7. However, when only small amounts of a morphology are present, it is impossible to distinguish from the predominantly present surface. Therefore, XRD was run to complement the SEM images. Figure 3.8 compares these XRD results for the a) pellets and b) fines with reference spectra for three different CaCO_3 morphologies (calcite, vaterite, and aragonite) and Ca(OH)_2 . Figure 3.8(a) also includes a curve for unreacted pellets. Here, it is evident that at all temperatures, the pellets are mainly calcite. Only a small peak appears in the 80°C results at a 2θ of 61. This small peak position is not one of the main peaks for vaterite, aragonite, or Ca(OH)_2 . Therefore, it is assumed that this small peak is from an impurity and that CaCO_3 is only present as calcite on the pellets.

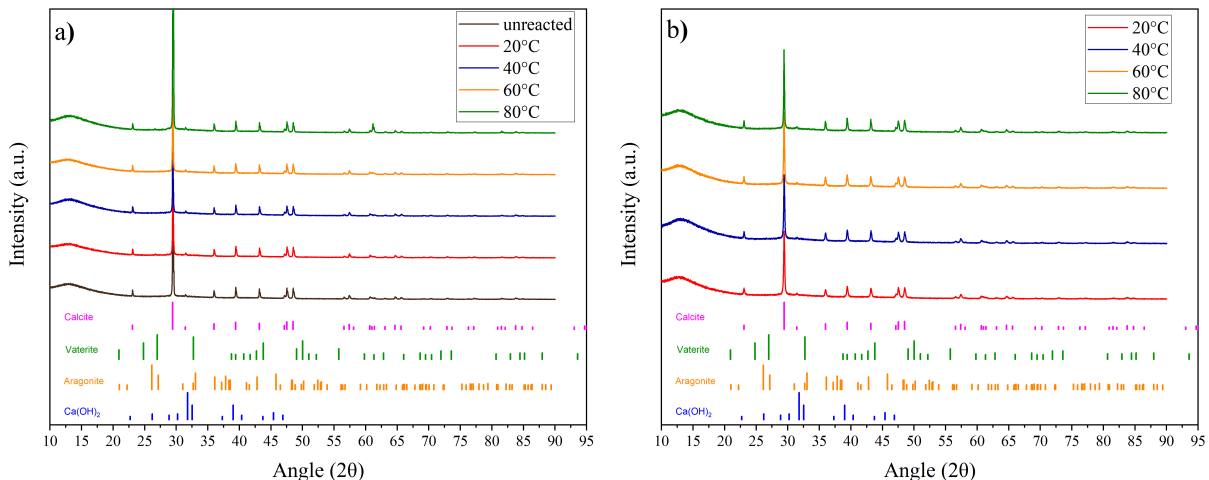


Figure 3.8: XRD results for (a) pellets, and (b) fines at different temperatures. Reference spectra for calcite (pink), vaterite (green), aragonite (orange), and Ca(OH)_2 (blue) are shown at the bottom.

For the fines, the XRD results (Figure 3.8(b)) were consistent with calcite at all temperatures. The fines are not seeded and consequently will form the morphology that is most favourable, kinetically and thermodynamically. In these results, only calcite is observed, and this suggests that at the high pH used in this work, only calcite will be formed both through spontaneous nucleation and as precipitation on CaCO_3 pellets. Therefore, in contrast to work at lower pH, the temperature does not change the morphology of CaCO_3 produced, and only modifies the nucleation rate causing lower retention at high temperatures.

When results at ambient and elevated temperatures are compared, a framework for achieving high retention can be found. This builds on the understanding that high retention is achieved by improving the conditions for precipitation on CaCO_3 particles while hindering spontaneous nucleation. These two processes have equal driving force, the supersaturation, F_d . Under the conditions used in this work, the supersaturation is high but locally confined around the Ca(OH)_2

particles. Thus, increased precipitation on the CaCO_3 pellets, with the resulting higher retention, is achieved by increasing the chance of a CaCO_3 pellet being near the $\text{Ca}(\text{OH})_2$ particle. This is a pure mass transport constraint. On the other hand, spontaneous nucleation is accelerated by increasing the kinetic driving force, demonstrated here by the temperature. High retention is achieved when the mass transport conditions are favorable and the kinetic driving force is low. The highest retention reported in this work is 73% and was achieved for seed size pellets at 100 g loading and at 20°C. A further retention improvement can be expected for smaller particle sizes, higher mass loadings of CaCO_3 pellets, and lower temperatures. This is a main result of this thesis.

3.2 Varied pH crystallization

Earlier in this chapter (Subsection 3.1.2.2), it was determined that in this highly alkaline environment, the morphology is no longer temperature dependent. To determine the alkalinity that ensures that all crystallization will occur as calcite (as we saw in Subsection 3.1.2.2), an experiment was designed to determine crystal morphology formed at room temperature at all possible pH values. The experiment was designed to precipitate CaCO_3 in the absence of seeding. Once the majority of carbonate ions become carbonic acid (see Figure 1.3), CaCO_3 precipitation is no longer the favoured reaction as ions would prefer to stay in solution. Additionally, CaCO_3 is known to dissolve in acidic solutions, thus any CaCO_3 crystals would dissolve in solutions with sufficiently low pH.

3.2.1 Experimental procedure

To grow crystals over a range of pH values, four solutions were necessary: process solution, K_2CO_3 solution, CaCl_2 solution, and HCl solution. The process solution was detailed earlier in

Section 3.1.1 of this chapter (1.0 M KOH and 0.5 M K₂CO₃). The K₂CO₃ solution was 0.5 M K₂CO₃ (Sigma Aldrich, 99%, reagent grade) aqueous solution, prepared with deionized water. A solution of 5.0 M CaCl₂, prepared with CaCl₂•2H₂O (Sigma Aldrich, ≥99%, ACS reagent) was prepared. The HCl solution was prepared at various concentrations ranging from 2 to 5 M by dilution of HCl stock solution (Sigma Aldrich, 37%, ACS reagent).

The first two experiments consisted of 200 mL of a solution: 1) process solution (pH of 14.5), and 2) K₂CO₃ solution (pH of 12.2). For three subsequent solutions on the range $12.2 \leq \text{pH} \leq 14.0$ a mix of solutions 1) and 2) was made to achieve pH values of 14.0, 13.4, and 12.9.

Thirteen subsequent solutions of pH 12.0, 11.5, ... 6.5, 6.0 were created, by using 200 mL of K₂CO₃ solution (to ensure equal initial CO₃²⁻ ions) and by adding HCl solution from a burette to reduce pH until the reaction stopped producing a usable amount of precipitate, this determined our endpoint of pH of 6.0. For these solution preparations, pH and temperature were measured using an Oakton pHTestr 30.

The prepared solution was added to a 500 mL Pyrex beaker. The beaker was stirred using an overhead mixer (JJ-1 Precise Strength Power Mixer) with a two-bladed stainless-steel impeller. Stirring speed was held constant. About 5.0 ± 0.2 mL of CaCl₂ solution was then added. After 10 minutes, the pH and temperature were measured again and the beaker contents were poured into a Buchner funnel and vacuum filtrated with a 9.0 cm Type 1 filter paper from Whatman. Precipitated material was placed in a glass petri dish for each reaction. These samples were dried overnight (at least 12 hours) at 105-110°C. Powder x-ray diffraction (XRD) was performed using a Bruker D8 Advance with $10 \leq 2\theta \leq 90$, step size 0.1, and scan time of 0.3 s per step.

3.2.2 Data processing method

Using Match! 3.7.0.124 software and the Crystallography Open Database (COD) (version from October 25, 2018) the spectra were matched with knowledge of possible morphologies and anticipated precipitates. The COD reference morphologies were calcite 96-900-9668, vaterite 96-900-7476, and calcium hydroxide 96-702-0139. Samples were scanned for aragonite but no acceptable figure-of-merit (FoM) values were found. To determine the relative percentages of each morphology, the software FullProf4Mac 2.5.4 was used within Match! for Rietveld refinement on each XRD data set. Rietveld refinement gives relative percentages of each morphology determined to be a match for each sample.

3.2.3 Results and discussion

The vaterite morphology, frequently found in earlier work [11], was found to be the dominant morphology when crystallization was performed for pH of 6.5 through 12.0 (see Figure 3.9). At a pH of 12.2 the morphologies reached a tipping point from primarily vaterite to then primarily calcite. This proceeded to 100% calcite at pH 13.4. At higher pH, there is the unexpected result of Ca(OH)_2 production. This was not seen in the earlier beaker experiments that used Ca(OH)_2 as a reactant (Subsection 3.1.2). In those, Ca(OH)_2 was entirely consumed. The observed Ca(OH)_2 production is attributed to a shorter reaction duration thus not allowing full thermodynamic equilibrium to be reached. In seeded experiments, Ca(OH)_2 production is hindered by the presence of CaCO_3 morphology.

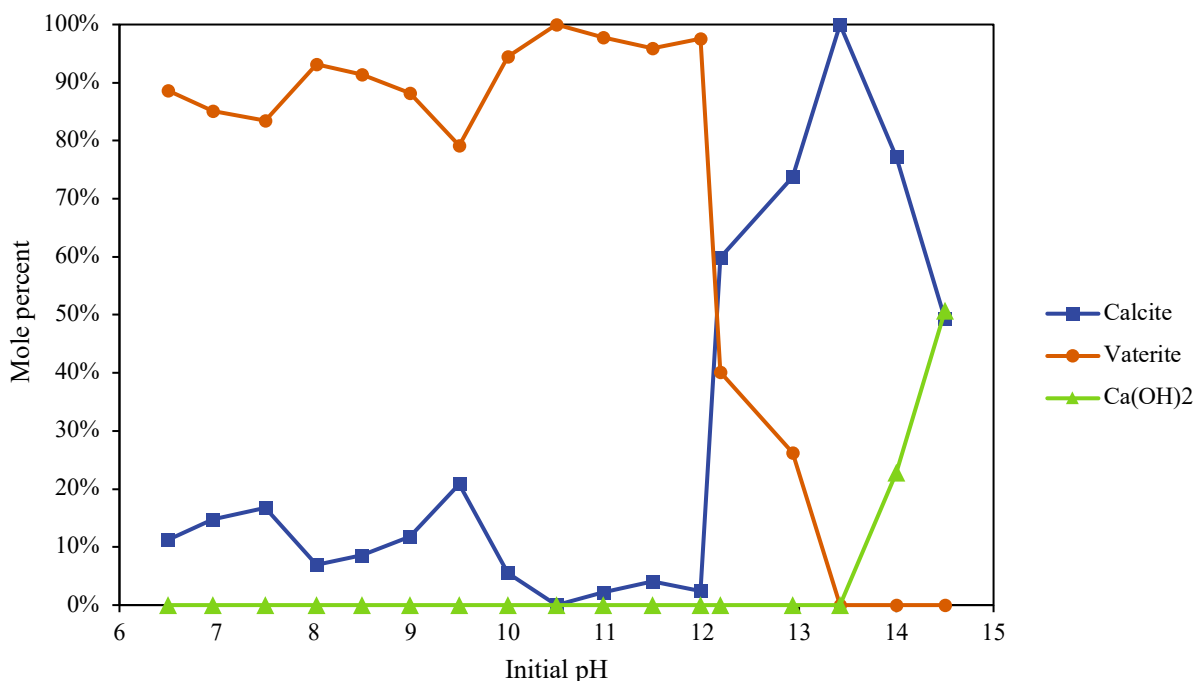


Figure 3.9: XRD Rietveld refinement mole fractions for relative prevalence of crystalline morphologies for $6.5 \leq \text{pH} \leq 14.5$.

