Spring 5-5-2023

Laboratory Study of Conditions Influencing Binder Formation and CO2 Sequestration During Carbonation With Hydrated Lime

Temitope Omokinde

University of Maine, temitope.omokinde@maine.edu

Follow this and additional works at: https://digitalcommons.library.umaine.edu/etd

Part of the Civil and Environmental Engineering Commons

Recommended Citation
Omokinde, Temitope, "Laboratory Study of Conditions Influencing Binder Formation and CO2 Sequestration During Carbonation With Hydrated Lime" (2023). Electronic Theses and Dissertations. 3804.
https://digitalcommons.library.umaine.edu/etd/3804

This Open-Access Thesis is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of DigitalCommons@UMaine. For more information, please contact um.library.technical.services@maine.edu.
LABORATORY STUDY OF CONDITIONS INFLUENCING BINDER FORMATION AND CO₂ SEQUESTRATION DURING CARBONATION WITH HYDRATED LIME

By
Temitope Babatunde Omokinde
M.Sc.University of Maine, 2023
B.Eng. Federal university of Technology Akure, 2019

A THESIS
Submitted in Partial Fulfillment of the Requirements for the Degree of Master of science (in Civil Engineering)

The Graduate School
The University of Maine
May 2023

Advisory Committee:
Prof. Aaron Gallant, Associate Professor of Civil and Environmental Engineering,
Advisor

Prof. Luiz Zambrano-Cruzatty, Assistant Professor of Civil and Environmental Engineering

Prof. Shaleen Jain, Professor of Civil and Environmental Engineering
LABORATORY STUDY OF CONDITIONS INFLUENCING BINDER FORMATION AND CO₂ SEQUESTRATION DURING CARBONATION WITH HYDRATED LIME

By Temitope Babatunde Omokinde

Dissertation Advisor: Dr. Aaron Gallant


The production of lime and cement used as additives in the chemical stabilization of soil emits 9% of the total CO₂ emissions. The utilization of lime in soil carbonation has a potential for soil improvement via the formation of calcium carbonate and also helps in the sequestration of an appreciable percentage of the process-related CO₂ (67% of the total emissions) emitted during the production of this alkali, which would help to reduce the carbon footprint associated with the production of alkali such as calcium and magnesium bearing materials used in chemical stabilization. The research focuses on understanding the optimum soil condition for soil carbonation which would help in the improvement of the engineering properties of weak, frost-susceptible, and expansive subgrade soil due to the modification of the soil fabric caused by the formation of calcite. This study investigates some factors affecting the formation of calcite and degree of carbonation such as lime content, degree of saturation, and density. It also investigates how the degree of saturation and the flow rate at which CO₂ is introduced influences the efficiency of CO₂ consumption and the formation of calcite during soil carbonation. Silt samples were treated with lime and varying lime content by weight of silt was used for the stabilization of silt which includes 1% lime by weight of silt, 5% lime by weight of silt, and 10% by weight of silt.
The lime-treated silt samples were prepared at various densities to capture the effect of density on the degree of carbonation. To capture the effect of increasing degree of saturation on the efficiency of CO₂ consumption, lime-treated silt samples were tested at different degrees of saturation and tested at an increased flow rate to check the effect of flow rate on the efficiency of CO₂ consumption. It was observed from the study that the degree of carbonation reduces as the lime content in the mix increases from 1% to 10%. It was also found from the study that the increasing degree of saturation enhances the formation of calcite and the degree of carbonation in samples treated with 5% and 10% lime by weight of silt but leads to the elongation of the mineral reaction time when the degree of saturation exceeds 50% due to gas mobility problem. The increasing density has a minor influence on the degree of carbonation, but elongates the duration for the completion of the mineral reaction. The elemental study also unveils that 60% to 98% of the process-related CO₂ emissions can be sequestrated via soil carbonation at optimum soil conditions with the degree of saturation and flowrate having a huge influence on the efficiency of CO₂ consumption.
DEDICATION

This dissertation is dedicated to God almighty for the grace bestowed on me from the day I was born to this present moment.
ACKNOWLEDGEMENTS

I would like to appreciate my advisor, Professor Aaron P. Gallant for his mentorship throughout my Master’s degree program and for his indelible support towards the completion of my research. Thanks to the transportation infrastructure durability center (TIDC) at the University of Maine for the summer funding provided which was instrumental to the completion of the research.

My appreciation would be incomplete without acknowledging the unflinching support showered on me by Dr. Zeki who was helpful during the laboratory work. My sincere appreciation goes to my research committee members Prof. Jain Shaleen and Prof. Luiz Zambrano-cruzzaty for their guidance.

Special appreciation goes to my parent Mr. and Mrs. Omokinde for their support from the start of my academic pursuit till this moment. I also want to use this medium to channel my appreciation to my siblings Lekan Omokinde, Taiwo Omokinde, and Kehinde Omokinde for the words of encouragement, I am super glad to have them as siblings.

Special appreciation goes to my parent Mr. Mrs. Omokinde for their support from the start of my academic pursuit till this moment. I also want to use this medium to channel my appreciation to my siblings Lekan Omokinde, Taiwo Omokinde, and Kehinde Omokinde for the words of encouragement, I am super glad to have them as siblings.

My profound gratitude goes to Engr. Mike Uduebor and Oluwawaierefunmi Olawolu during my master’s degree program.
# TABLE OF CONTENTS

DEDICATION ........................................................................................................... v

ACKNOWLEDGEMENTS ...................................................................................... vi

LIST OF TABLES ................................................................................................. x

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

1. INTRODUCTION ............................................................................................... 1
   1.1 Research objectives ..................................................................................... 5
   1.2 Research Questions .................................................................................... 5
   1.3 Hypotheses ................................................................................................ 6

2. LITERATURE REVIEW ................................................................................... 11
   2.1 Soil stabilization .......................................................................................... 11
      2.1.1 Soil stabilization techniques ................................................................. 12
   2.2 Chemical stabilization .................................................................................. 13
      2.2.1 Lime stabilization ................................................................................ 13
      2.2.2 Cement stabilization .......................................................................... 16
      2.2.3 Chemical stabilization with Fly Ash .................................................... 19
      2.2.4 Carbonation ....................................................................................... 21
      2.2.4.1 Ca-CO$_2$-H$_2$O system ................................................................. 24
      2.2.4.2 Mg-CO$_2$-H$_2$O system ................................................................. 25
   2.3 Carbon Emission associated with chemical stabilizers ............................ 28
3. METHODOLOGY ........................................................................................................ 30
  3.1 Experimental set up .......................................................................................... 30
  3.2 Materials ......................................................................................................... 35
  3.3 Sample preparation .......................................................................................... 35
  3.4 Method used for the determination of Calcium carbonate content formed and the degree of carbonation of a carbonated soil sample ................................................. 38
  3.5 Testing of hypotheses ..................................................................................... 44

4. RESULTS AND DISCUSSION ................................................................................. 51
  4.1 Introduction ....................................................................................................... 51
  4.2 Limitation of instrumentation used in the study .............................................. 51
    4.2.1 Technique use to deduce what steady state of gas properties indicates using the result from the flowmeter ............................................................. 54
    4.2.2 Effect of degree of saturation on calcite formation and degree of carbonation ........................................................................................................... 57
    4.2.3 Effect of lime content on calcite formation and degree of carbonation .............................................................................................................. 63
    4.2.4 Effect of density on the degree of carbonation .......................................... 66
  4.3 Technique used for the determination of Global efficiency of CO₂ consumption ......................................................................................................................... 70
  4.4 Justification of end of Mineral carbonation with Flow meter result ................ 75
    4.4.1 Growth of the carbonation depth with time ............................................ 79
    4.4.2 Effect of increasing flow rate of CO₂ gas on Calcite formation and Global efficiency of CO₂ consumption ................................................................. 85
4.4.3 Efficiency of CO$_2$ consumption with increasing degree of saturation... 92

4.4.3.1 Global Efficiency of CO$_2$ Consumption and the Local

   efficiency of CO$_2$ consumption during soil carbonation......... 94

5. SUMMARY AND CONCLUSIONS ................................................................. 97

   5.1 Major Findings ........................................................................ 97

   5.2 Conclusions........................................................................... 100

   5.3 Limitation of study................................................................. 101

   5.4 Recommendations for Future Work ............................................ 101

REFERENCES .................................................................................. 102

APPENDIX A – RESULTS FROM FLOW METER TS 5300 USED DURING

   THE ELEMENTAL TESTING ..................................................... 110

BIOGRAPHY OF THE AUTHOR ....................................................... 175
LIST OF TABLES

3.1 Testing soil matrix for the determination of the end of mineral carbonation ................................................................. 45

3.2 Test Matrices for the determination of effect of Lime content on the degree of carbonation................................................. 46

3.3 Test Matrices for the determination of effect of degree of saturation on the degree of carbonation and efficiency of CO$_2$ consumption. .......... 47

3.4 soil properties for the determination of the effect of density on the degree of carbonation with samples having constant mass of lime and varying mass of water with constant degree of saturation ......................... 48

3.5 Soil testing matrix for the determination of the effect of density on the degree of carbonation with samples having constant mass of lime and constant mass of water with varying degree of saturation ................. 48

3.6 Soil testing matrix to determine the effect of increasing flowrate on the efficiency of CO$_2$ consumption for a loose lime-treated silt ............ 50

3.7 Soil testing matrix to determine the effect of increasing flowrate on the efficiency of CO$_2$ consumption for a dense lime-treated silt .......... 50
LIST OF FIGURES

2.1 Lime life cycle showing the production of lime from the calcination of limestone leads to the emission of CO\textsubscript{2} into the atmosphere, and the hydrated lime formed also has the potential to sequester CO\textsubscript{2} gas to form calcite ................................................................. 23

2.2 Scanning electron microscope picture of PCCs ........................................ 25

2.3 Scanning electron microscope picture of HMCs ................................. 27

2.4 CO\textsubscript{2} emissions during the production of cement and lime ........... 29

3.1 Experimental set up ........................................................................ 31

3.2 Experimental set up used in this study .............................................. 32

3.3 Flow meter used in the study which helped in capturing CO\textsubscript{2} gas properties and the volume introduced during the carbonation. ............ 33

3.4 (a) The introduction of CO\textsubscript{2} gas leads to the formation of carbonic acid while the lime particles dissolved into the water in the soil to produce divalent calcium carbonate ions (b) The reaction between the carbonic acid formed and the divalent calcium carbonic lead to the formation of calcite which enhance the engineering properties of the treated soil ........................................................................... 34

3.5 Mechanical mixing of lime treated samples to ensure homogenization of mix .................................................................................. 36

3.6 Mold housing the lime-treated samples which is similar to the thickness of a subgrade in a field scenario .......................................... 37
3.7 Standard calcium carbonate curve used in the study to determine the mass of calcite formed after the carbonation test. Varying masses of pure Calcite were reacted with 1 N of diluted hydrochloric acid which emitted CO$_2$ gas, a relationship between CO$_2$ and mass of calcite was obtained.

3.8 Illustration of point where samples were retrieved from carbonated samples for the determination of calcium carbonate content to show the effect of lime content, degree of saturation and density o the degree of carbonation.