The morphology inversion in Figure 3.9 is a critical result of this work as earlier morphology work had not explored beyond a pH of 10 [13]. This inversion occurs, within error, at an equivalence point: 11.8. An *equivalence point* is the pH value where the conversion of all ions from one form to the next is complete. Equivalence point pH values were found for the process solution using 18 data sets of pH titrations run. These experiments were run to determine ion concentrations in the process solution, however they also provided a statistically significant sample for equivalence point data. A sample of one of these 18 sets is provided in Figure 3.10 alongside the experimentally found equivalence points.

For the process solution, the KOH equivalence point occurs at $\text{pH } 11.8 \pm 0.2$ and the ion conversion is from hydroxide (OH^-) to water (H_2O). For the carbonate ion, the conversions are from carbonate (CO_3^{2-}) to bicarbonate (HCO_3^-) ($\text{pH } 7.9 \pm 0.2$) and from bicarbonate to carbonic acid (H_2CO_3) ($\text{pH } 3.9 \pm 0.3$). See Appendix Figure C.1 for more on equivalence points.

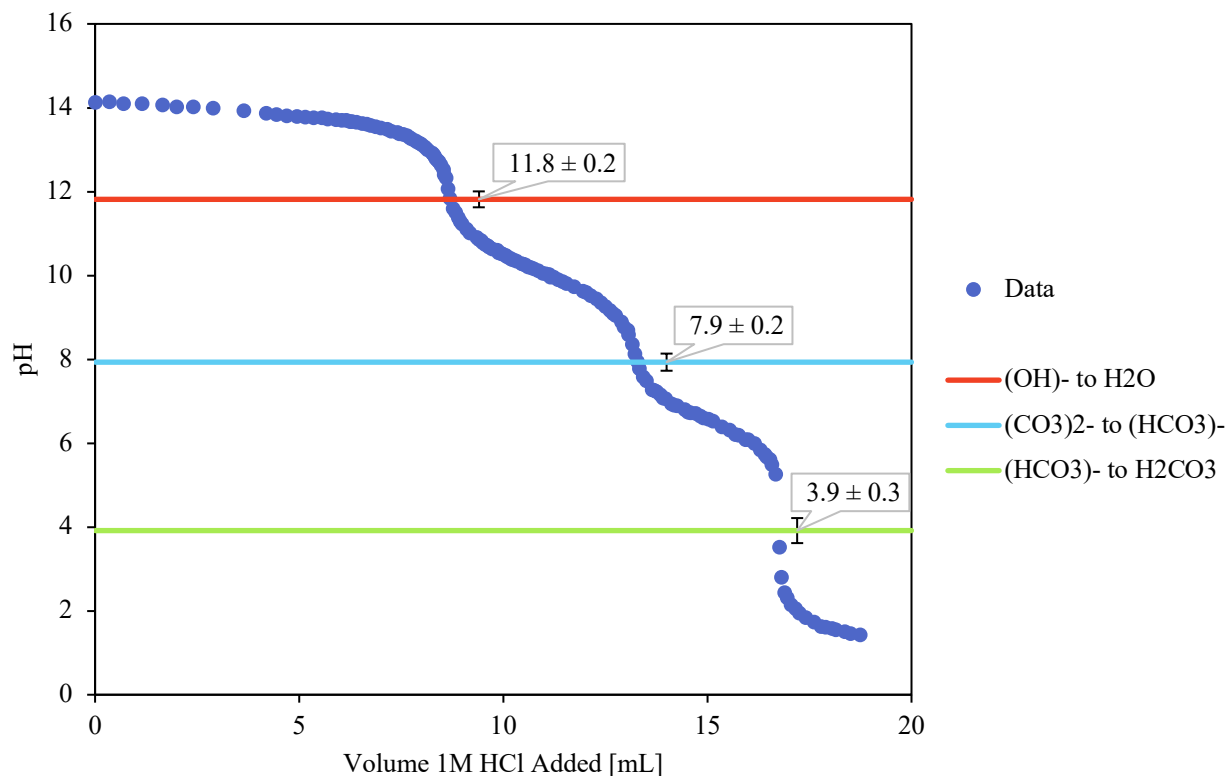


Figure 3.10: Equivalence point pH for OH^- to H_2O , CO_3^{2-} to HCO_3^- , and HCO_3^- to H_2CO_3 determined from 18 pH experimental titrations performed to with Oakton pHTestr 30. Data set is representative sample of pH versus volume added for a 1.0 M KOH and 0.5 M K_2CO_3 solution.

The most precise burette use, to bring the pH to the desired value, was required to reach pH values of 8.0, 8.5, and 9.0. This is around the next equivalence point: 7.9 ± 0.2 . The pH varied over each 10 minute reaction period. Ion precipitation from solution yielded these pH variations.

These deviations of pH are plotted with respect to the initial pH in Figure 3.11. From this figure we learn that maintaining a constant pH in this range is not feasible due to small changes of ion concentration having observable effects on the pH. These thus move the reaction pH to beyond the initial pH of other experiments (see Figure 3.12).

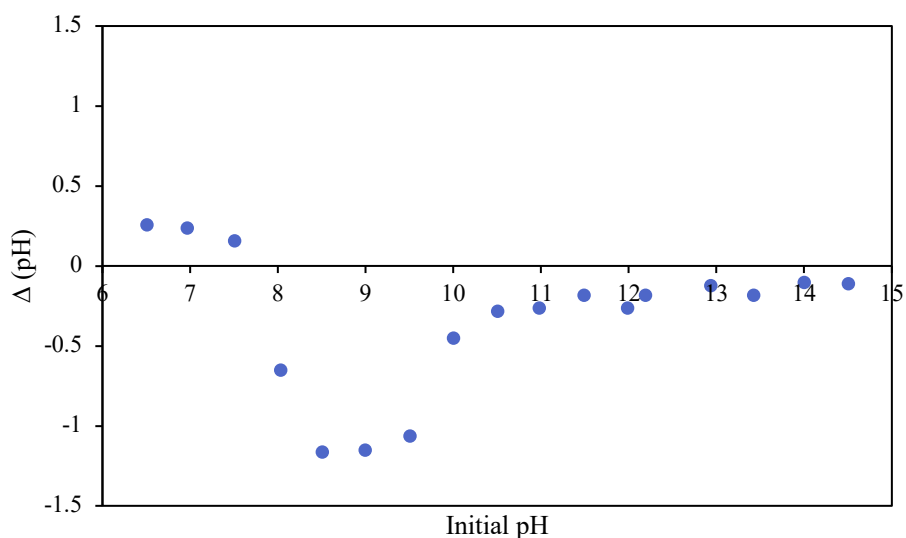


Figure 3.11: Experimental pH change of solution during 10 minute crystallization.

The final equivalence point, of $\text{pH } 3.9 \pm 0.3$, is not reached by these experiments. At a pH of 6.0, the acidity is sufficient to disfavour precipitation.

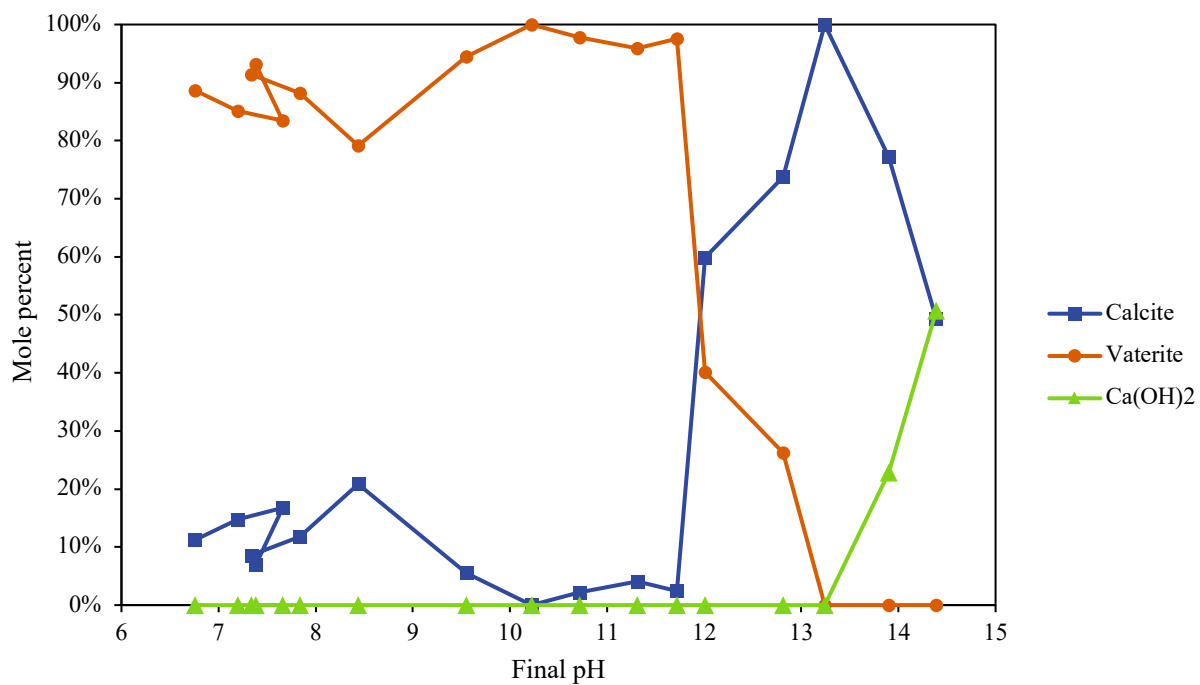


Figure 3.12: XRD Rietveld refinement mole fractions for relative prevalence of crystalline morphologies at the final pH of the reaction for the reactions starting at $6.5 \leq \text{pH} \leq 14.5$, on pH 0.5 intervals (see Figure 3.9).

Chapter 4: Lab-scale reactor construction and operation

To ensure a flow regime analogous to the fluidized bed that is used as the pelletizer at Carbon Engineering, Ltd., a lab-scale pellet reactor (LPR) model was built and used with pH and temperature monitoring (see Figure 4.1). This reactor is an embodiment of [7]. This chapter reports on the calcium retention in this LPR.

4.1 Construction

A fluidized bed is constructed from a vertically oriented 2-inch diameter schedule 40 clear PVC pipe that is 10 feet long (see Figure 4.1). This reactor tube is mounted on the wall adjacent to a fume hood. PVC glue is used to attach the fittings to the reactor bottom. A disengagement zone is glued on at the top. This disengagement zone consists of a PVC pipe expansion fitting and a 1-foot section of 3-inch diameter schedule 40 clear PVC pipe (see Figure 4.2). The top of this disengagement zone has a plumbing male pipe thread (MPT) drain cover which can be removed for pellet loading. Within the 1-foot pipe section of the disengagement zone there is a ½-inch spillover line at 6 inches above the top of the pipe expansion. The spillover line (outflow) (right side, grey in Figure 4.1) consists of rigid polyethylene pipe with PVC elbows. At 4 feet from the reactor bottom, this outflow line ends in a hose barb to which steel-reinforced PVC tubing is attached. This tubing guides effluent to the right side of the settling tank (see Figure 4.4). The settling tank consists of a 68L Rubbermaid™ bin with 6 baffles inserted into slots in two submerged, plastic strips. The entire reactor setup and settling tank is contained by a 100L secondary containment spill pan (grey in Figure 4.1).

At the reactor bottom, a 3-way “T” receives process solution from the left and empties reactor contents to the drain valve (see Figure 4.3). The process solution pipe, from the left, contains a ball valve (V6) that is shut prior to turning off the pump, to prevent pellet backflow into the ½-inch diameter pipes leading to the reactor. Process solution is fed to the reactor by a Greylor Co. Model 200 positive displacement pump.

Slurry is fed into the reactor at a height of 8.0 cm. Slurry is fed by a Mec-O-Matic VSP12 positive displacement pump with nominal output of 12 gallons per day. The slurry reservoir is a 500 mL beaker, stirred at 350 rpm, on a Corning PC-420D stir plate.

Steel-reinforced PVC tubing of ½-inch inner diameter is used at both input and output of the process solution pump (Greylor Co. Model 200). The input tubing draws process solution from the left side of the settling tank (see Figure 4.4). The output tubing connects the pump to the reactor piping network which begins with a hose barb.

Within the ½ inch line there is a needle valve for control of flow, and vertically mounted flowmeter (Polysulfone Tube Flowmeter, King Instruments 7330 series, 42W) that measures flowrates between 0.1 and 1.0 gallons per minute (see Figure 4.5). Conversions of volumetric flow (from flowmeter) to superficial velocity, (F_w/A), are done and posted next to the flowmeter for convenience. These conversions can be found in Appendix Table C.1.

Turbidity probes were installed, in-line, to measure fine particles during the experiment duration (see Figure 4.5). To calibrate these, sampling ports were also installed. Both sampling ports, inlet and exit, are hose barbs at the end of a branch from the process solution line piping (see Figure

4.6). Thirty minutes into the first reaction, the turbidity probes developed enough scaling for their data to reach a maximum, and, upon removal after the reaction duration, were found to be coated in a cloudy film of CaCO_3 which would disable their ability to be used in these experiments. Since the probes were already built into the reactor at this point, the piping was not altered, and the probes remained as a source of minor loss.

Additional valves ($\frac{1}{2}$ -inch PVC Econo ball valves), were installed 10 pipe diameters away from all in-line components to allow for cleaning if needed. The length of 10 pipe diameters allows fluid to reach a laminar flow around each component, undisrupted from the valve.



Figure 4.1: Lab scale reactor at hour 2 of a mid-sized pellet trial.



Figure 4.2: Disengagement zone of LPR.



Figure 4.3: Bottom of LPR.



Figure 4.4: Settling tank of LPR while operating.



Figure 4.5: Flowmeter and turbidity probe setups in LPR.



Figure 4.6: LPR inlet sampling port.

4.2 Experimental

4.2.1 Reactants

The process solution for these reactor experiments is identical to the process solution in Chapter 3 {1.0 M KOH (Sigma Aldrich, 99%, 45wt% solution) and 0.5 M K₂CO₃ (Sigma Aldrich, 99%, reagent grade) aqueous solution}. Pellets used in this Chapter match those of Chapter 2 (see Table 3.1). The lime slurry in Chapter 4 comprises 16wt% of Ca(OH)₂ powder (Sigma Aldrich, 95+%, ACS) within a 1.0 M KOH solution.

4.2.2 Operation

A 4L white plastic bucket serving as the DI water reservoir is placed next to the settling tank as a temperature control (see lower right corner of Figure 4.1). The process solution concentrations are confirmed via equilibrium point analysis of a titration (see Appendix C). The control water reservoir and process solution must sit overnight before a reactor run commences, to allow each to reach thermal equilibrium. Density of the lime slurry, ρ_{slurry} , is confirmed with mass and volume measurements in a graduated cylinder.

At start up, all reactor valves were open, except V-5 and V-10, the sampling ports. The process solution pump was activated by plugging it in. The reactor is allowed to half fill (to approximately 5 feet) with process solution, then we close V-6 and turn off the process solution pump. From the reactor top, using the ladder seen in Figure 4.1, we remove the reactor lid (drain cover in Figure 4.2) and use a funnel to pour in the sieved, washed, and weighed pellet sample. Temporarily homogenize the slurry by shaking and then pour 500 mL of this into a beaker with a stir bar at 350 rpm on a Corning PC-420D stir plate. The slurry pump draws from this continuously-stirred beaker through a 1/4-inch inner diameter tube. We then purge the tubing line and slurry pump of any residual cleaning solution with the slurry.

Meanwhile, we turn the process solution pump on, and then open V-6. Adjust needle valve, V-1, to give a flowrate of 0.56 GPM. Allow reactor to reach steady state after which, we measure fluidized bed height and record flowmeter reading at top of float. We then take a 100 mL sample at the exit sampling port spout (at V-10), close V-6, and take another 100 mL sample from the inlet port (V-5). When sampling, the sampling ports are purged with 300-500 mL of solution before the 100 mL sample is taken. Meanwhile, the pellets in the bed should have settled. We

then measure the fixed bed height of the settled particles. Temperature and pH measurements are taken, in-situ, with the Oakton pHTestr 30 in the second from the right region of the settling tank (between the two rightmost baffles, see Figure 4.4). We next record the temperature of the water reservoir and settling tank, as well as the pH of the settling tank.

Once all these initial conditions have been recorded, open V-6 and allow steady state to, once again, be reached. We then insert the slurry pump output line (operating at minimum speed, 5.5 mL/min) into the slurry port at the bottom right of the reactor (see Figure 4.3). The reactor start time is the slurry line insertion time.

To deepen the reader's understanding of LPR operation, we include a representative table of raw data for one run (Table 4.1). At one-hour intervals, each row of Table 4.1 is collected as described earlier within this section.

Table 4.1: Hourly measurements from reactor run R6. Initial solids: 4500.15 g at mature size (see Table 3.1).

Calcium retention for this trial was 35.0%.

Time [h]	Fluidized bed height [cm]	Fixed height [cm]	Settling Tank Temp [°C]	Control Water Temp [°C]	pH	Flow [GPM]
0	177.0	139.0	20.8	20.3	14.54	0.540
1	177.5	145.4	21.2	20.2	14.35	0.540
2	181.9	149.6	21.3	20.3	14.23	0.570
3	180.4	150.2	21.8	20.4	14.26	0.560
4	183.4	152.0	21.9	20.2	14.22	0.570

5	184.3	153.0	22.1	20.3	14.20	0.575
6	186.0	154.8	22.6	20.7	14.25	0.585

After six hours of operation, and the final row of Table 4.1 is collected, V-6 is closed and the slurry line is removed. Pellets are drained from the bottom using the drain valve, V-7, and rinsed with DI water over a sieve of mesh 120. The thoroughly rinsed pellets are placed in glass petri dishes in a drying oven at 105°C overnight, after which their mass is recorded and LPR calcium retention is calculated from:

$$R_{LPR} = \frac{m_{\text{pellets,after}} - m_{\text{pellets,before}}}{m_{\text{pellets,after}} + n_{\text{Ca(OH)}_2}(\text{MW}_{\text{CaCO}_3})} \quad (4.1)$$

where the molecular weight of CaCO_3 is $\text{MW}_{\text{CaCO}_3}$ and $n_{\text{Ca(OH)}_2}$ gives the total number of moles of calcium fed:

$$n_{\text{Ca(OH)}_2} = t_{\text{run}} \left(\frac{\rho_{\text{slurry}} \dot{V}_{\text{slurry}} w}{\text{MW}_{\text{Ca(OH)}_2}} \right) \quad (4.2)$$

where t_{run} is the reaction duration, ρ_{slurry} , the lime slurry mass density, $\dot{V}_{\text{slurry}}$, the volumetric flowrate of slurry, w , the weight fraction of Ca(OH)_2 in the slurry (16% in this Chapter), and $\text{MW}_{\text{Ca(OH)}_2}$ the molecular weight of Ca(OH)_2 . The denominator is the only difference between retention reported by Equation (3.1), R_{beaker} , and by Equation (4.1), R_{FPR} , mass obtained and mass expected, respectively. This distinction is made because beaker reaction vessel was a closed system while the LPR is an open system.

4.2.3 Experimental matrix

The experiments run in the LPR are given in Table 4.2. Three experiments were run with each pellet size category.

Table 4.2: Experiments run in the LPR.