3.9 (a) Plot showing the effect of the sample size used on the amount of calcite extracted. Different sizes of carbonated samples were tested and the carbonated sample with the least size has the highest % calcite. (b) The plot of the sample size against degree of carbonation, the degree of carbonation reduces as the sample size increases.

3.10 1 g of Carbonated sample in Calcium carbonate chamber

3.11 Calcium carbonate chamber with a pressure inducer

4.1 Plot showing the results obtained from the flow meter used during soil carbonation with the inlet and outlet flow meter calibrated to capture the CO$_2$ properties during and after the reaction.

4.2 Plot showing the results obtained from the flow meter used during soil carbonation with the inlet flow meter calibrated to capture the CO$_2$ properties during and after the reaction and the outlet flow meter assigned to read the properties of air with the aim of justifying the limitation of instrumentation.
4.3  (a) Plot of showing CO₂ flow rate during carbonation against the carbonation time captured by a flow meter during the carbonation test. (b) The plot of the temperature from the inlet and outlet flowrate against the carbonation time, the temperatures from both flow meter attained steady state. (c) The plot of the absolute pressure against the carbonation time showing the absolute pressure approaching steady state. (d) The plot showing the carbonation period against the % binder content approaching steady state indicating formation of calcite stopped as soon as the gas temperature and absolute pressure attained steady state in Figure 4.3a, Figure 4.3b and Figure 4.3c  

4.4  (a) Plot showing the effect of increasing degree of saturation on the average % calcite formed for both samples treated with 5% and 10% lime content by weight of silt. The samples were tested at increasing degrees of saturation for a carbonation period of 1hr with a similar void ratio of 1.30  (b) Plot showing the effect of increasing degree of saturation on the average degree of carbonation for both samples treated with 5% and 10% lime content by weight of silt. The samples were tested at increasing degrees of saturation for a carbonation period of 1hr with a similar void ratio of 1.30
4.5 (a) Plot showing the change in the water content if all lime particles are converted into calcite due to mineral reaction for samples prepared at similar void ratio of 1.30 at different % lime content. The final water content was obtained using stoichiometry and soil properties as presented in Table.3.3. (b) Plot showing the change in the degree of saturation if all lime particles are converted into calcite due to mineral reaction for samples prepared at similar void ratio of 1.30 at different % lime content. The final degree of saturation was obtained using stoichiometry and the soil properties presented in Table.3.3.

4.6 (a) Plot showing the effect of lime content on the % average calcite formed. Silt samples were treated with 1%, 5%, and 10% by weight of silt at different degrees of saturation with carbonation period of 1hr. (b) Plot showing the effect of lime content on the average degree of carbonation. Silt samples were treated with 1%, 5%, and 10% by weight of silt at different degrees of saturation with carbonation period of 1hr.
4.7 Plots showing the effect of increasing density on the average % calcite and average degree of carbonation. Samples with different densities were tested to capture the effect of increasing density on calcite formation. The samples were all tested for a continuous carbonation period of 1hr. The samples were tested having a similar mass of water as density increases. For samples prepared with a constant mass of water, samples with densities of 14.05 kN/m$^3$, 13.61 kN/m$^3$, 12.92 kN/m$^3$, 12.24 kN/m$^3$, 11.62 kN/m$^3$ having degrees of saturation of 42%, 41%, 38%, 36%, 35% respectively with a similar mass of water of 117 g, while samples prepared with a constant degree of saturation has a degree of saturation of 42% with a varying mass of water of 111 g, 115 g, 123 g, 128 g, and 134 g for densities 14.05 kN/m$^3$, 13.61 kN/m$^3$, 12.92 kN/m$^3$, 12.24 kN/m$^3$ and 11.62 kN/m$^3$ respectively, ........ 68

4.8 Plots showing the change in water content and degree of saturation as density increases due to mineral reaction provided all lime particles are converted to calcite. The final water content and degree of saturation was obtained with the initial soil properties presented in Table.3.5 and stoichiometry for samples prepared with similar mass of water. .......................................................... 69
4.9 (a) Plot showing the % binder content formed at different duration through a sample depth of 15.6cm. The duration of testing of 15mins was obtained after a continuous test which indicates the end of the mineral reaction. Samples were tested between 0mins to 15mins to see how the growth of carbonation depth occurs during soil carbonation. The mass of calcite formed at each duration of carbonation was obtained using the integration of the area under the curve method (b) Plot showing the volume of CO$_2$ introduced during the carbonation test against the time, plot obtained from the flow meter was used in this study; the volume of CO$_2$ introduced was obtained with the aid of the flow meter which was important in computing the efficiency of CO$_2$ consumption.

4.10 Plot showing the % binder content formed at different duration through a sample depth of 15.6cm. The area under the curve represents the calcite mass formed. The area under each curve was calculated using the integral method. The summation of all areas gives the total calcite mass formed due to soil carbonation. The integration of the area under the curve method helps us obtain the mass of Calcite formed at each shaded region.

4.11 Interpretation using flow meter result to obtain the Mass of CO$_2$ introduced for efficiency of CO$_2$ calculations.

4.12 Continuous testing for 1hr of sample tested at target flow rate of 1.25L/mins with degree of saturation of 42% and initial void ratio of 0.82.

4.13 Representative analysis of the samples carbonated at degree of saturation of 42% and initial void ratio of 0.82.
4.14 Plot of the percentage calcite formed throughout a sample depth of 15.6cm with the CO_2 flowrate increasing. The tested samples were prepared at 35% degree of saturation and initial void ratio of 0.82. The samples all possess similar mass of silt and mass of lime. ............ 81

4.15 Plot of the percentage calcite formed throughout a sample depth of 15.6cm with the CO_2 flowrate increasing with samples prepared at 35% degree of saturation and initial void ratio of 1.20. The samples all possess similar mass of silt and mass of lime. ............................. 82

4.16 Flowmeter results for samples tested to see the effect of flowrate on the efficiency of CO_2 consumption for samples having void ratio of 1.20 and a degree of saturation of 35% ................................. 83

4.17 Flowmeter results for samples tested to see the effect of flowrate on the efficiency of CO_2 consumption for samples having void ratio of 0.82 and a degree of saturation of 42% ................................. 84

4.18 (a) Plot showing the effect of increasing flow rate on the formation of calcite in a lime-treated silt in loose configuration. The increased flow rate leads to the reduction in the mass of calcite formed. All samples possess same mass of lime of 70g and mass of silt (734g) with similar degree of saturation of 35% (b) plot showing the effect of the increasing flow rate on the efficiency of CO_2 consumption in a Loose configuration, the increased flow rate cause a reduction in the efficiency of CO_2 consumption. ................................. 88

4.19 Plot of the mass of CO_2 introduced during carbonation against mass of CO_2 consumed for samples with initial void ratio of 1.20. ................. 89
4.20 (a) Plot showing the effect of increasing flow rate on the efficiency of CO₂ consumption in lime treated silt in a dense configuration. The increased flow rate posses a negative impact on calcite formation, an increased flow rate leads to reduction in the mass of calcite formed. All samples possess same mass of lime of 70g and mass of silt (817g) with similar degree of saturation of 42%. (b) Plot showing the effect of increasing flow rate on the efficiency of CO₂ consumption for a dense configuration, the increased flow rate leads to a reduction in the efficiency of CO₂ consumption.

4.21 Plot of the mass of CO₂ introduced during carbonation against mass of CO₂ consumed for samples with initial void ratio of 0.82.

4.22 (a) Plot showing the effect of increasing degree of saturation on degree of carbonation and efficiency of CO₂ consumption for samples of void ratio e = 1.30 treated with 5% Lime content by weight of silt tested for a duration of 1hr (b) Plot showing the effect of increasing degree of saturation on degree of carbonation and efficiency of CO₂ consumption for samples of void ratio e = 1.30 treated with 10% Lime content by weight of silt tested for a duration of 1hr.
(a)% Calcite formed throughout a sample tested at a gas flowrate presented above with samples having initial void ratio of \( e=0.82 \) and \( \text{Sr}=42\% \). The sample was tested for different duration which were deduced from a continuous test (b) Local efficiency of \( \text{CO}_2 \) consumption between two carbonation periods during the carbonation of a lime-treated silt having a void ratio of 0.82 and a degree of saturation of 42% (c) Global efficiency of \( \text{CO}_2 \) consumption throughout a carbonation period of 25mins of a lime-treated silt having a void ratio of 0.82 and a degree of saturation of 42% , tested at a gas peak flow rate which ranges between .................................... 96

A.1 Flow meter results for the determination of the end of mineral reaction with testing duration of 7.5 minutes. Testing condition is presented in Table.3.1. The measurement from the outlet flow meter is invalid until the end of mineral reaction.................................... 111

A.2 Flow meter results for the determination of the end of mineral reaction with testing duration of 15 minutes. Testing condition is presented in Table.3.1. The measurement from the outlet flow meter is invalid until the end of mineral reaction.................................... 112

A.3 Flow meter results for the determination of the end of mineral reaction with testing duration of 30 minutes. Testing condition is presented in Table.3.1. The measurement from the outlet flow meter is invalid until the end of mineral reaction.................................... 113

A.4 Flow meter results for the determination of the end of mineral reaction with testing duration of 60 minutes. Testing condition is presented in Table.3.1. The measurement from the outlet flow meter is invalid until the end of mineral reaction.................................... 114
A.5 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=12%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................. 115

A.6 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=16%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................. 116

A.7 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=20%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................. 117

A.8 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=24%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................. 118

A.9 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=28%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................. 119
A.10 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=42%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................. 120

A.11 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=50%. Testing condition is presented in Table.3.2. Testing condition is presented in Table.3.2 ................................ 121

A.12 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=12%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ....................................................... 122

A.13 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=16%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ....................................................... 123

A.14 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=20%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ....................................................... 124
A.15 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=24%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 125

A.16 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=28%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 126

A.17 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=42%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 127

A.18 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=50%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 128

A.19 Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=60%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 129
A.20 Flow meter results for the determination of effect of Lime content on degree of carbonation for sample treated with 1% Lime content at Sr=16%. Testing condition is presented in Table.3.3. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 130

A.21 Flow meter results for the determination of effect of Lime content on degree of carbonation for sample treated with 1% Lime content at Sr=24%. Testing condition is presented in Table.3.3. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 131

A.22 Flow meter results for the determination of effect of Lime content on degree of carbonation for sample treated with 1% Lime content at Sr=42%. Testing condition is presented in Table.3.3. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 132

A.23 Flow meter results for the determination of effect of density on degree of carbonation for sample with e=0.82 at Sr=40% (varying mass of water). Testing condition is presented in Table.3.4. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 133

A.24 Flow meter results for the determination of effect of density on degree of carbonation for sample with e=0.88. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ............... 134
A.25 Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.98$ at $Sr=40\%$ (varying mass of water). Testing condition is presented in Table.3.4. The measurement from the outlet flow meter is invalid until the end of mineral reaction.

A.26 Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=1.09$ at $Sr=40\%$ (varying mass of water). Testing condition is presented in Table.3.4. The measurement from the outlet flow meter is invalid until the end of mineral reaction.

A.27 Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=1.20$ at $Sr=40\%$ (varying mass of water). Testing condition is presented in Table.3.4. The measurement from the outlet flow meter is invalid until the end of mineral reaction.