Trial number	Pellet size	Pellet mass [g]	Retention [%]
R1	Mid-size	2327.99	45.0
R3	Mature	4500.50	38.7
R4	Seed	1200.21	58.3
R5	Seed	1200.62	54.0
R6	Mature	4500.15	35.0
R9	Mid-size	2500.72	59.8
R10	Mature	4500.72	38.8
R11	Seed	1202.16	54.8
R12	Mid-size	2500.71	59.8

4.3 Results and Discussion

Figure 4.7 shows that, when pellet size is accounted for, retention and total pellet surface area in the LPR are not positively related. This is consistent with our beaker results reported in Chapter 3 (see Figure 3.4). Figure 4.8 shows that the deviations in temperature between the settling tank and DI water reservoir, over the course of all 9 reactions reported in this chapter, increase. From Figure 4.8, we learn that the deviations for mid-size pellets exceed those for both seed and mature. In particular, the deviations for seed and mature pellets match. This suggests that, since the reaction is exothermic (see Equation (1.1)), the reaction may be proceeding more rapidly or more completely when the reactor is loaded with mid-size pellets. This may also reflect a lesser fines production from the mid-size pellet trials, since fines production consumes more energy for surface area generation.

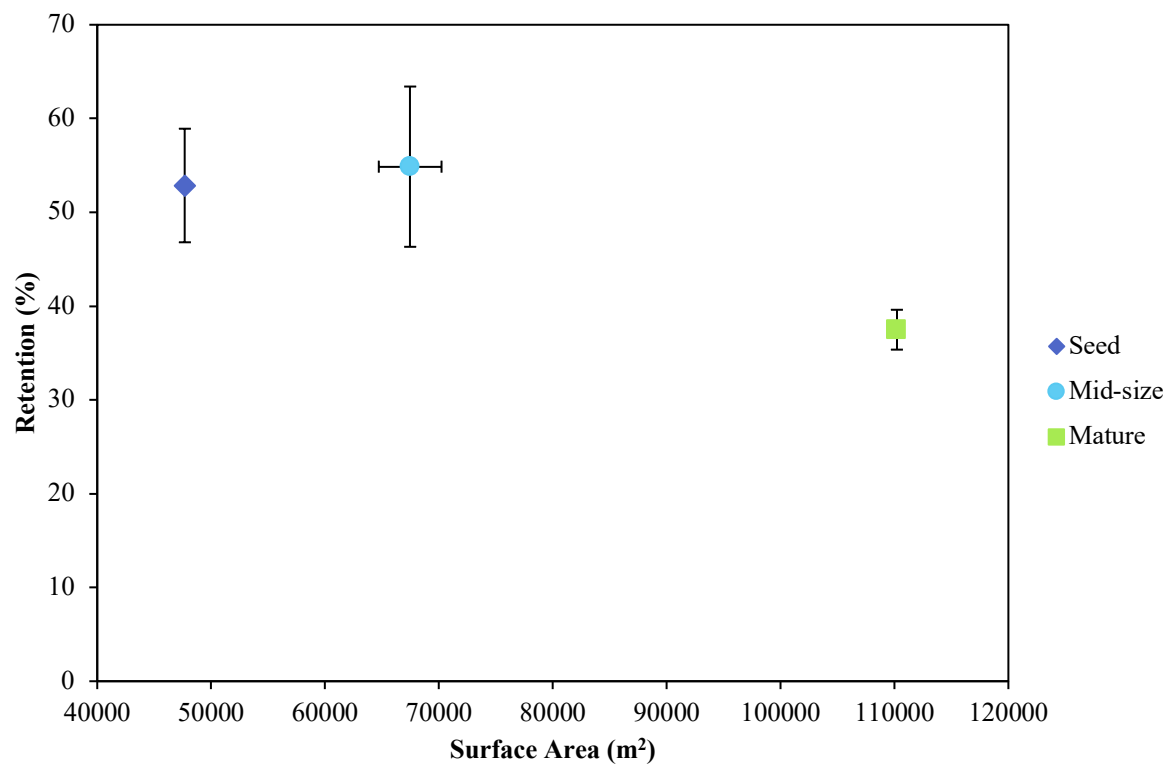


Figure 4.7: Reactor retentions, R_{LPR} , versus available initial surface area. Surface area determined using BET isotherm analysis (see Table 3.1) and initial pellet mass.

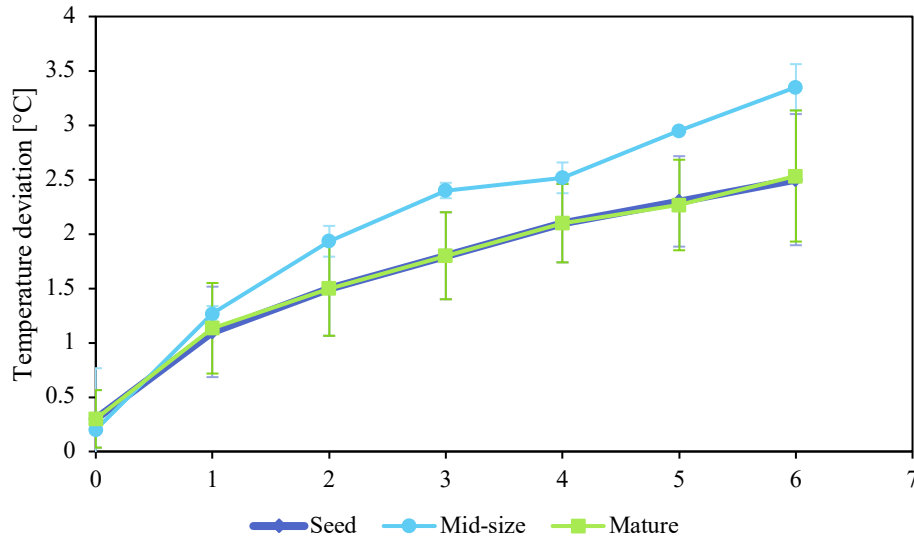


Figure 4.8: Average temperature deviation, settling tank minus DI water reservoir, hourly, for reaction duration in LPR.

Figure 4.9 shows that for all trials the fluidized bed height, within one standard deviation, was approximately the same for all pellet sizes. Thus, we succeeded in controlling the fluidized bed height for all trials. With a flow velocity of 60 m/h (1 m/min), the solution residence time for the pellet populated region of the bed is around 2 minutes at the bed heights in Figure 4.9.

Figure 4.10 shows the pH evolution over the reaction durations in the LPR, for all nine trials. From Figure 4.10, we learn that the process solution pH decreases, for all pellet sizes, at the same rate. This suggests an even consumption of CO_3^{2-} ions for all trials. Figure 4.10 can be used in conjunction with Figure 3.9 to determine that all CaCO_3 formed at these high pH values is expected to be of the calcite morphology. This result is also consistent with XRD analysis of pellets grown in the BPR, reported in Burhenne et al. [6]

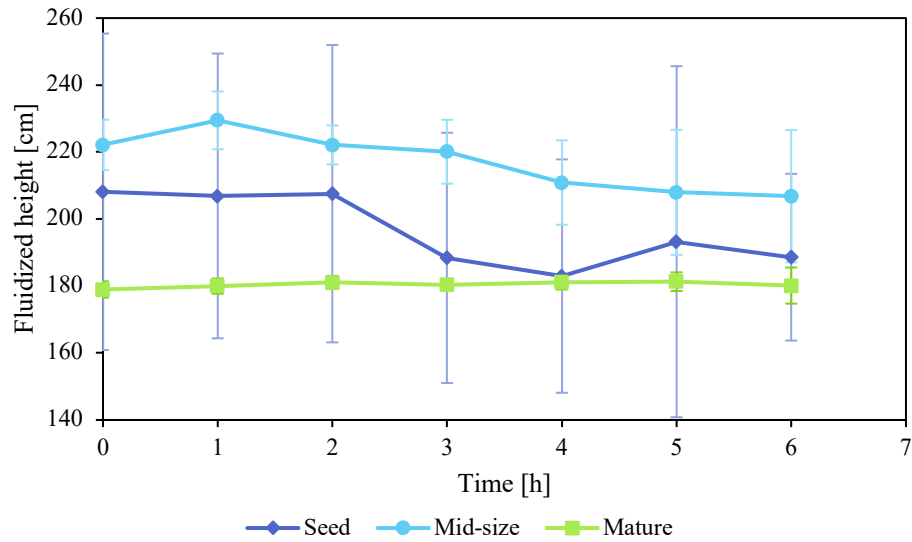


Figure 4.9: Within one standard deviation (error bars), the fluidized bed height was held constant for all three pellet sizes tested. This was done by approximating bed porosity at 60 m/h and determining the mass of pellets to be added to control this fluidized height in the LPR.

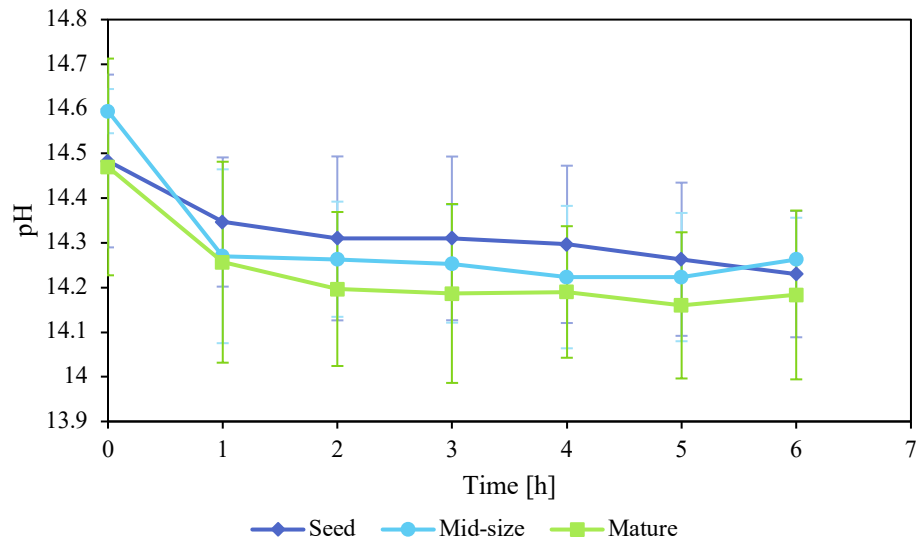


Figure 4.10: Settling tank pH as calibrated to USA standard and measured with Oakton pHTestr 30 with two-minute measurement to allow reading stabilization. Measured hourly for reaction duration in LPR.

Shown in Figure 4.11 is the particle size distribution, expressed as mass fraction, of pellets found in each size of sieve pre and post LPR reaction for a seed sized trial. The x-axis is labelled by the sieve mesh size. For sieve sizes, see Appendix Table C.3. Some fraction of the pellets, post reaction, is found to be smaller than their initial diameters. This can be attributed to: (i) fines that grew to critical size, or (ii) pellet breakage, or (iii) due to inefficiency of the sieve shaker.

Shown in Figure 4.12 and Figure 4.13 are the particle size distributions of pellets pre and post LPR reaction run for a mid-sized trial and a mature-sized trial, respectively. In Figure 4.13, due to the large diameter range of material caught in the sieve with mesh 25, the growth is not well quantified.

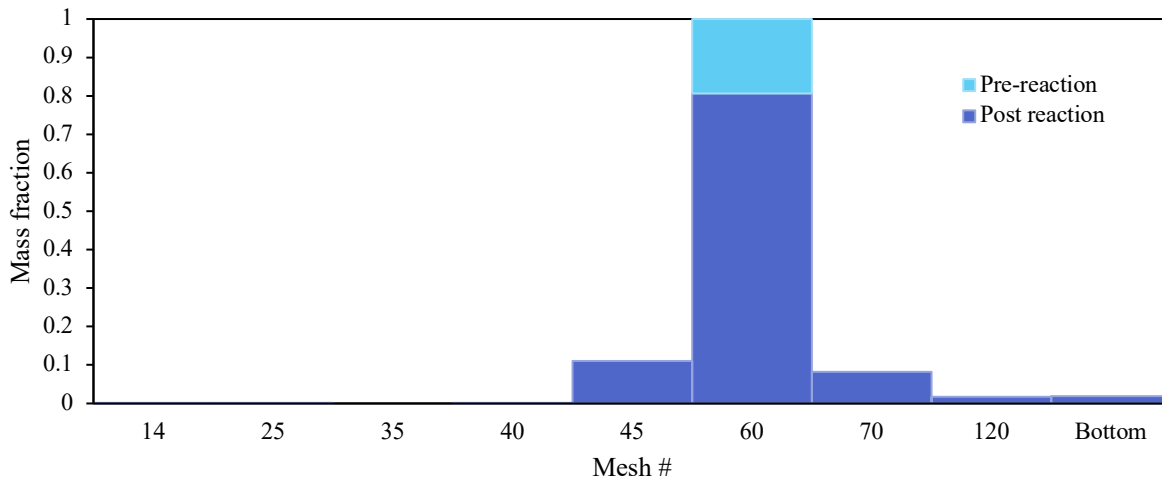


Figure 4.11: Mass fraction of pellets found in each sieve for R4, a representative size distribution change for a seed pellet size trial. R4 had a retention, R_{LPR} , of 58.3% (corresponding to a mass gain of 289.10 g) and a starting mass of 1200.21 g.

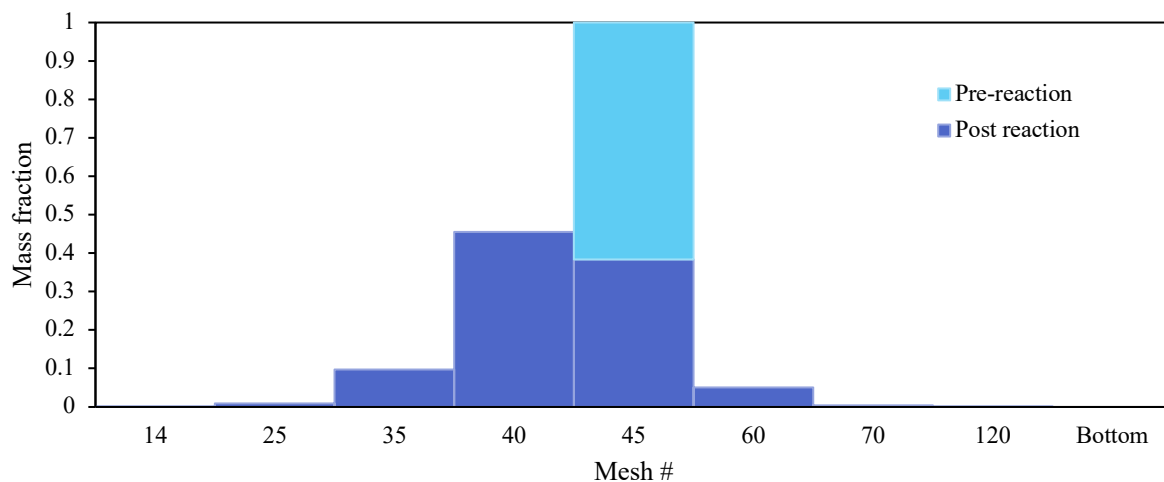


Figure 4.12: Mass fraction of pellets found in each sieve for R9, a representative size distribution change for a mid-size pellet trial. R9 had a retention, R_{LPR} , of 59.8% (corresponding to a mass gain of 295.51 g) and a starting mass of 2500.72 g.

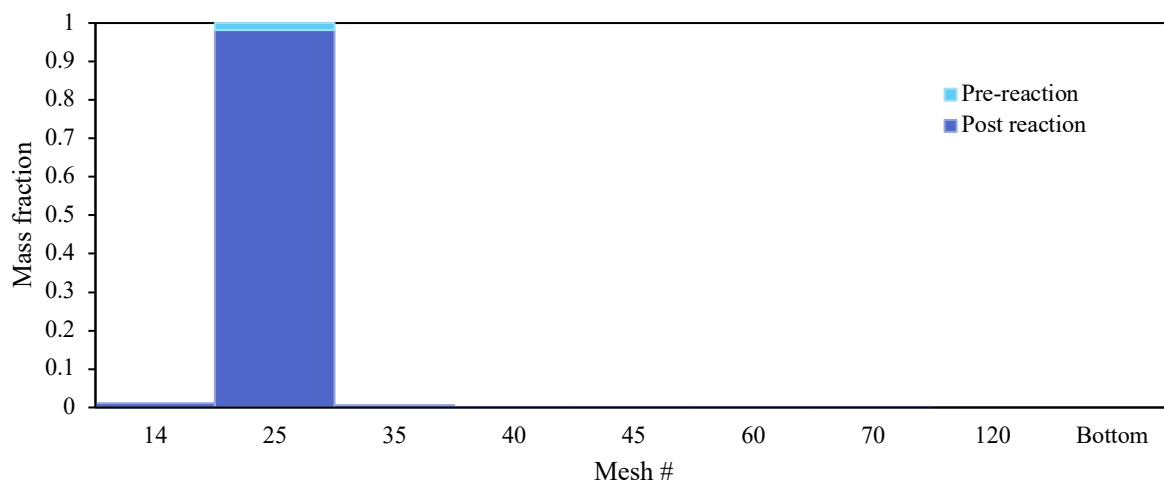


Figure 4.13: Mass fraction of pellets found in each sieve for R3, a representative size distribution change for a mature pellet size trial. R3 had a retention, R_{LPR} , of 38.7% (corresponding to a mass gain of 203.10 g) and a starting mass of 4500.50 g.

Figure 4.12 shows the largest proportion of pellets being found in a larger mesh post reaction, therefore we determine the optimum pellet seed size is the mid-size range used herein which is just above the optimum pellet seed size of 250 μm for water softening [17].

4.4 Industrial relevance

When there is a particle size distribution within the reactor, the reactor bottom contains the largest pellets. Thus, the LPR calcium retention will decrease because the calcium injection point is near the reactor bottom.

Chapter 5: Conclusion

Crystallization of $\text{CaCO}_3(\text{s})$ from an alkaline liquid, relevant for a direct air capture, was studied experimentally as a function of temperature, CaCO_3 pellet loading, CaCO_3 pellet size, and pH at three scales. The measurements were evaluated in terms of calcium retention: the fraction of CaCO_3 formed that grows on pellets.

In Chapter 2, we developed a MATLAB code (Appendix A) and by use of this, found the empirical constants α and β (Equation (2.11)). The applicability of these empirical constants to various scales of pelletizers was then validated (Figure 2.4). These empirical constants, α and β , allow us to predict pellet diameters within Carbon Engineering's pelletizer, based on in-situ bed density measurements. Further, we calculate specific surface area and bed porosity by use of our MATLAB code. The specific surface area stops increasing at 96 h, indicating a critical pellet size (Figure 2.5). Bed density increases throughout the entire BPR run (Figure 2.5).

From Chapter 3, we find that the most favorable conditions for high retention were for experiments with the smallest pellet size, highest mass loading, and lowest temperature (Figure 3.4). Total pellet surface area had a limited effect on retention (Figure 3.3(c)). We found higher temperatures reduced the diameter of fines produced (Figure 3.6). The experimental results suggest that crystallization on pellets is mass transport controlled, while spontaneous nucleation is controlled kinetically, and guides directions for further direct air capture process optimization. Our understanding of the effect of pH on morphology was extended by exploring a pH range that

now includes the pH used in direct air capture. We find a calcite-vaterite morphology inversion at the carbonate to bicarbonate equivalence point (Figure 3.9).

From Chapter 4, we find that, in a fluidized bed environment, the results from Chapter 3, pertaining to pellet size and surface area, remain true (Figure 4.7). At high surface areas, LPR calcium retention is low when mature pellets are used. Smaller pellets should therefore be conveyed to the calciner. We find a greater temperature increase for LPR trials run with mid-size pellets (Figure 4.9). We find matching pH reduction trends over LPR operation for all initial pellet sizes (Figure 4.11).

All results (Chapters 2, 3, and 4) lead to the industrial recommendations of pellet size reduction and longer reactor residence time.

5.1 Applications

The growth of calcium carbonate pellets under the conditions tested here is hindered by increased temperature. Based on this work it is recommended that Carbon Engineering consider investigating this topic further in their process.

A longer fluid residence time in a fluidized bed can be achieved by flow velocity reduction. To maintain volumetric flow within the current direct air capture system, flow velocity can be reduced by (i) increasing bed diameter, or (ii) increasing bed height or (iii) increasing the number of pelletizers.

5.2 Limitations

We acknowledge that the particle flows in this thesis are polydisperse and that additional work in the field of complex fluid dynamics, including population density modelling, is called for. This interesting path is beyond the scope of this master's thesis.

5.3 Future directions

Insights from this thesis provoke recommendations for future directions. Additional experiments with the constructed LPR to investigate an optimum residence time for fluid in the reactor should be designed. Chilled reactions may also be run to explore the lower operating limit. The influence of pH on crystallized CaCO_3 structure should be investigated to provide additional data for the morphology inversion uncovered in Figure 3.9 and Figure 3.12.