A.28 Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.82$ at $Sr=42\%$ (Constant mass of water). Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.

A.29 Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.88$ at $Sr=40\%$ (Constant mass of water). Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
A.30 Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.98$ at $Sr=38\%$ (Constant mass of water). Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 140

A.31 Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=1.09$ at $Sr=36\%$ (Constant mass of water). Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 141

A.32 Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=1.20$ at $Sr=35\%$ (Constant mass of water). Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 142

A.33 Flowmeter results for the sample with $e=0.82$ tested at a gas flowrate of 1.44 L/mins for 2mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 143

A.34 Flowmeter results for the sample with $e=0.82$ tested at a gas flowrate of 0.98 L/mins for 10mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................................................................. 144
A.35 Flowmeter results for the sample with e=1.30 tested at a gas flowrate of 1.02L/mins for 15mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 145

A.36 Flowmeter results for the sample with e=0.82 tested at a gas flowrate of 0.98L/mins for 20mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 146

A.37 Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.81L/mins for 25mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 147

A.38 Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.77 L/mins for 30mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 148

A.39 Flowmeter results for the sample with e=0.82 tested at a gas flowrate of 1.5 L/mins for continuous testing. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ................. 149

A.40 Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.55L/mins for 2mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................................. 150
A.41 Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.37L/mins for 5mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 151

A.42 Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.15L/mins for 10mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 152

A.43 Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.22L/mins for 15mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 153

A.44 Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.10 L/mins for 20mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 154

A.45 Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.61L/mins for 25mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 155

A.46 Flowmeter results for the sample with e=0.82 tested at a gas flowrate of 2L/mins for 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction. .............................................. 156
A.47 Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 1.98L/mins for 2 mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................................. 157

A.48 Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 1.87L/mins for 5 mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................................. 158

A.49 Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 1.56L/mins for 10 mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................................. 159

A.50 Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 1.25L/mins for 15mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................................. 160

A.51 Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 2.08L/mins for 20mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................................. 161

A.52 Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 2L/mins for 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction................................................. 162
A.53 Flow meter results for the sample with e= 1.20 tested at a gas flow rate of 1.74L/mins for 2mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 163

A.54 Flow meter results for the sample with e=1.20 tested at a gas flow rate of 1.56L/mins for 5mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 164

A.55 Flow meter results for the sample with e=1.20 tested at a gas flow rate of 1.23L/mins for 10mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 165

A.56 Flow meter results for the sample with e=1.20 tested at a gas flow rate of 1.53 L/mins for 15mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. The measurement from the outlet flow meter is invalid until the end of mineral reaction. ....................... 166

A.57 Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2L/mins for 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 167

A.58 Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2.78 L/mins for 2mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction............................................... 168
Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2.58L/mins for 5mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.......................... 169

Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2.44L/mins for 10mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.......................... 170

Flow meter results for the sample with e=1.20 tested at target flowrate of 4l/mins 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction.......................... 171

Flow meter results for the sample with e=1.20 tested at a gas flow rate of 3.13L/mins for 2mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.......................... 172

Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2.70L/mins for 5mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.......................... 173

Flow meter results for the sample with e=1.20 tested at a gas target flow rate of 5L/mins for 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction.......................... 174
CHAPTER 1
INTRODUCTION

The production of lime and cement emits 9% of the global Co2 emissions caused by humans (Olivier et al., 2017), manufacturing of 1 tonne of ordinary portland cement emits about 0.8-1.0 tonnes of CO2 while the production of 1 mega-tonne of lime generates about 0.86 mega-tonne of CO2 (Latifi et al., 2017). Chemical stabilization has been used extensively over the years to enhance the engineering properties or the performance of soils, the production of ordinary Portland cement is energy-intensive, which contributes to an increment in atmospheric CO2 concentration (Betts et al., 2016) causing climate change and health-related issues. Global warming causes a lot of harmful effects on humans and our environment from increasing temperature, heightened disease outbreaks, tropical storms, and melting of ice and snow causing an increment in the sea water level (Mohammed et al., 2021). It has been found that the major stimulant of global warming is the greenhouse gases from agricultural activities, the production of cement and lime which contributes massively to the amount of emission into the ozone layer (Fagerlund & Zevenhoven, 2011). CO2 contributes over 50% of the total effect on climate changes (Goh, 2004). To reduce the Co2 emissions due to the production of lime, the use of cementitious materials for soil carbonation where a fraction of the CO2 emitted during its production can be sequestration should be encouraged. One of the methods used for sequestrating CO2 entails storing CO2 inside saline aquifers, depleted oil, and impervious rocks (Boot-Handford et al., 2014).

The CO2 emitted during the production of lime happened due to the calcination of limestone and the emissions from fuels and energy used, the emission of CO2 due to lime production is categorized into two which are the process-related emissions caused by the burning of limestone which takes about two-thirds of the whole emission (Stork et al., 2014) and the combustion-related due to emissions from machinery and fuels used during
production which takes about one-third of the whole emission (Elias et al., 2018).
Recapturing the whole CO\(_2\) emitted during lime production seems byzantine, however,
some of the process-related emission can be recaptured and reused in lime-based soil
carbonation which will help to reduce the carbon footprint associated with the production
of Calcium and magnesium-bearing materials and enhance weak sub-grade, expansive and
frost-susceptible subgrade soil. In geotechnical engineering, soil carbonation is also a means
of capturing CO\(_2\) (Sanna et al., 2014) and helps in the formation of calcium carbonate
which acts as a binder, the binder is formed when a calcium based-material such as cement
or Portlandite Ca(OH)\(_2\) reacts with carbonic acid produced when CO\(_2\) get dissolved in
water within the soil matrix for soil improvement (Ji et al., 2014). Carbonation is one of
the chemical stabilization methods that has received massive attention over years (Xu
et al., 2020). The reaction of any metal-bearing oxides or divalent cation such as calcium
oxide (CaO) and Magnesium oxide (MgO) with carbon dioxide produces insoluble solid
carbonates (Azdarpour et al., 2015).These minerals formed such as Calcite (CaCO\(_3\)) ,
dolomite (Ca\(_{0.5}\)Mg\(_{0.5}\)CO\(_3\)), magnesite (MgCO\(_3\)) and siderite (FeCO\(_3\)) have been
considered as carbonate minerals capable of capturing CO\(_2\) for a long time (Mohammed
et al., 2021; Oelkers et al., 2008). The carbonation depth obtained after soil carbonation has
been said to be affected by chemical composition, mix proportion in porous materials,
temperature, partial pressure, concentration, and relative humidity of CO\(_2\) in external
environments (Ta et al., 2016). Hyvert et al. (2010) also proves the effect of CO\(_2\) pressure
on carbonation depth which indicates the sequestration of CO\(_2\) is influenced due to the
variation of carbonation depth. The examination of soil carbonation indicates that the
formation of an insoluble salt of CaCO\(_3\) caused a reduction in the pore size which affects
the diffusivity of the CO\(_2\) (Du et al., 2012).

According to Ji et al. (2014), the carbonation process happens in two phases, the first
stage involves the dissolution of carbon dioxide in water to form carbonic acid accompanied
by the second phase which involves the reaction of lime with the carbonic acid to produce a
binder called calcite which enhances the soil properties. The diffusivity of the CO$_2$ gas depends on the void ratio and the amount of water present in the soil matrix (Deneele et al., 2021). Van Balen et al. (1997) found that the CO$_2$ effective diffusion coefficient decreases almost linearly between the mortar and the capillary water content because more water is produced during the carbonation reaction hence the diffusion efficiency of the gas in the soil matrix depends on the drying rate of sample and the rate of water production caused by the carbonation reaction. The calcium carbonate film formed after the reaction precipitate at the surface of the hydrated lime Ca (OH)$_2$ particles which lowered the diffusion of CO$_2$ and affect the total conversion of Ca(OH)$_2$ into CaCO$_3$ (Dheilly et al., 2002).

According to Xu et al. (2020) the micro-structural analysis indicates that CaCO$_3$ was produced mostly by the carbonation of Ca(OH)$_2$ and the rapid increase in the strength initially was because of the increase in the amount of CaCO$_3$ provided by portlandite Ca(OH)$_2$ which confirms the hypothesis that CO$_2$ is sequestrated during soil carbonation. The carbonation reaction products are CaCO$_3$ and modified silica gel performs as the binding phase and hardened the soil matrix (Ashraf et al., 2019), this hardened soil matrix or cementitious composite has been proven to store 18% (by weight) of CO$_2$ which serves as a means of sequestration (Shao et al., 2006). During soil carbonation, the modification of soil fabric occurs and the formation of cementitious compounds which enhances the cohesion and resistance of the soil making the process suitable for stabilizing soil for embankment construction and other earthworks (Deneele et al., 2021). In modern construction, to achieve durable transportation infrastructure, lime has been increasingly incorporated into stabilizing soil due to its cost-effectiveness and stability characteristics in either the short or long run (Rogers et al., 2006b). According to (Arabi & Wild, 1986), the chemistry in the reaction between lime and silicate, aluminate component of expansive soils is complex and the factors the chemical reaction depends on include cation exchange,
agglomeration, flocculation, pozzolanic reaction, and carbonation. (MANUAL, 2004) presented that lime stabilization is not suitable for all types of soils, the utilization of lime in the stabilization of weak and expansive soil is more effective when the plasticity index is greater than 10% and the grain size of the material is lesser than the 74mm sieve size. Lime and cement stabilization based on previous research causes an improvement in soil properties, however, the production of lime and cement emits massive carbon dioxide into the atmosphere, to lessen the carbon footprint associated with the production of lime and cement, the use of lime in soil carbonation should be critically examined which might serve as a great means of capturing Carbon-dioxide. Factors that influence the amount of CO$_2$ sequestrated during soil carbonation should be investigated which will enable geotechnical engineers to know how efficiently CO$_2$ is sequestrated. Calcium-based soil carbonation is represented as follows in Eqn. 1.1

$$Ca(OH)_2[s] + H_2O[l] + CO_2[g] \rightarrow CaCO_3[s] + 2H_2O[l]$$ (1.1)

The equation presented above represents the exothermic reaction between the reactants which consists of the Ca(OH)$_2$, water, and the introduced captured process-related CO$_2$ emitted during the calcination of limestone when lime is produced. The outcome of this reaction produces calcite which enhances the engineering properties of the soil and also serves as a means of carbon sequestration.

This study aims at determining the optimum condition for soil carbonation and optimal gas flow. It will help us know how factors such as the degree of saturation of the soil, lime content, void ratio or dry density and flow rate at which the Co$_2$ gas is introduced into the soil matrix affects the degree of carbonation and how some of these factors affect the efficiency of CO$_2$ consumption were investigated.
1.1 Research objectives

The thesis aimed at identifying the best condition for soil carbonation and efficient consumption of CO$_2$. The specific objective include the following items listed below:

1. To understand the influence of soil properties such as lime content, degree of saturation, density or void ratio on the degree of carbonation DOC.

2. To understand conditions influencing the efficiency of CO$_2$ consumption during soil carbonation.

1.2 Research Questions

The following questions were answered by this thesis, which give a great insight about some factors influencing the formation of calcium carbonate and CO$_2$ sequestration during soil carbonation.

1. What is the relationship between lime content in the mix and the degree of carbonation?

2. What is the relationship between degree of saturation and the degree of carbonation?

3. What is the relationship between density of soil and the degree of carbonation?

4. What is the relationship between Sr and e with efficiency of CO$_2$ consumption
1.3 Hypotheses

1. The degree of carbonation may decrease as lime content increases.

The soil matrix consists of lime-treated silt with water for the dissolution of CO$_2$ gas, the lime is first dissolved into the available solution which offers divalent calcium ions (Ca$^{2+}$) and then followed by the introduction of CO$_2$ gas which gets dissolved into the water to form H$_2$CO$_3$ acid (Ji et al., 2014). As the lime content in the mix increases, more calcium carbonate will be produced because more lime is dissolved in the water and also available to react with the carbonic acid to form calcite. The sample with 5% lime content by weight of silt would produce less calcium carbonate than that of samples treated with 10% lime by weight of silt but the conversion rate of lime particles into calcite will be higher in samples with less lime content because as more calcite is produced in samples with 10% lime by weight of silt, more lime particles will be covered by the calcite films produced which makes it difficult for the carbonic acid to react with all the lime particle. Also as the lime content increases, more Calcium ions and carbonate ions will be released into the available solution in the soil matrix which affects the dissolution rate of CO$_2$ gas this then affects the quantity of CO$_2$ gas dissolved in solution to react with the lime in the soil matrix which affects the extent or degree of carbonation. Conclusively, the higher the lime content the more difficult to transform the lime into calcite i.e the higher the lime content the lesser the degree of carbonation. Also, as the lime content increases in the mix, more calcite is produced which clogs the pore space, therefore, reducing the diffusivity of the CO$_2$ gas.
2. It maybe impossible to attain a full transformation of all lime particles in the mix into calcium carbonate. It is impossible to convert all the lime in the soil matrix into calcium carbonate because during mineral reaction there is a formation of calcite which shields the other lime particles yet to be transformed into calcite, so the shielding of the unconverted lime caused by the calcite films made it impossible for the carbonic acid to react with the remaining lime covered to produce calcite. As soon as the precipitation of calcite occurs and it covers other lime particles yet to be converted into calcite, the reaction ends.

3. Increasing degree of saturation may enhance the formation of calcite and the degree of carbonation. The degree of carbonation and the calcium carbonate content will increase by the increasing degree of saturation but at a certain degree of saturation, the gas mobility problem would arise which would cause a drastic reduction in the degree of carbonation. The amount of lime dissolved initially before the exothermic reaction involving dissolved CO$_2$ gas in water occurs plays a huge role in the formation of calcite. Samples treated with lime by weight of silt would witness an increasing calcite formation and an increasing degree of carbonation as the degree of saturation increases because more solution is available for the initial dissolution of the lime which will aid the formation of more calcite and increase the degree of carbonation as the saturation rate increases. Also, as the degree of saturation increases more water will be available for the dissolution of the CO$_2$ gas leaving more carbonic acidic in the system to react with the dissociated calcium ions from the lime to form calcite.
4. Increasing density would have a negative influence on calcite formation

The increasing density would cause a reduction in void space meant for the mobility of CO₂ gas which would have a negative influence the average % calcite due to the reduction in the amount of CO₂ dissolved for the reaction to occur.

5. Increasing flow rate of CO₂ gas during soil carbonation may lead to reduced efficiency of CO₂ consumption and calcite formation.

An increment in the flow rate at which the CO₂ gas moves into the soil matrix will reduce the efficiency of CO₂ consumption and the degree of carbonation. During the reaction, the CO₂ gas moves into the soil matrix and dissolves into the available solution, as the flow rate increases, the diffusivity rate of CO₂ would increase which will lower the quantity of CO₂ gas that would dissolve in the solution present in the system, it makes the quantity of Carbonic acid (H₂CO₃) available to react with the lime reduced therefore reducing the degree of carbonation. Also, increased diffusivity caused by the increased flow rate will make the CO₂ gas diffuse faster in the soil matrix leaving less quantity of CO₂ gas to be dissolved in the solution in the soil system. It gives the gas more energy to egress the system easily via the unclogged pores before calcite formation will occur. As the flow rate of the CO₂ gas increases, the quantity of CO₂ gas consumed will be reduced hence reducing the efficiency of CO₂ consumption and the degree of carbonation. Another reason the efficiency of CO₂ consumption and the degree of carbonation would degree when the flow rate increase is that the reaction would occur faster and ends faster because calcite is produced abruptly and a high amount of lime would be covered by the calcite formed abruptly making it difficult for more lime to be carbonated, while the reduction in the flow rate would make the formation of calcite slow, therefore the rate at which the precipitation of calcite over lime would be slow giving more room for more lime
to be carbonated which would enhance the degree of carbonation and efficiency of CO₂ consumption.

6. The increasing degree of saturation would enhance the consumption of CO₂ due to increased amount of water to dissolve more CO₂ and lime particles.

7. Calcium carbonate formation may not occur throughout a continuous flow of gas. Calcium carbonate formation will not occur all through the carbonation continuous flow of gas for one hour if the flow of CO₂ gas is uninterrupted. The formation of calcium carbonate would be completed before one hour because the mineral carbonation is a fast process. After the reaction in the soil matrix which includes the dissolution of lime into the water in the system, divalent calcium ions are formed which react with the carbonic acid formed from the dissolution of CO₂ in water to form calcite, the calcium carbonate particles formed will precipitate over the remaining unconverted lime and reduces the porosity of the soil matrix. As more CO₂ gas keeps moving into the soil matrix but could not react with the covered lime, so immediately in the first few minutes the CO₂ gas dissolves into the available solution to form carbonic acid and then react with the dissolved lime to produce calcite. After the formation of calcite in the first few minutes, the CO₂ gas that moves in keeps flowing in and out without reacting with the remaining lime until temperature remains steady because the remaining lime has been covered by the calcite formed in the first few minutes.

This dissertation includes five chapters, including the introduction (chapter 1), background information (Chapter 2), research chapters (3-4), and summary and conclusions (Chapter 5).

Chapter 2 provides relevant background information about Soil stabilization and chemical stabilization. Chapter 3 presents provides information of the testing methods used and the hypotheses were tested.
Chapter 4 presents the results and the discussion about the results obtained from the study.

Chapter 5 presents the Summary of major findings, conclusions deduced from the study and recommendations.
2.1 Soil stabilization

According to Patel et al. (2012), Soil stabilization is the alteration or preservation of the properties of the soil to enhance its engineering properties such as strength to reach the required value for a specific purpose. The term soil stabilization encompasses the various techniques or methods used for modifying the properties of the soil. It also refers to the process of adding special soil, cementing material, or other chemical materials and can be achieved mechanically by mixing stabilizing material and the natural soil to achieve a homogeneous mixture (Perloff & Baron, 1976). It is mostly used to enhance the shear strength and the bearing capacity of soil intended to carry structural loads. Also, it can be used to reduce the Compressibility of the soil in expansive soil such as clay and can help in reducing the settlement magnitude in structures. Most times, additives can improve the properties of less-desirable pavement sub-grade materials, when used they help in improving soil particle cohesion, maintain water content, and serve as a cementing and waterproofing agent (Addo et al., 2004) which enhances the shear strength and reduces the permeability of the soil. According to Sherwood (1993), fine-grained granular materials are the easiest to stabilize due to their large surface area to their particle diameter, but Silty materials are sensitive to small variations in moisture which might prove difficult during stabilization. Organic and peat soils possess high water-holding capacity, high porosity, and high organic content and have high exchange capacity which can hinder the hydration process by retaining the calcium ions liberated during the hydration of calcium silicate and calcium aluminate to satisfy the exchange capacity in the cement during a cement-based stabilization. In this type of soil, the proper selection of the type of additive and amount would determine its success (Hebib & Farrell, 2017).
2.1.1 Soil stabilization techniques

According to Estabragh et al. (2014), there exist two major stabilization techniques which include the mechanical stabilization and chemical stabilization, both techniques may be incorporated based on the required properties to be achieved. Some may include electrical stabilization and thermal stabilization. Apart from the improvement in soil shear strength and other physical properties of the soil, soil stabilization should also provide a defense mechanism to the soil from the seasonal temperature and moisture changes and even biological activities (Winterkorn & Pamukcu, 1991). The selection of any of these methods depends on the mission, terrain, equipment, and the time available (Onyelowe Ken & Okafor, 2006). Mechanical stabilization involves mixing at least two or more types of natural soil to change its gradation which enhances the soil properties. The method combines the engineering properties of the mixed soil as one. This method helps to reduce the void ratio by filling up the spacing between larger granular soil with finer soil particles followed by intense compaction, the compaction of the stabilized sample reduces the porosity, and permeability and enhances the shear strength parameters of the soil such as the cohesion and angle of internal friction (Arora, 2005). According to Arora (2005), Soils are usually grouped into two during Mechanical stabilization which includes the aggregates and binders. The aggregates are soils with strong, well-graded, and angular particles with sizes greater than 75 microns which provides a skeletal framework providing internal friction to the soil. While the binders are soils with particle sizes lesser than 75 microns, they provide primary cohesion and plasticity to the shear strength properties of the soil, and factors like the strength of aggregates, binder mineral composition, and gradation of mixture affect the efficiency of mechanical stabilization. According to (Barman & Dash, 2022), mechanical stabilization also known as physical stabilization involves compaction, pre-wetting, reinforcement, and electro-kinetic treatment, in this method of stabilization the soil performance and properties are improved without changing
the chemistry of the soil components while chemical stabilization alters the chemistry of
the soil to enhance the strength and stability of the soil (Abduljauwad, 1993).

2.2 Chemical stabilization

This is a widely used method of soil stabilization that involves the use of chemical
additives such as fly-ash, cement, and lime, a pozzolanic type of material with a significant
quantity of silica and aluminum. These materials react with calcium hydroxide with the
addition of water to produce a cementitious gel known as calcium silicate hydrates and
calcium aluminate hydrates (Walker & Pavía, 2011). The gels produced from the chemical
reaction form a gel that helps bond the particles of soil together enhancing the strength
and lowering the swelling index in expansive soils by reducing the impact of double diffuse
layer (Zainuddin et al., 2016). The most common chemical stabilizers used to improve soil
properties are cement and lime, cement is the most popular chemical stabilizer used in Asia
due to its cheapness and high effectiveness. (Raftari et al., 2014). The additives used during
chemical stabilization are classified as traditional, by-products, and non-traditional, Petry
& Little (2002) classified cement, fly Ash and lime as traditional stabilizers, classified
Portland cement dust, Lime kiln dust, and slags as By-product stabilizers and classified
sulfonated oils, polymers, and salt as Non-traditional stabilizers. This dissertation will be
dwelling much on traditional stabilizers.