Operating in a different flow regime, such as an expanded bed (lower superficial velocity, denser bed), should be investigated to, effectively, increase pellet loading near the slurry injection. A change of slurry injection point height should also be attempted. Lastly, trials of longer duration should be done to determine when growth stalls in the LPR.

Bibliography

- [1] H. N. S. Wiechers, P. Sturrock, and G. v R. Marais, “Calcium carbonate crystallization kinetics,” *Water Res.*, vol. 9, no. 9, pp. 835–845, 1975.
- [2] J. F. Richardson and W. N. Zaki, “Sedimentation and fluidisation, Part 1,” *Trans. Ins. Chem. Engrs*, vol. 32, pp. 35–53, 1954.
- [3] S. Brunauer, P. H. Emmett, and E. Teller, “Adsorption of Gases in Multimolecular Layers,” *J. Am. Chem. Soc.*, vol. 60, pp. 309–319, 1938.
- [4] K. van Schagen, L. Rietveld, R. Babuška, and E. Baars, “Control of the fluidised bed in the pellet softening process,” *Chem. Eng. Sci.*, vol. 63, no. 5, pp. 1390–1400, 2008.
- [5] H. T. Bi and J. R. Grace, “Flow regime diagrams for gas-solid fluidization and upward transport,” *Int. J. Multiph. Flow*, vol. 21, no. 6, pp. 1229–1236, 1995.
- [6] L. Burhenne, C. Giacomini, T. Follett, J. Ritchie, J. S. J. McCahill, and W. Mérida, “Characterization of reactive CaCO₃ crystallization in a fluidized bed reactor as a central process of direct air capture,” *J. Environ. Chem. Eng.*, vol. 5, no. 6, pp. 5968–5977, 2017.
- [7] K. R. Heidel, D. W. Keith, J. A. Ritchie, N. Vollendorf, and E. Fessler, “Recovering a caustic solution via calcium carbonate crystal aggregates,” U.S. Patent No. 9,637,393, 02-May-2017.
- [8] D. W. Keith, G. Holmes, D. St. Angelo, and K. Heidel, “A Process for Capturing CO₂ from the Atmosphere,” *Joule*, vol. 2, pp. 1–22, 2018.
- [9] S. Atsumi, W. Higashide, and J. C. Liao, “Direct photosynthetic recycling of carbon dioxide to isobutyraldehyde,” *Nat. Biotechnol.*, vol. 27, pp. 1177–1180, Nov. 2009.
- [10] S. Leahy, “Carbon Engineering Makes Gasoline by Capturing Carbon Dioxide From the Air,” *National Geographic*, 2018. [Online]. Available:

<https://news.nationalgeographic.com/2018/06/carbon-engineering-liquid-fuel-carbon-capture-neutral-science/>.

- [11] R. Ševčík, M. Pérez-Estébanez, A. Viani, P. Šásek, and P. Mácová, “Characterization of vaterite synthesized at various temperatures and stirring velocities without use of additives,” *Powder Technol.*, vol. 284, pp. 265–271, 2015.
- [12] R. H. G. Perry, D. W. Green, and J. O. Maloney, *Perry’s Chemical Engineers’ Handbook (7th Edition)*. 1997.
- [13] N. Spanos and P. G. Koutsoukos, “Kinetics of Precipitation of Calcium Carbonate in Alkaline pH at Constant Supersaturation. Spontaneous and Seeded Growth,” *J. Phys. Chem. B*, vol. 102, no. 34, pp. 6679–6684, 1998.
- [14] C. Y. Tai and H. P. Hsu, “Crystal growth kinetics of calcite and its comparison with readily soluble salts,” *Powder Technol.*, vol. 121, no. 1, pp. 60–67, 2001.
- [15] K. L. Mercer, Y. P. Lin, and P. C. Singer, “Enhancing calcium carbonate precipitation by heterogeneous nucleation during chemical softening,” *J. Am. Water Work. Assoc.*, vol. 97, no. 12, pp. 116–125, 2005.
- [16] G. H. Nancollas and M. M. Reddy, “The crystallization of calcium carbonate. II. Calcite growth mechanism,” *J. Colloid Interface Sci.*, vol. 37, no. 4, pp. 824–830, 1971.
- [17] K. M. Van Schagen, R. Babuška, L. C. Rietveld, and A. M. J. Veersma, “Model-based dosing control of a pellet softening reactor,” in *IFAC Proceedings Volumes*, 2009, vol. 42, no. 11, pp. 267–272.
- [18] K. M. Van Schagen, L. C. Rietveld, and R. Babuška, “Dynamic modelling for optimisation of pellet softening,” *J. Water Supply Res. Technol. - AQUA*, vol. 57, no. 1, pp. 45–56, 2008.
- [19] J. Chen and L. Xiang, “Controllable synthesis of calcium carbonate polymorphs at

- different temperatures,” *Powder Technol.*, vol. 189, no. 1, pp. 64–69, 2009.
- [20] Y. F. Ma, Y. H. Gao, and Q. L. Feng, “Effects of pH and temperature on CaCO₃ crystallization in aqueous solution with water soluble matrix of pearls,” *J. Cryst. Growth*, vol. 312, no. 21, pp. 3165–3170, 2010.
- [21] U. S. University, “Carbon Dioxide - Carbonic Acid Equilibrium,” 2009. [Online]. Available: <http://ion.chem.usu.edu/~sbialkow/Classes/3600/Overheads/Carbonate/CO2.html>.
- [22] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena, Revised 2nd Edition*. Wiley, 2006.
- [23] K. M. van Schagen, L. C. Rietveld, R. Babuška, and O. J. I. Kramer, “Model-based operational constraints for fluidised bed crystallisation,” *Water Res.*, 2008.
- [24] L. Schiller and A. Naumann, “Über die Grundlegenden Berechnungen bei der Schwerkraftaufbereitung,” *Zeitschrift Des Vereines Dtsch. Ingenieure*, vol. 77, pp. 318–320, 1933.
- [25] M. D. Mikhailov and A. P. S. Freire, “The drag coefficient of a sphere: An approximation using Shanks transform,” *Powder Technol.*, 2013.
- [26] R. B. Bird, W. E. Stewart, E. N. Lightfoot, and D. J. Klingenberg, *Introductory Transport Phenomena*. Wiley, 2015.
- [27] O. J. I. Kramer, P. J. de Moel, E. T. Baars, W. H. van Vugt, J. T. Padding, and J. P. van der Hoek, “Improvement of the Richardson-Zaki liquid-solid fluidisation model on the basis of hydraulics,” *Powder Technol.*, vol. 343, pp. 465–478, Feb. 2019.
- [28] J. F. Richardson and W. N. Zaki, “Sedimentation and fluidisation: Part I,” *Chem. Eng. Res. Des.*, vol. 75, pp. S82–S100, 1997.
- [29] R. Di Felice and R. Kehlenbeck, “Sedimentation velocity of solids in finite size vessels,”

- Chem. Eng. Technol. Ind. Chem. Equipment-Process Eng.*, vol. 23, no. 12, pp. 1123–1126, 2000.
- [30] R. D. van der Weijden, A. E. van der Heijden, G. J. Witkamp, and G. M. van Rosmalen, “The influence of total calcium and total carbonate on the growth rate of calcite,” *J. Cryst. Growth*, vol. 171, no. 1, pp. 190–196, 1997.
- [31] C. Y. Tai, “Crystal growth kinetics of two-step growth process in liquid fluidized-bed crystallizers,” *J. Cryst. Growth*, vol. 206, no. 1–2, pp. 109–118, 1999.
- [32] C. Y. Tai, J. F. Wu, and R. W. Rousseau, “Interfacial supersaturation, secondary nucleation, and crystal growth,” *J. Cryst. Growth*, vol. 116, no. 3–4, pp. 294–306, 1992.
- [33] S. Al-Jibbouri and J. Ulrich, “The growth and dissolution of sodium chloride in a fluidized bed crystallizer,” *J. Cryst. Growth*, vol. 234, no. 1, pp. 237–246, 2002.
- [34] J. W. Mullin, *Crystallization*, 4th ed. Oxford: Butterworth-Heinemann, 2001.
- [35] C. Y. Tai, W. C. Chien, and C. Y. Chen, “Crystal growth kinetics of calcite in a dense fluidized-bed crystallizer,” *AIChE J.*, vol. 45, no. 8, pp. 1605–1614, 1999.
- [36] T. L. Threlfall and S. J. Coles, “A perspective on the growth-only zone, the secondary nucleation threshold and crystal size distribution in solution crystallisation,” *Org. Process Res. Dev.*, vol. 18, no. 3, pp. 369–378, 2016.
- [37] D. Binev, A. Seidel-Morgenstern, and H. Lorenz, “Study of crystal size distributions in a fluidized bed crystallizer,” *Chem. Eng. Sci.*, vol. 133, pp. 116–124, 2015.
- [38] C. E. Giacomini, L. Burhenne, and W. Mérida, “Capturing atmospheric CO₂: a validated scale up model,” in *Generate 2017*, 2017, p. Poster.
- [39] C. E. Giacomini, T. Holm, L. Burhenne, and W. Mérida, “Alkaline Crystallization of CaCO₃ in a Direct Air Capture Process,” in *AIChE Conference Proceedings, Session: Particle Formation and Crystallization Processes from Liquids, Slurries, and Emulsions*,

Paper No. 528336, 2018, pp. 1–8.