2.2.1 Lime stabilization

The use of lime stabilization started in the early 20th century (Bell, 1996). Its
utilization in modern geotechnical engineering was scarce until 1945 due to an inadequate
understanding of the material (Herrin & Mitchell, 1961). According to Wilkinson et al.
(2010), Lime stabilization has become so popular in the field of geotechnical engineering
that it is now used during the construction of highways, airports, railways, foundation
bases, slope protection, and canal linings. This chemical additive is the best stabilizer for
expansive soils (Johnson, 1949). In modern construction, to achieve durable transportation infrastructure, lime has been increasingly incorporated into stabilizing soil due to its cost-effectiveness and stability characteristics in either the short or long run (Rogers et al., 2006b). According to (Arabi & Wild, 1986), the chemistry in the reaction between lime and silicate, aluminate component of expansive soils is complex and the factors the chemical reaction depends on include cation exchange, agglomeration, flocculation, pozzolanic reaction, and carbonation. MANUAL (2004) presented that lime stabilization is not suitable for all types of soils, the utilization of lime in the stabilization of weak and expansive soil is more effective when the plasticity index is greater than 10% and the grain size of the material is lesser than the 74 mm sieve size. The chemical theory involved in the reaction between the chemical stabilizer which is lime the silicate and aluminate component of the expansive soil is complex that depends on several factors such as cation exchange, flocculations, agglomeration, pozzolanic reaction, and carbonation (Arabi & Wild, 1986). But carbonation is not desired in lime stabilization, it has been found that it possesses a detrimental effect on the strength gain or behavior (Diamond & Kinter, 1965).

According to Boardman et al. (2001), the reaction mechanisms that cause the improvement in the expansive soil properties are divided into two stages which include the modification of plasticity and solidification. The achieved modifications in the plasticity have been found by Deka (2011) to be reversible while the process causing the solidification remains irreversible. The modification of the expansive soil is caused by the flocculation and cation exchange while solidification occurred due to pozzolanic reactions (Salehi & Sivakugan, 2009). The use of lime in expansive soil reduces the liquid limit, and plastic limit plasticity index of the soil which affects the diffuse hydrous double layer surrounding the clay particles (Wang et al., 1963). According to Bhasin et al. (1978), through physio-chemical modification, Lime stabilization help to reduce the swelling of expansive soil, modifies the swelling characteristic and plasticity, it also improves the soil properties through cementation which leads to an increase in the strength and stiffness (Consoli et al.,
2011) due to pozzolanic reactions (Rogers et al., 2006a). however it was found by Herrin & Mitchell (1961), that an increment in the lime content to a certain limit would decrease the strength gain. Dash & Hussain (2012) stated that lime stabilization depends on some factors such as soil type, mineralogy, lime content, and curing period which needs to be considered for effective stabilization.

Diamond & Kinter (1965), stated that the addition of water to quick lime (CaO) causes an exothermic reaction that generates heat of about 280 calories/gram that produces hydrated lime Ca(OH)₂ in Eq. (2.1)

\[ CaO(s) + H₂O(l) \rightarrow Ca(OH)_2(s) + Heat \text{ (280 calories/gram)} \]  \hfill (2.1)

\[ Ca(OH)_2(s) \rightarrow Ca^{2+} + 2OH^- \]  \hfill (2.2)

The existing monovalent cations of the soil minerals are replaced by Ca²⁺ formed in Eq. (2.2) leading to an increment in the interparticle attractive forces which reduces the thickness of the diffuse double layer of clay particles (Rogers & Glendinning, 2000). The dissolution of silicas and alumina from clay particles in an alkaline environment produces pozzolanic reactions. The dissociated component of lime Ca²⁺ and OH⁻ reacts with the dissolved silica (SiO₂) and alumina (Al₂O₃) from the clay promoting the production of hydrated gelatinous cementitious compounds of silicates and aluminates called Calcium silicate hydrate (CSH) and Calcium aluminate hydrate (CAH) respectively (Boardman et al., 2001). The calcium silicates and illuminate hydrate are formed based on the chemical reaction expressed below in Eq. (2.3) and Eq. (2.4),

\[ Ca^{2+} + 3OH^- + SiO_2 \rightarrow 3CaO.2SiO_2.3H_2O \text{ or CSH} \]  \hfill (2.3)

\[ Ca^{2+} + 3OH^- + Al_2O_3 \rightarrow 3CaO.Al_2O_3.3H_2O \text{ or CAH} \]  \hfill (2.4)

The calcium silicates and aluminate hydrate formed binds the clay particles together leading to long-term property improvement in shear strength, bearing capacity, and stability (Eades & Grim, 1960). The treatment of soil using Lime has been found to
improve the dynamic resilient modulus of soil subjected to freeze and thaw, Zhang et al. (2018) obtained that after 10F-T cycles, the dynamic resilient modulus of the lime-treated soil increases by 120.6% exceedingly much larger than the resilient modulus of untreated soil. According to Locat et al. (1990), The lime content is a factor that affects the results of lime stabilization, at low lime content only the modification of soil properties occurs while at higher lime content both modification and solidification take place (Boardman et al., 2001) which leads to a higher degree of flocculations and increment in cementitious pozzolanic compounds. Lime-stabilization mechanism is reduced when used as stabilizers in soil with high organic matter, Organic matter also affects the free water for hydration of lime (Barman & Dash, 2022).

Hilt & Davidson (1960) presented the Eq. (2.5) below to select the lime content for lime-stabilization

\[
\text{Optimum lime content} \% = \frac{\text{Clay content} \%}{35} + 1.25
\]

### 2.2.2 Cement stabilization

Ordinary Portland cement is also a type of chemical additive used for the modification of soil properties, which has been massively used for about 100 years (Estabragh et al., 2014). Ordinary Portland cement is a fine non-homogeneous compound that is made up of four different oxides such as tricalcium silicate (C\(_3\)S), di-calcium silicate (C\(_2\)S), tricalcium aluminate (C3A), and tetra calcium ferrate (C4AF), where C represents the calcium oxide (CaO), S represents silica S\(_2\)O\(_2\), A is alumina Al\(_2\)O\(_3\), F represents Iron oxide (Fe\(_2\)O\(_3\)) and H represents water H\(_2\)O (Barman & Dash, 2022). According to Estabragh et al. (2012), the mechanism that leads to the improvement of soil properties in lime stabilization and cement stabilization is almost similar. Cement is mostly used due to its easy availability and rapid strength gain (Zhang et al., 2018). The stabilization mechanism includes hydration, cation exchange, flocculation, and pozzolanic reaction. According to Barman & Dash (2022), during the stabilization of clay with cement, hydration takes place first when the clay soil is mixed with cement and water, followed by the reaction of the tricalcium silicate (C\(_3\)S),
di-calcium silicate (C\textsubscript{2}S) present in the cement reacts with water and release Ca\textsuperscript{2+} into the clay mixture leading to the production of cementitious gel such as calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) Chew \textit{et al}. (2004). These gelatinous cementitious hydration products contribute massively to the rapid strength improvement and ordinary Portland cement contains more of (C\textsubscript{3}S) than (C\textsubscript{2}S) which reacts quickly with water to contribute to strength improvement, therefore (C\textsubscript{3}S) contributes more to the rapid strength development (Barman & Dash, 2022). The cementitious hydration that causes rapid strength development is expressed below in Eq. (2.6) and Eq. (2.7)

\begin{align*}
2C\textsubscript{3}S + 6H\textsubscript{2}O + SiO\textsubscript{2} & \rightarrow CSH + Ca(OH)\textsubscript{2} \quad (2.6) \\
2C\textsubscript{2}S + 4H\textsubscript{2}O + SiO\textsubscript{2} & \rightarrow CSH + Ca(OH)\textsubscript{2} \quad (2.7)
\end{align*}

The reaction is exothermic and the temperature increases as the initial water content and curing temperature Abbas & Majdi (2017). The hydrated lime (Ca(OH)\textsubscript{2}) formed from the hydration of (C\textsubscript{3}S) and (C\textsubscript{2}S) dissociate into Ca\textsuperscript{2+} and OH\textsuperscript{-} with Ca\textsuperscript{2+} contributing to soil flocculation (Barman & Dash, 2022). The calcium ions Ca\textsuperscript{2+} also react with pozzolans such as the silica (Si\textsubscript{O\textsubscript{2}}) and alumina (Al\textsubscript{2}O\textsubscript{3}) to form Cementitious gel compounds such as CSH and CAH which increases in the interparticle bond causing strength improvement (Estabragh \textit{et al}.., 2014). According to Ouhadi \textit{et al}. (2014), cement-stabilized soil posses more resistance than soil treated with lime, because both the cementitious gels from hydration and pozzolanic reaction as time progress contributes to strength improvement in cement-treated soils (Barman & Dash, 2022). The stabilization of expansive soil with cement significantly reduces the liquid limit, and plasticity of the soil while the shrinkage and strength increase (Goodarzi \textit{et al}.., 2016). Factors affecting this method of chemical stabilization include curing period, cement content and type, sulfate, organic matters, and compaction delay. Cement stabilization is amenable for all types of soil but it is more suitable for soils with enough fines and clay having a plasticity ranging from low to medium mainly due to their ease of mixing (Chittoori, 2008). Cement can be used to
stabilize gravel when it’s the percentage retained on the sieve size 4.75mm is limited to or at most 45% (Little & Nair, 2009). According to Association (2003), they suggested cement as a stabilizer is effective practically and economically when the plasticity index of the soil to be treated is not beyond 20%. The reaction is exothermic and the temperature increases as the initial water content and curing temperature (Abbas & Majdi, 2017). The hydrated lime (Ca(OH)$_2$) formed from the hydration of (C$_3$S) and (C$_2$S) dissociate into Ca$^{2+}$ and OH$^-$ with Ca$^{2+}$ contributing to soil flocculation (Barman & Dash, 2022). The calcium ions Ca$^{2+}$ also react with pozzolans such as the Silica (S$_i$O$_2$) and Alumina (Al$_2$O$_3$) to form Cementitious gel compounds such as CSH and CAH which increases in the interparticle bond causing strength improvement (Estabragh et al., 2014). According to Ouhadi et al. (2014), cement-stabilized soil posses more resistance than soil treated with lime, because both the cementitious gels from hydration and pozzolanic reaction as time progress contributes to strength improvement in cement-treated soils (Barman & Dash, 2022). The stabilization of expansive soil with cement significantly reduces the liquid limit, and plasticity of the soil while the shrinkage and strength increase (Goodarzi et al., 2016). Factors affecting this method of chemical stabilization include curing period, cement content and type, sulfate, organic matters, and compaction delay. Cement stabilization is amenable for all types of soil but it is more suitable for soils with enough fines and clay having a plasticity ranging from low to medium mainly due to their ease of mixing (Chittoori, 2008). Cement can be used to stabilize gravel when it’s the percentage retained on the sieve size 4.75mm is limited to 45% (Little & Nair, 2009). According to Association (2003), they suggested cement as a stabilizer is effective practically and economically when the plasticity index of the soil to be treated is not beyond 20%. Terrel et al. (1979) presented the Eq. (2.8) below as a criteria for selecting the cement-stabilization.

\[
P.I = 20 + \frac{50 - Fines \ content \ (\text{grain} \ size < 0.075mm)}{4}
\]  

(2.8)
2.2.3 Chemical stabilization with Fly Ash

Fly Ash is also a chemical additive used to improve soil properties, it’s a non-expansive finely graded material usually formed from the burning of coal in a thermal plant (Cokca, 2001). Fly ash has a spherical grain with sizes ranging from 1 to 50 microns usually classified as silt based on the Unified soil classification system (Joshi, 2000). Based on Phanikumar & Sharma (2007) evaluation, FA consists of silica (SiO\textsubscript{2}) and alumina (Al\textsubscript{2}O\textsubscript{3}) with little content of Calcium oxide (CaO), Iron oxide (Fe\textsubscript{2}O\textsubscript{3}), titanium oxide (TiO\textsubscript{2}), Potassium oxides (K\textsubscript{2}O), Magnesium oxide (MnO), Sulphur trioxide (SO\textsubscript{3}) and Sodium oxide (Na\textsubscript{2}O). FA is usually classified into two depending on the nature and chemical composition of the burnt coal such as the Class F and Class C types. According to Cabrera & Woolley (1994), the Class F types are produced from the burning of bituminous coal while Class C types are produced from the calcination of Fresh Lignite or sub-bituminous coal. The class F Fly ash is called (FFA) while the class C Fly ash type is tagged (CFA), CFA consists of high content which is at least 20% high content of Lime (CaO), rich in alkali and sulfate. The combination of the proportion of (Al\textsubscript{2}O\textsubscript{3}), (Fe\textsubscript{2}O\textsubscript{3}), and (SiO\textsubscript{2}) present in CFA ranges between 50% to 70% while FFA has more than 70% of these minerals with less lime content lesser than 10% (Barman & Dash, 2022). CFA can form a cementitious compound with time in the presence of water that leads to strength gain in treated soil while FFA needs an activator such as lime or cement to produce a cementitious compound which makes it less good compared to CFA (Joshi, 2000). Due to the high sensitivity of clay with high plasticity with calcium ions, the addition of a Significant quantity of FA reduces the swelling potential and liquid limit but the addition of FA alone would not be sufficient to eliminate the swelling potential of expansive clay (Binal, 2016). The values of the California bearing ratio and the resilient modulus increased for all types of soil when treated with FA including high plastic clay and silt clays. An increment in the clay content of FA-stabilized soil would help in increasing the strength properties of the soil due to the alumina and silica content present in the soil (Dermatas & Meng, 2003).
Prabakar et al. (2004) discovered that treating the soil with expansive soil helps lower the cohesion and increase the friction angle while in Lean clays (CL), these two shear strength properties are increased. During the stabilization of soil with FA, the increase in the FA content has been found to increase the maximum dry density MDD and decrease the optimum moisture content OMC of the treated soil during compaction where the increment in the MDD has been attributed to the finer FA particles filling the void between particles and the reduction in the OMC is associated with the elevated consumption of water by fine grains due to the added FA which causes the Specific surface area of the grains increases (Mir & Sridharan, 2019). Treatment of soil with FA has been found to reduce the duration of primary consolidation of soil with an increment in FA content, which reduces the settlement of the soil when used to support structures (Phanikumar & Sharma, 2007) with an increase CFA content enhancing the drainage properties of clays (Mohanty et al., 2016).
2.2.4 Carbonation

Carbonation is one of the chemical stabilization methods that has received massive attention over years (Xu et al., 2020). The reaction of any metal bearing oxides or divalent cation such as calcium oxide (CaO) and Magnesium oxide (MgO) with CO$_2$ under the natural or accelerated condition to produce insoluble solid carbonates (Azdarpour et al., 2015). These minerals formed such as Calcite (CaCO$_3$), dolomite CaMg(CO$_3$)$_2$, magnesite (MgCO$_3$) and siderite (FeCO$_3$) have been considered as carbonate minerals capable of capturing CO$_2$ for a long time (Mohammed et al., 2021; Oelkers et al., 2008). Azdarpour et al. (2015) presented a carbonation reaction in its simplest form in Eq. (2.9)

\[ \text{Metal oxide} + \text{CO}_2 \rightarrow \text{Metal carbonate} + \text{Heat} \quad (2.9) \]

Application of carbonation technology in geotechnical engineering indicates that carbonation can occur in three systems calcium-based system, magnesium-based system, and other composite-based systems (Mohammed et al., 2021). Carbonation reactions in these systems can occur in gas-solid routes and gas-liquid-solid routes. The carbonation can occur through the gas-solid routes when carbon-dioxide infiltrate into the soil via the pores, it reacts with the metal oxide-bearing minerals which are regarded as the most-straight forward routes of carbonation in soil. The carbonation reaction in calcium and magnesium-bearing material through the gas-solid route leading to the formation of calcite and magnesite binder is expressed below in Eq. (2.10) and Eq. (2.11)

\[ CaS_iO_3 + CO_2 \rightarrow CaCO_3 + S_iO_2 \quad (2.10) \]

\[ MgS_iO_3 + CO_2 \rightarrow MgCO_3 + S_iO_2 \quad (2.11) \]

The reaction in Eqn. 2.10 and Eqn. 2.11 are very slow and it does contribute to the improvement of the soil properties effectively. Carbonation through the gas-liquid-solid route occurs when there exists water in the pores, which is faster than the gas-solid route
An example of carbonation through a gas-liquid-solid route in a Calcium-bearing system and magnesium-bearing system is described below in Eq. (2.12) and Eq. (2.13) respectively

\[
Ca(OH)_2[s] + H_2O[l] + CO_2[g] \rightarrow CaCO_3[s] + 2H_2O[l] \tag{2.12}
\]

\[
Mg(OH)_2[s] + H_2O[l] + CO_2[g] \rightarrow MgCO_3[s] + 2H_2O[l] \tag{2.13}
\]

Eq. (2.14) and Eq. (2.15) indicate soil carbonation of a lime-treated soil, the lime in the mix gets dissolved in the $H_2O$ to produce divalent calcium ions $Ca^{2+}$ in the solution

\[
Ca(OH)_2[s] + H_2O \rightarrow Ca^{2+}[aq] + 2OH^{-}[aq] \tag{2.14}
\]

\[
CO_2[g] + H_2O \rightarrow H^+[aq] + HCO_3^-[aq] \tag{2.15}
\]

As soon as the CO$_2$ gas is introduced to the available water, the formation of carbonic acid occurs, a reaction between the product side of Eq. (2.14) and the product side of Eq. (2.15) produces calcium carbonate which enhances the properties of soils. According to the investigation done by Cui $et$ $al.$ (2015); Hyvert $et$ $al.$ (2010), it was found that the insoluble salt of calcite formed causes clogged pored with reduced Investigations on carbonation mechanism showed that the formation of an insoluble salt of CaCO$_3$ resulted in clogged pores with reduced pore size, causing changes in the carbonation depth and rate of propagation also increasing the strength of the material stabilized (Du $et$ $al.$, 2012; Thiery $et$ $al.$, 2007; Hossen $et$ $al.$, 2020). Carbonation can be affected by some factors which include, chemical compositions, mix proportions of porous-materials, relative humidity, and Partial pressure of CO$_2$ in the external environment (Lu $et$ $al.$, 2018; Chang $et$ $al.$, 2004). Carbonation reaction has been found to reduce the PH of treated material which obstructs the formation of hydration products that may hamper strength development (Ruan & Unluer, 2017; Liska & Al-Tabbaa, 2008).

It has been found that grain sizes of different types of soil affect carbonation, the high porosity in sand enables carbon dioxide to move smoothly compare to fines with lesser
porosity which causes lower absorption of carbon dioxide (Yi et al., 2013a,b). Du et al. (2016) discovered in his study that the increase in the concentration of zinc and lead negatively affects the strength gain due to carbonation and also stated that soil contaminated with lead Pb affects the strength gain more than when the soil is contaminated by zinc. Fig. 2.1 indicate that during soil carbonation with a calcium bearing material such as Hydrated lime, calcium carbonate is formed via the sequestration of CO₂ gas.

Figure 2.1: Lime life cycle showing the production of lime from the calcination of limestone leads to the emission of CO₂ into the atmosphere, and the hydrated lime formed also has the potential to sequestrate CO₂ gas to form calcite (Stork et al., 2014)
2.2.4.1 Ca-CO$_2$-H$_2$O system

This is the carbonation reaction that involves the reaction of calcium and CO$_2$ in the presence of water under natural or accelerated conditions to form calcite. The products are usually called precipitated calcium carbonates (PCC). The formation of these precipitated calcium carbonates depends on the temperature ca$^{2+}$, and carbonation period (Mohammed et al., 2021). The calcium carbonate formed possesses various crystal morphologies, but the main morphology includes vaterite, calcite, and aragonite. Calcite is the most stable of all under ambient atmospheric conditions, aragonite is usually formed under heightened temperature while vaterite is unstable and usually changes to calcite (Jimoh et al., 2018; Mattila, 2014). Based on the micro-structural analysis, aragonite looks like a needle, vaterite is spherical in shape while the shape of calcite varies depending on the Ph during precipitation. If it has a Ph of 13 during precipitation, it possesses a scalenohedral while at low PH, it possess a rhombohedral shape as shown in Fig. (2.2).

According to (Mattila, 2014), the calcium carbonate polymorph named aragonite is usually formed at a temperature greater than 50 degrees Celsius while calcite and vaterite are produced at a lower temperature that is influenced by the ratio of Ca$^{2+}$ to CO$_3^-$ ion, also a higher concentration of calcium favors the production of calcite. In this system, the strength of the treated soil sample increases as time prolongs with the rate of strength development declining as time goes on. The reduction in strength may be a result of loss of moisture which affects the pozzolanic reaction. This loss of moisture which causes the reduction in strength can be controlled by accelerated carbonation where moisture loss will be less (Mohammed et al., 2021).
2.2.4.2 Mg-CO$_2$-H$_2$O system

This involves the use of magnesium-rich material such as MgO to form hydrated magnesium carbonates HMCs (Yi et al., 2013b; Yan et al., 2013). Magnesium carbonate is available in two forms which are hydrated or non-hydrated, the non-hydrated exists as geologic material in its anhydrous carbonate form existing in two physical forms as amorphous magnesite and crystalline magnesite (Unluer & Al-Tabbaa, 2013). Hänchen et al. (2008) presented in his study that at various levels of temperature and partial CO$_2$ pressure, magnesite is the most stable carbonate whose formation at ambient temperature is impossible but hydrated magnesium carbonate can be precipitated. The end product of the hydration of magnesium is the magnesium hydroxide also called brucite which can
react with CO$_2$ to produce one of the products of the Mg-CO$_2$-H$_2$O system called the Hydrated magnesium carbonates HMC, which includes lansfordite, dypingite, nesquehonite and hydromagnesite. (Unluer & Al-Tabbaa, 2015). Nesquehonite can be formed at a low temperature which becomes unstable at a temperature above 50 degrees celsius, it transformed into dypingite and hydromagnesite at a temperature above 50 degrees celsius.