Appendices

Appendix A: Codes

A.1 Minimizer

The function minimizer.m runs the curve fitting of alpha and beta parameters at 1.5 calcium loading are reasonably close to the alpha and beta at calcium loading 3.0. This function is minimizes the MSE in Pelletizer.m when alpha and beta are set as variables to be changed.

```
function minimizer
%alpha=0.1;
beta=1;
diffbeta=1;

while abs(diffbeta)>0.01
    i=1;
    for alpha=0.05:0.01:.15
        sumchi(i)=Pelletizer(alpha, beta);
        varied(i)=alpha;
        i=i+1;
    end
    [W,index]=min(sumchi);
    alpha=varied(index);
    j=1;
    betaold=beta;
    for beta=.90:0.005:1.2

        sumchib(j)=Pelletizer(alpha, beta);
        variedb(j)=beta;
        j=j+1;
    end
    [W,indexb]=min(sumchib);
    beta=variedb(indexb);

    diffbeta=beta-betaold;

    alpha
    beta

    figure(5)
    hold on
    grid on
    plot(variedb(:),sumchib(:),'.b','LineWidth',2);
    title('Chi squared values produced on a range of betas')
    xlabel('beta') % x-axis label
    ylabel('Chi squared') % y-axis label
```

```

figure(6)
hold on
grid on
plot(varied(:),sumchi(:),'.k','LineWidth',2);
title('Chi squared values produced on a range of alphas')
xlabel('alpha') % x-axis label
ylabel('Chi squared') % y-axis label
end

```

A.2 Pelletizer

The function Pelletizer.m runs, independently with inputted alpha and beta found through curve fitting.

```

function [MSE] = Pelletizer
%close all
format short

%% Varying parameters **** Will need to be optimized with curve fitting
alpha=.1515; %% Initial estimate value %% Van Shagan
beta=1.0035; %% Initial estimate value %% Van Shagan

%% Specific System Constants

dr=0.1016; %% m %% inner diameter of reactor
xports=1.0; %% m %% distance between ports
dseed=0.00015; %(to 0.0005) %% m %% initial/seed pellet diameters
flowspeed=60; %% m/h %% flow velocity
psolu=1100; %% kg/m3 %% density solution (entering, no pellets)
swtperc=0.2; %% wt% %% Slurry weight percent Ca(OH)2 of influent
slurryin=15; %% mL/min %% volumetric flow of slurry
slurryin=slurryin/60/(100^3); %% m3/s %% volumetric flow of slurry
liquidin=8.2; %% L/min %% Volumetric flow of
liquidin=liquidin*(10^3)/60/(100^3); %% m3/s %% Volumetric flow
TotVin=slurryin+liquidin; %% m3/s
CaLoad=6; %% mol/m3 %% Calcium entering
CaMols=CaLoad*TotVin; %% mol/s %% Calcium entering
%dpAVE=0.00015;
%% Known Constants
g=9.81; %% m/s2 %% Gravity %% does not need negative in this case
(terminal velocity direction not noted)
pcaco3=2711; %% kg/m3 %% density caco3
% pcaoh2=2211; %% kg/m3 %% density Ca(OH)2
% MWcaoh2=.074093; %% kg/mol %% molecular weight of Ca(OH)2;
MWcaco3=.1000869; %% kg/mol %% molecular weight of CaCO3
% MWca=0.04008; %% kg/mol %% molecular weight of Ca;
% MWoh=.001700; %% kg/mol %% molecular weight of OH;
% MWco3=.06001; %% kg/mol %% molecular weight of CO3;
kv=0.0000015; %% m2/s %% kinematic viscosity
%% Derived Constants
A=pi*(dr/2)^2; %% m2 %% cross sectional area of the reactor
Vflow=flowspeed*A/60/60; %% m3/s %%

```

```

iter=0;
error=1;
%-----
%%% Bring in data matrices
%%% DATA INPUTS
%%% Pellet diameter at each sampling port
data=xlsread('Data Set avg.xlsx','Pellets');
[Nports, Ntimes]=size(data);
Nports=Nports-1;
Ntimes;
for i=1:1:Nports
    for t=1:1:Ntimes
        dp(i,t)=data(i+1,t);
    end
end
dp=dp/1000; %%% m %%% pellet diameters
times(1,:)=data(1,:);
times=times'; %%% Transpose times matrix
Ntimes=length(times);
%%% Sampling port heights
h=xlsread('Data Set avg.xlsx','Port heights');
h;
%%% Density at each sampling port
data=xlsread('Data Set avg.xlsx','Densities');

for i=1:1:Nports %%% put all density data into a matrix.
    for t=1:1:Ntimes
        den(i,t)=data(i+1,t);
    end
end

% Unit Conversion for density
den=den*1000000; %%% g/m3 %%% densities
den=den/1000; %%% kg/m3 %%% densities

err=xlsread('Data Set avg.xlsx','Error'); %%% Read error from excel sheet.

%%% Average measured diameter of pellets
dpAVE0=mean(dp,2);
dpAVE=mean(dpAVE0); %% For R-Squared calculations

%%% Preallocate Arrays
v=zeros(Nports,Ntimes); %%% Terminal velocity at each point
P=zeros(Nports,Ntimes); %%% Porosity
Cw=zeros(Nports,Ntimes); %%% Drag coefficient
Re=zeros(Nports,Ntimes); %%% Reynolds#
mpel=zeros(Nports,Ntimes+1); %%% mass of the pellets
massflow=zeros(Nports+1,Ntimes); %%%
dmpelDt=zeros(Nports,Ntimes); %%% change in mass of pellets by change in time
n=zeros(Nports,Ntimes); %%% Richardson-Zaki parameter matrix
chisq=zeros(Nports,Ntimes); %%% Chisquared matrix
%count=zeros(Nports,Ntimes); %%% artifact of earlier versions
%countcw=zeros(Nports,Ntimes);
dpcalc=zeros(Nports,Ntimes+1);
massflow(1,:)=psolu*TotVin;

```



```

dpcalc(:,1)=dseed;
%SUMCHI=0; %%artifact

%-----
%%% Minimize chisq
for t=1:Ntimes;
    for i=1:Nports
        %%% Porosity calculation %%% wiki eqn
        P(i,t)=(pcaco3-den(i,t))/(pcaco3-psolu);

        %%% Mass of solids in each Cv at each time
        MCV(i,t)=(1-P(i,t))*(A*xports)*pcaco3;

        %%% Retention based on porosity (density measurements)
        if t==1
            PRet(i,t)=0;
        else
            PRet(i,t)=MCV(i,t)-MCV(i,t-1);
        end

        %%% Calc massflows
        massflow(i+1,t)=den(i,t)*TotVin;

        %%% Calc mass retained rate
        retention(i,t)=massflow(i,t)-massflow(i+1,t);

        %%% Use porosity to find pellet mass
        if t==1
            mpel(i,t)=pcaco3*(1-P(i,t))*xports*A;
        end
        mpel(i,t+1)=pcaco3*(1-P(i,t))*xports*A;

        %%% Use pellet masses to find difference with respect to time
        dmpelDt(i,t)=mpel(i,t+1)-mpel(i,t);

        %%% Guess an n and CW
        n(i,t)=3;
        Cw(i,t)=12;

%-----
% Find terminal velocity values based on recorded pellet diameters
% Gives initial Cw to work with
% [termvel]= DataCw (alpha, beta, pcaco3, psolu, kv, dp(i,t), g);
% voDat(i,t)=termvel;
% ReDat(i,t)=voDat(i,t)*dp(i,t)/kv;
% Cw(i,t)=24/ReDat(i,t)*(1+alpha*ReDat(i,t)^beta);
% Removed for time purposes, just set generic drag, Cw initial guess
error=1;
while error>0.001
    %%% Use porosity to determine terminal velocity %%% Richardson-
Zaki
    v(i,t)=Vflow/(P(i,t)^n(i,t)*A);

    CwError=1;
    while CwError>0.001

```

```

    %% Use terminal velocity and guessed Cw to find calculated
    %% pellet diameter
    dpcalc(i,t+1)=(v(i,t)^2*(3/4)*psolu*Cw(i,t)/(pcaco3-
psolu)/g);

    Cwold=Cw(i,t);

    %% Use terminal velocity and calc-ed pellet diameter to find
    %% Reynolds
    Re(i,t)=v(i,t)*dpcalc(i,t+1)/kv;

    %% Use Reynolds to calculate a Cw
    Cw(i,t)=24/Re(i,t)*(1+alpha*Re(i,t)^beta);

    %% Does Cw calc match Cw old?
    CwError=Cw(i,t)-Cwold; % Because this is not an absolute
value, the potential negative allows the Cw value to be adjusted up OR down
    Cw(i,t)=Cw(i,t)-.5*CwError; % Put new Cw to halfway between
old guess and new Cw
    v(i,t)=sqrt((4/3)*dpcalc(i,t+1)*(pcaco3-
psolu)/psolu*g/Cw(i,t));
    %countcw(i,t)=countcw(i,t)+1;
end

    testn=n(i,t);

    %% Alpha and beta are parameters to be fit to data.
    if Re(i,t)<0.2
        n(i,t)=4.6;
    elseif Re(i,t)>=0.2 & Re(i,t)<1
        n(i,t)=4.4*Re(i,t)^(-.03);
    elseif Re(i,t)>=1 & Re(i,t)<500
        n(i,t)=4.4*Re(i,t)^(-.1);
    elseif Re(i,t)>=500
        n(i,t)=2.4;
    end
    error=abs(n(i,t)-testn);
    %count(i,t)=count(i,t)+1;
end
    chisq(i,t)=((dp(i,t)-dpcalc(i,t+1))^2);
    MSEdiff(i,t)=((dp(i,t)-dpcalc(i,t+1))/dp(i,t))^2;
    aver(i,t)=((dp(i,t)-dpAVE)^2); %% difference between average and
each data point squared
end

end

%% Counts of pellets per CV
SolidVol=A*xports.*(1.-P(:,1)); %% m3 %% volume of pellets in each control
volume
volseed=(4/3*pi*(dp(:,1)./2).^3); %% volume at t=1
NumPellet=SolidVol./volseed;

%% Overall R-squared value
SSres0=sum(chisq,2); %% sum the rows (aka, sum the chi squared at each port)

```

```

SSres=sum(SSres0); %%% sum the residuals
SStot0=sum(aver,2); %%% sum the rows
SStot=sum(SStot0); %%% sum the
Rsquared=1-(SSres/SStot);

%% Find Rsquared for each port
RsqCV=1.-SSres0./SStot0;

MSE0=sum(MSEdiff,2); %%% Mean squared error sum of rows (aka, sum of error at
each CV)
MSE=sqrt(1/(Ntimes*Nports)*sum(MSE0));

chisq;
%-----

sumPret=zeros(Ntimes,1);
dpcalcgraph=zeros(Nports,Ntimes);
for w=1:1:Nports
    for k=1:1:Ntimes
        %%% Adjust dpcalc values to be in columns to correspond with time
matrix
        dpcalcgraph(w,k)=dpcalc(w,k+1);
        %%% Find specific Surface Area
        S(w,k)=6*(1-P(w,k))/dpcalc(w,k+1); %%% Units?
        %%% Sum of retained mass based on Porosity
        sumPret(k)=Pret(w,k)+sumPret(k);
        %%% Added mass of CaCO3 by volume change of pellet
        Vol_new(w,k)=(4/3*pi*(dp(w,k)/2)^3)-volseed(w)*NumPellet(w);
        Mass_new(w,k)=Vol_new(w,k)*pcaco3;
    end
end
end