These HMCs have been found to have a lower CO$_2$/Mg ratio compared to that of Nesquehonite but still contribute to strength improvement (Unluer & Al-Tabbaa, 2013). Unluer & Al-Tabbaa (2013) also found that Co$_2$ concentration, temperature, water activity, and PH value can influence the formation of HMCs During the Mg-CO$_2$-H$_2$O system, the HMC formed fills the pores and enhances the strength of the stabilized material. The Nesquehonite formation causes volume expansion leading to a reduction in porosity and increment in the stiffness, its ability to cause much strength improvement when formed is due to the needle-like shape as shown in Fig.(2.3) compared to others which are rounded or otherwise (Mohammed et al., 2021). According to Unluer & Al-Tabbaa (2013), the formation of HCCs is in the sequence below

\[ \text{Nesquehonite} \rightarrow \text{dypingite} \rightarrow \text{hydromagnesite} \rightarrow \text{magnesite} \]
Figure 2.3: Scanning electron microscope picture of HMCs
a) Magnesite b) Nesquehonite c) dypingite d) hydromagnesite (Unluer & Al-Tabbaa, 2014)
2.3 Carbon Emission associated with chemical stabilizers

According to Initiative (2009), the cement industry accounts for 3.8% of the total Greenhouse gases emission or about 5% of the world CO$_2$ emissions. The emissions from the production of cement are divided into two types which include the industrial energy-use CO$_2$ and the industrial process CO$_2$. The industrial energy-use CO$_2$ are the emissions from the combustion of fuel during the manufacturing process while the emissions chemically-produced CO$_2$ that is not related to fuel. The energy-related CO$_2$ emission takes about 10% of the total emission (Schokker, 2010). According to the Initiative (2009), PCC has an embodied CO$_2$ range of 866 kg CO$_2$/t of clinker.

The emissions from the clinker manufacture consist of the process-related CO$_2$ released by the calcination of carbonate minerals (limestone) in a kiln which accounts for about 60% of the whole direct CO$_2$ emissions and the energy-generated CO$_2$ emission is released during the burning or combustion of fuel which takes about 40% of the total direct CO$_2$ emissions (Initiative, 2009). The Process-related emissions are the emission formed by the chemical reaction that breaks down limestone into calcium oxide. According to the Survey (2012), the quantity of cement produced hit 3.4 billion tonnes in 2011. For every production of one ton of cement produced, 900 kg of CO$_2$ is generated (Hasanbeigi et al., 2010) which accounts for 5-7% of the anthropogenic carbon-dioxide emission. Cement production witnessed a 54% increment between the year 2000 to 2006, due to the increase in population and the global demand for concrete, cement production is projected to increase annually by 0.8% to 1.2% (Initiative, 2009). The cons of the growing population on the production of cement were obvious as cement production witnessed a sudden surge by increasing from 576 million tons in 1990 (Boden et al., 2011) to 1.88 billion tons in 2006, if this trend is not curbed, by 2050 the amount of CO$_2$ emissions from cement industry would hit 2.34 billion tons (Initiative, 2009). In cement plants during the production of lime and cement, the process-related CO$_2$ (Emissions from the chemical disintegration of limestone) is generated mainly from the expression in Eq. (2.16) and Eq. (2.17).
\[ CaCO_3[s] \rightarrow CaO + [aq] + CO_2[g] \]  \hspace{1cm} (2.16)

\[ MgCO_3[s] \rightarrow MaO + [aq] + CO_2[g] \]  \hspace{1cm} (2.17)

Figure 2.4: CO\textsubscript{2} emissions during the production of cement and lime (Habert et al., 2010)
3.1 Experimental set up

The experimental set up shown in Figure 3.2 and Figure 3.1 was used for this study. The CO$_2$ gas flows from the tank into the mold through an inlet flow meter which captures the properties of the gas before the gas moves into the mold housing the treated silt sample, while the outlet flow meter captures the gas properties leaving the mold. The valve which allows the gas into the mold housing the lime-treated silt was opened and the flow meter was launched to start reading the CO$_2$ gas properties such as the temperature, absolute pressure and STD flow meter. The reaction between the materials in the mold which includes the lime, silt, water, and the introduced CO$_2$ is exothermic. The temperature and absolute pressure data collected after the carbonation test play an important role in the determination of end of mineral reaction. The meter's flow accuracy is specified with an offset of 0.05 L/min (or 50 mL) and the totalizer measurement from the flow meter shown in Figure 3.3 has its tolerance specified at +/- 4% of reading based on the manufacturer’s specifications. The absolute pressure of the gas was 100 kPa which was carefully controlled to remain constant throughout the test.

The flow meters were flushed with CO$_2$ to get rid of the air trapped inside the flow meters. Before the commencement of some of the test, CO$_2$ gas was introduced into the system to flush out the air, this procedure was done for samples with testing condition in the Table.3.4, Table.3.5, Table.3.6, Table.3.7.
Figure 3.1: Experimental set up
Figure 3.2: Experimental set up used in this study
Figure 3.3: Flow meter used in the study which helped in capturing CO$_2$ gas properties and the volume introduced during the carbonation.
Figure 3.4: (a) The introduction of CO$_2$ gas leads to the formation of carbonic acid while the lime particles dissolved into the water in the soil to produce divalent calcium carbonate ions (b) The reaction between the carbonic acid formed and the divalent calcium carbonate lead to the formation of calcite which enhance the engineering properties of the treated soil.
3.2 Materials

The materials used in this study are Silica SiO$_2$ with a grain size of 40 microns and hydrated lime in a solid state also called portlandite Ca(OH)$_2$ both having a specific gravity of 2.65 and 2.24 respectively. The hydrated lime is pure (ninety-nine percent calcium hydroxide and one percent of crystalline silica), which was obtained from Graymont located at shell bridge way Richmond BC V6X 3C6 in Canada while the Silica was purchased from the United States silica company at 8480 progress drive, suite 300 Frederick MD 21701.

3.3 Sample preparation

This study was conducted using a silt treated with lime. Water was added to the treated silt to replicate the presence of moisture in the soil in the field scenario. The percentage of hydrated lime used to treat the silt used in this study was measured based on the weight of the silt. The lime-treated silt was mixed uniformly with water for about 2 minutes as shown in Figure 3.5 to ensure homogenization of the blend of lime with silt with the aid of a mechanical mixer. The weight of water added to each sample prepared was based on the total weight of the soil mix which varies depending on the desired saturation rate to be achieved. Distilled water was used for the sample preparation to prevent the lime from reacting with impurities. The samples were prepared at varying lime content, void ratio, and degree of saturation, which was obtained by filling the mold in Figure 3.6 with the prepared samples and also targeting a certain height in the mold which will give the desired soil properties needed with the aid of phase relationships. The height of the samples prepared was 15.6cm with a diameter of 0.71cm throughout the test. During the preparation of samples for testing, the samples were carefully introduced into the mold and filled in layers with tamping until they attained the expected height of 15.6 cm to achieve the desired soil properties such as void ratio, density, and degree of saturation. During the preparation of samples with different densities to check the effect of density on the degree of carbonation, the samples were prepared having similar heights while the mass of solids...
increases as the density increases. To achieve void ratios of 0.82 which were the densest, the samples were compacted thoroughly achieving a dry density of 14.02 kN/m$^3$ with the highest mass of solid. As shown in Table (3.4), the loosest sample prepared was the sample with a void ratio of 1.20 which was lightly compacted having a dry density of 11.43 kN/m$^3$ with the lowest mass of solid but both density configurations were prepared with similar sample height and diameter. The samples were prepared at room temperature, in an enclosed area to prevent the lime from absorbing CO$_2$ from the atmosphere.

Figure 3.5: Mechanical mixing of lime treated samples to ensure homogenization of mix
Figure 3.6: Mold housing the lime-treated samples which is similar to the thickness of a subgrade in a field scenario.
3.4 Method used for the determination of Calcium carbonate content formed and the degree of carbonation of a carbonated soil sample

The carbonate content formed in the soil due to carbonation reaction was determined with the aid of the ASTM (D4373, 2021) standard test method for the rapid determination of carbonate content in the soil.

After the test, samples were taken at strategic positions, the top of the sample, middle, and bottom to see if carbonation is homogeneous in all parts of carbonated samples, taking the samples at those three points will be a way to ensure that the average degree of carbonation obtained after carbonation is representative of the whole specimen. Also to know how the carbonation is formed at different duration and to determine the efficiency of CO\textsubscript{2} consumption, samples were taken at 0 cm, 3.9 cm, 7.8 cm, 11.7 cm, and 15.6 cm representing the carbonation front. The samples taken were oven dried for 24hrs to get rid of the moisture added initially and the quantity of water generated due to the reaction and also to get the original weight of solids. After 24hrs of drying in the oven, the samples were pounded with the aid of the mortar and pestle in order to break lumps into the fine grain. The pounded samples were sieved through sieve no. 40, then transferred into the Calcium carbonate chamber shown in Figure 3.10 for testing. 1g of the carbonated sample was used for the test which reacts with the hydrochloric acid enclosed in a calcium carbonate chamber. The reaction between calcium carbonate in the sample and the 1N of hydrochloric acid emits CO\textsubscript{2} whose pressure is observed from the pressure gauge and the measured CO\textsubscript{2} is converted into mass of calcite using the standard calcium carbonate curve in Fig. (3.7).

The standard calcium carbonate curve in Figure 3.7 was obtained using a pure calcium carbonate where various masses of pure calcite ranging from 0.1g to 1g reacted with the dilute HCL which produces CO\textsubscript{2} pressure, therefore from the test there exists a CO\textsubscript{2} pressure for every mass of carbonate. A linear relationship between the CO\textsubscript{2} pressure induced in the chamber and the mass of calcium carbonate formed was obtained. The linear equation was used to convert CO\textsubscript{2} pressure generated from a calcium carbonate
chamber test into a corresponding mass of carbonate formed due to soil carbonation. The Eqn. 3.1 represents what happens during the reaction of Carbonate minerals with dilute HCL during the calcium carbonate standard test.

\[
CaCO_3[s] + 2HCl[l] \rightarrow CO_2[g] + CaCl_2 + 2H_2O[l] \quad (3.1)
\]

Figure 3.7: Standard calcium carbonate curve used in the study to determine the mass of calcite formed after the carbonation test. Varying masses of pure Calcite were reacted with 1 N of diluted hydrochloric acid which emitted CO\textsubscript{2} gas, a relationship between CO\textsubscript{2} and mass of calcite was obtained.

\[ y = 60.71x \quad (3.2) \]

The Equation 3.2 presented above was used to obtain the mass of CaCO\textsubscript{3} formed using the CO\textsubscript{2} pressure induced in the calcium carbonate chamber during the reaction between the calcite formed and the HCL. \( x \) represents the mass of calcite formed in grams and \( y \) represents the CO\textsubscript{2} pressure induced in the chamber in kPa. The CO\textsubscript{2} pressure-induced \( (y) \) was obtained from the calcium carbonate test, and the mass of calcite \( (x) \) was obtained using Equation 3.2.
To know the sample size to be tested after carbonation which would enables us to accurately determine the mass of calcite formed due to carbonation, a sacrificial test was conducted and different sizes of samples were taken from the carbonated soil mass. The sizes of carbonated samples used range between 1g, 2g, 5g, and 10g, the result indicates as the size of carbonated samples reacting with the 1 N of dilute hydrochloric acid increases the calcium carbonate content present in the mix reduces which leads to a lesser ratio of calcite to the weight of soil, hence the degree of carbonation reduces as the sample size increases as shown in Figure 3.9b. it yielded a linear relationship indicating this method is consistent and suitable or can be used as a proxy to determining the amount of calcite in the soil. Based on this result as shown in Figure 3.9a the least size of samples yielding the highest % calcite equivalent. To know the carbonated sample size to be used to determine the amount of calcite formed and also to be able to capture the optimum degree of carbonation in this study, the smallest size of the sample sizes tested i.e 1 g of carbonated samples were selected for the calcium carbonate test. In summary, the result shows the
higher the size of the sample tested, the lesser the degree of carbonation. As the sample size collected for the calcium carbonate test reduces, it enables us to capture optimum % calcite formed due to the reduced amount of soil available that would reduce the CO$_2$ pressure generated during the calcium carbonated chamber test.