```

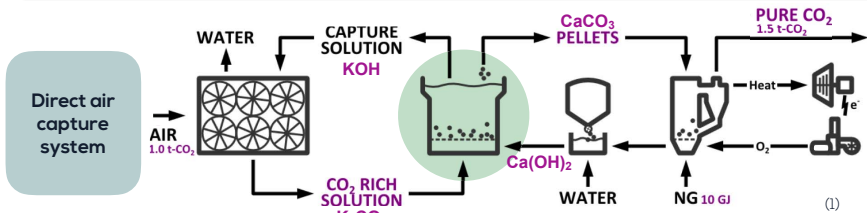
Appendix B: Generate 2017 Conference Poster



Capturing atmospheric CO₂: a validated scale up model

Caroline E. Giacomini, Luisa Burhenne, and Walter Mérida

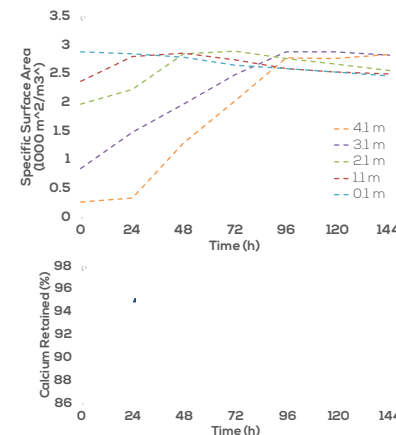
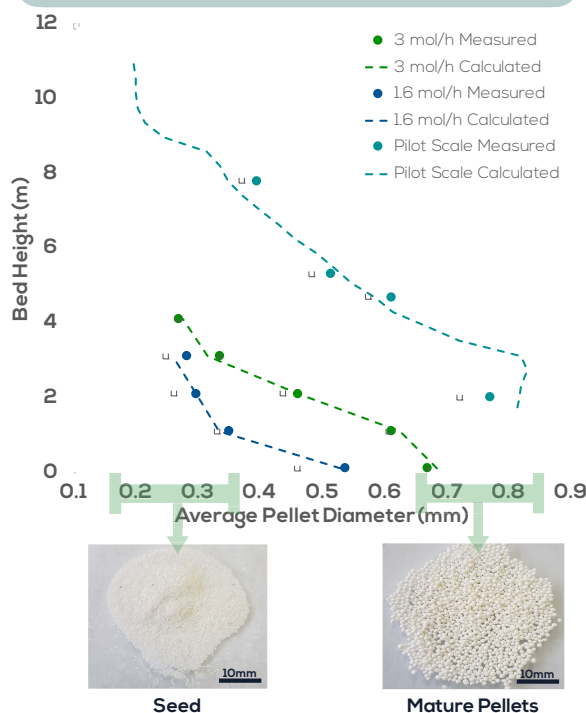
University of British Columbia, Carbon Engineering Ltd., Clean Energy Research Centre



$$\alpha = 0.1515 \quad \beta = 1.0035$$

Model validation:

The found α and β are used to predict pellet size against height for calcium loading 16 mol/h and for a pilot scale system.



Additional results:

Specific surface areas were calculated with the growth model adapted from water softening processes (2).

Corresponding to calcium retention reduction, the surface area remains constant from day 4 onwards.

Motivation:

The development of a mathematical model of pellet growth for the fluidized bed used in the direct air capture process above allows for:

- Optimizing pellet replacement time and sizes.
- Modelling bed and individual pellet growth
- Relating air capture pellet growth to well established water softening pellet growth.
- Mass balance tracking for reactants and products within the fluidized bed.

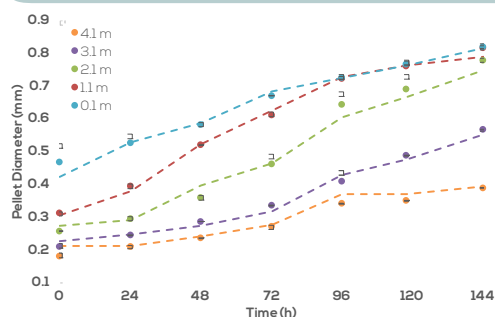
Mathematical modelling:

The Richardson-Zaki model for pellet growth in a fluidized bed for water softening employs two reaction specific constants: α and β (2). Adaptation of these constants translates the model to be useful in an alkaline CO₂ capture fluidized bed (3).

$$C_{w2} = \frac{24}{Re} (1 + \alpha Re^\beta)$$

Determining α and β :

Optimization of mean square error at 3 mol/h calcium feed rate yields α and β . The figure below shows the calculated fits alongside the averaged data from the trials run (3).



Bench top scale reactor:

Isolated from the system a bench-top scale reactor is used to collect data. The reactor consists of a 5 inch diameter pipe that is just over 5 meters in height.

Samples from the reactor bed are taken at five equally spaced points along the reactor height every 24 hours for 1-week of operation. Density and pellet sizes of the sample are recorded.

Conclusion:

The Richardson-Zaki model for pellet growth is adaptable to the fluidized bed used in this direct air capture system. The model can accurately predict pellet growth for system scale-up and parameter changes.

Future work:

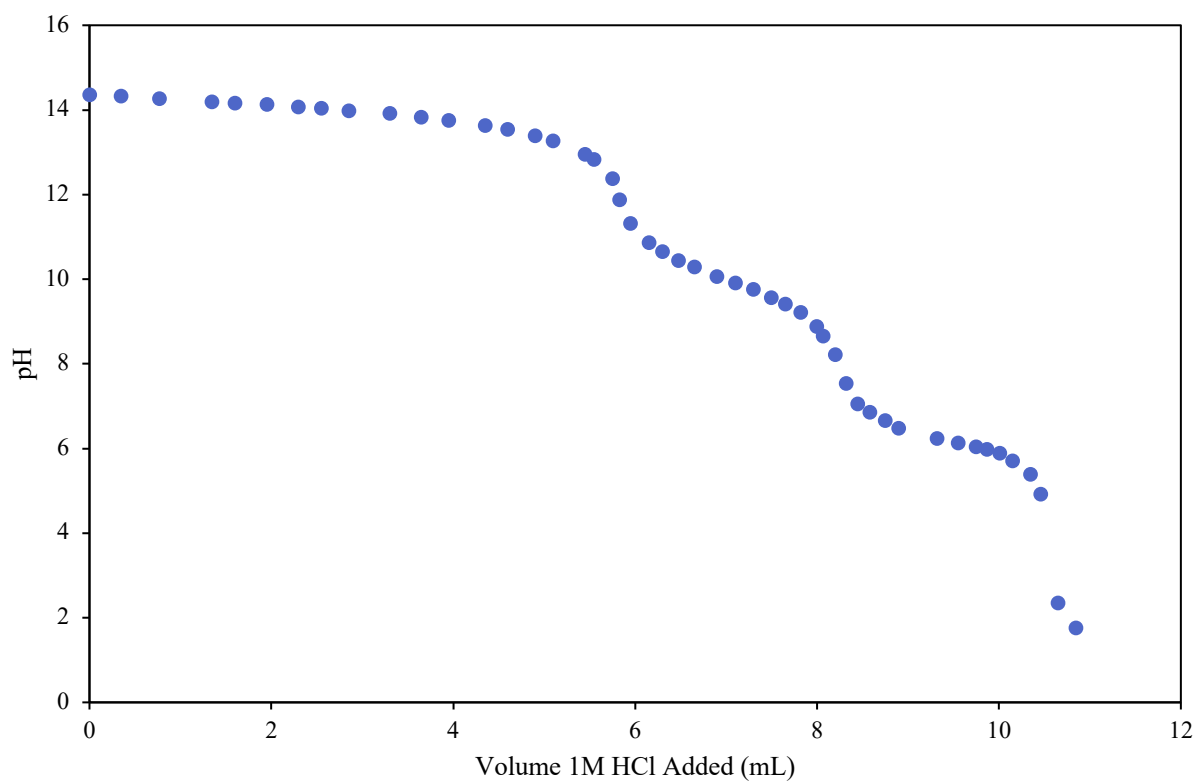
Temperature, pellet size, porosity, and injection heights will be tested at the lab scale, and these altered variables can be run in the model to hypothesize improvement at the large scale.

References:

- (1) Carbon Engineering Direct Air Capture. Retrieved from <http://carbonengineering.com/about-dac/>
- (2) K. van Schagen, L. Rietveld, R. Babuška, E. Baars, Control of the fluidised bed in the pellet softening process, Chem. Eng. Sci. 63 (2008) 1390-1400. doi:10.1016/j.ces.2007.07.027.
- (3) L. Burhenne, C. Giacomini, T. Follett, J. Ritchie, J.S.J. McCahill, W. Mérida, Characterization of reactive CaCO₃ crystallization in a fluidized bed reactor as a central process of direct air capture, J. Environ. Chem. Eng. 5 (2017) S968-S977. doi:https://doi.org/10.1016/j.jece.2017.10.047.

Appendix C: Experimental procedures

C.1 Equivalence points for carbonate titration



Appendix Figure C.1: Titration of process solution sample post reaction run 10 for determining replenishing amounts for KOH and K_2CO_3 .

C.2 Reactor flow conversion

Appendix Table C.1: Conversion of flowmeter readings to superficial velocity

Volumetric flow rate [GPM]	Superficial velocity [m/h]
0.19	20
0.37	40
0.56	60
0.75	80
0.93	100

C.3 Reactor operation

Appendix Table C.2: Initial, final, and average solution pH for experiments conducted in Subsection 3.2.

Initial pH	Final pH	Average pH of crystallization environment
14.50	14.39	14.45
14.00	13.9	13.95
13.42	13.24	13.33
12.93	12.81	12.87
12.19	12.01	12.10
11.98	11.72	11.85
11.49	11.31	11.40
10.98	10.72	10.85
10.50	10.22	10.36
10.00	9.55	9.78

9.50	8.44	8.97
8.99	7.84	8.42
8.50	7.34	7.92
8.03	7.38	7.71
7.50	7.66	7.58
6.96	7.2	7.08
6.5	6.76	6.63
5.99	7.11	6.55

C.4 Sieve sizes

Appendix Table C.3: Order of stacked sieve meshes, and the size of opening found in each.

Mesh	Opening size [μm]
14	1410
25	700
35	500
40	425
45	350
50	300
60	250
70	210
120	125