Figure 3.9: (a) Plot showing the effect of the sample size used on the amount of calcite extracted. Different sizes of carbonated samples were tested and the carbonated sample with the least size has the highest % calcite. (b) The plot of the sample size against degree of carbonation, the degree of carbonation reduces as the sample size increases.
The degree of carbonation was determined using the equation below.

\[
\text{Degree of carbonation} = \frac{\text{CaCO}_3 \text{ obtained from the carbonation reaction}}{\text{Maximum theoretical CaCO}_3} \quad (3.3)
\]

The maximum theoretical calcite equivalent was computed with the equation expressed below.

\[
= \frac{\text{Theoretical mass of CaCO}_3 \text{ to be formed from the mix}}{\text{Mass of silt}} \quad (3.4)
\]

The theoretical mass of calcium carbonate to be formed from a mix containing silt and lime was obtained using mass of the available lime and stoichiometry using the Eqn (3.5), which is expressed in percentage

\[
= \frac{\text{Molar mass of CaCO}_3 \times \text{Mass of Ca(OH)}_2 \text{ in the mix}}{\text{Molar mass Ca(OH)}_2} \quad (3.5)
\]

The Calcium carbonate from the reaction can be obtained with the equation below which is expressed in percentage.

\[
= \frac{\text{Mass of CaCO}_3 \text{ measured from reaction}}{\text{Mass of carbonated Soil tested} - \text{Mass of CaCO}_3 \text{ measured from reaction}} \quad (3.6)
\]

The mass of calcium carbonate measured was obtained using the Eqn 3.2 based on the CO$_2$ pressure obtained during each test.
Figure 3.10: 1 g of Carbonated sample in Calcium carbonate chamber

Figure 3.11: Calcium carbonate chamber with a pressure inducer
3.5 Testing of hypotheses

1. To confirm that the formation of calcite does not occur throughout a continuous carbonation period, samples of similar properties were prepared and tested at different duration as shown in Table.3.1. Samples prepared to have similar soil properties such as the lime content, degree of saturation, and void ratio and tested at varying duration to show the evolution of the calcite formed during soil carbonation. The samples were tested at an increasing duration of carbonation as presented in Table.3.1. To determine the % calcite formed during continuous testing of one hour, at each carbonation duration for each sample prepared, 1g of carbonated samples were taken at strategic positions in the sample for calcium carbonate determination. These procedures are repeated for each carbonation duration shown in Table.3.1.
Table 3.1: Testing soil matrix for the determination of the end of mineral carbonation

<table>
<thead>
<tr>
<th>Soil properties</th>
<th>Carbonation time t(mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime content</td>
<td>10%</td>
</tr>
<tr>
<td>Total mass of solid</td>
<td>700</td>
</tr>
<tr>
<td>(g)</td>
<td></td>
</tr>
<tr>
<td>Mass of Silt (g)</td>
<td>636</td>
</tr>
<tr>
<td>Mass of Lime (g)</td>
<td>64</td>
</tr>
<tr>
<td>Void ratio e</td>
<td>1.30</td>
</tr>
<tr>
<td>Water content %</td>
<td>16%</td>
</tr>
<tr>
<td>Mass of water (g)</td>
<td>112</td>
</tr>
<tr>
<td>Degree of saturation%</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>7.5, 15, 30, 60</td>
</tr>
</tbody>
</table>

2. To determine the effect of the lime content on the calcite formation and degree of carbonation, silt samples were treated using varying percentages of lime measured by the weight of silt to indicate the effect of increasing lime content on the efficiency of carbonation or degree of carbonation. The calcium carbonate content will be determined using the calcium carbonate chamber test based on ASTM D4373-14, samples will be taken from the top, middle, and bottom of the carbonated sample to show the homogeneity of carbonation and the average values will be used. The three lime content by weight of silt used and other testing conditions are shown in Table 3.2. The samples were prepared at a similar void ratio as seen in Table 3.2 which means that the height of samples is homogeneous, obtained via uniform tapping of treated silt introduced into the mold.
Table 3.2: Test Matrices for the determination of effect of Lime content on the degree of carbonation

<table>
<thead>
<tr>
<th>Lc %</th>
<th>M_solids (g)</th>
<th>M_silt (g)</th>
<th>M_lime (g)</th>
<th>e</th>
<th>Wc %</th>
<th>S_r %</th>
<th>t</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
<td>693</td>
<td>7</td>
<td>1.30</td>
<td>8,12,21</td>
<td>16,24,42</td>
<td>1hr</td>
</tr>
<tr>
<td>5</td>
<td>700</td>
<td>667</td>
<td>33</td>
<td>1.30</td>
<td>8,12,21</td>
<td>16,24,42</td>
<td>1hr</td>
</tr>
<tr>
<td>10</td>
<td>700</td>
<td>636</td>
<td>64</td>
<td>1.30</td>
<td>8,12,21</td>
<td>16,24,42</td>
<td>1hr</td>
</tr>
</tbody>
</table>

3. To understand how the degree of saturation enhances the formation of calcium carbonate and degree of carbonation, lime-mix silt samples of similar void ratio at the increasing degree of saturation was tested. Different lime contents such as 5% lime content and 10% lime by weight of silt were used to show the effect of increasing the degree of saturation on the formation of calcium carbonate. The samples were tested at an increasing degree of saturation ranging from 12% to 60% to show the positive and negative effects of increasing the degree of saturation on the degree of carbonation. The testing matrices and conditions are shown in Table 3.3. The calcium carbonate content will be determined using the calcium carbonate chamber test based on ASTM D4373-14, samples will be taken from the top, middle, and bottom of the carbonated sample to show the homogeneity of carbonation, and the average values were be used.
Table 3.3: Test Matrices for the determination of effect of degree of saturation on the degree of carbonation and efficiency of CO$_2$ consumption.

<table>
<thead>
<tr>
<th>Lc %</th>
<th>$M_{\text{solids}}$ (g)</th>
<th>$M_{\text{silt}}$ (g)</th>
<th>$M_{\text{lime}}$ (g)</th>
<th>e</th>
<th>$S_r$ %</th>
<th>(t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>700</td>
<td>667</td>
<td>33</td>
<td>1.30</td>
<td>12,16,20,24,28,42,50,60</td>
<td>1hr</td>
</tr>
<tr>
<td>10</td>
<td>700</td>
<td>636</td>
<td>64</td>
<td>1.30</td>
<td>12,16,20,24,28,42,50,60</td>
<td>1hr</td>
</tr>
</tbody>
</table>

4. To determine the relationship between density and the degree of carbonation or the effect of density on the degree of carbonation, samples with a similar mass of lime, and a similar mass of water with varying degrees of saturation were tested for a duration of one hour to capture the effect of increasing density. The density of the prepared sample increases as the mass of silt increases in the mix with the lime content reducing with increasing density. The five samples treated with lime were prepared in a loose state to dense state which ranges from 11.65 kN/m$^3$ to 14.02 kN/m$^3$. The amount of binder formed was determined using the ASTM D473-14, where samples will be taken from the carbonation fronts with the average value being used. The testing matrices and conditions are presented in the table below. To ascertain the effect of density on the degree of carbonation, the samples were also prepared in a different form as initially presented above with samples treated with a similar mass of lime and varying mass of water, to make the samples have a similar degree of saturation. The samples were prepared to have a similar degree of saturation of 40%, the mass of silt increases as the density increases with reducing lime content in the mix. The testing conditions and soil matrices are shown in the Table.3.4 and Table.3.5
Table 3.4: soil properties for the determination of the effect of density on the degree of carbonation with samples having constant mass of lime and varying mass of water with constant degree of saturation

<table>
<thead>
<tr>
<th>$M_{\text{Solid}}$ (g)</th>
<th>$M_{\text{silt}}$ (g)</th>
<th>$M_{\text{lime}}$ (g)</th>
<th>$L_c$ %</th>
<th>$\gamma_d$ kN/m$^3$</th>
<th>e</th>
<th>$S_r$ %</th>
<th>$W_C$ %</th>
<th>$M_{\text{water}}$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>734</td>
<td>664</td>
<td>70</td>
<td>10.5</td>
<td>11.65</td>
<td>1.20</td>
<td>40</td>
<td>18.31</td>
<td>134</td>
</tr>
<tr>
<td>770</td>
<td>700</td>
<td>70</td>
<td>10</td>
<td>12.22</td>
<td>1.09</td>
<td>40</td>
<td>16.74</td>
<td>129</td>
</tr>
<tr>
<td>810</td>
<td>740</td>
<td>70</td>
<td>9.5</td>
<td>12.86</td>
<td>0.98</td>
<td>40</td>
<td>15.15</td>
<td>123</td>
</tr>
<tr>
<td>856</td>
<td>786</td>
<td>70</td>
<td>8.9</td>
<td>13.59</td>
<td>0.88</td>
<td>40</td>
<td>13.52</td>
<td>116</td>
</tr>
<tr>
<td>887</td>
<td>817</td>
<td>70</td>
<td>8.6</td>
<td>14.02</td>
<td>0.82</td>
<td>40</td>
<td>12.51</td>
<td>111</td>
</tr>
</tbody>
</table>

Table 3.5: Soil testing matrix for the determination of the effect of density on the degree of carbonation with samples having constant mass of lime and constant mass of water with varying degree of saturation

<table>
<thead>
<tr>
<th>$M_{\text{Solid}}$ (g)</th>
<th>$M_{\text{silt}}$ (g)</th>
<th>$M_{\text{lime}}$ (g)</th>
<th>$L_c$ %</th>
<th>$\gamma_d$ kN/m$^3$</th>
<th>e</th>
<th>$S_r$ %</th>
<th>$W_C$ %</th>
<th>$M_{\text{water}}$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>734</td>
<td>664</td>
<td>70</td>
<td>10.5</td>
<td>11.65</td>
<td>1.20</td>
<td>35</td>
<td>16</td>
<td>117</td>
</tr>
<tr>
<td>770</td>
<td>700</td>
<td>70</td>
<td>10</td>
<td>12.22</td>
<td>1.09</td>
<td>36</td>
<td>15.25</td>
<td>117</td>
</tr>
<tr>
<td>810</td>
<td>740</td>
<td>70</td>
<td>9.5</td>
<td>12.86</td>
<td>0.98</td>
<td>38</td>
<td>14.5</td>
<td>117</td>
</tr>
<tr>
<td>856</td>
<td>786</td>
<td>70</td>
<td>8.9</td>
<td>13.59</td>
<td>0.88</td>
<td>40</td>
<td>13.72</td>
<td>117</td>
</tr>
<tr>
<td>887</td>
<td>817</td>
<td>70</td>
<td>8.6</td>
<td>14.02</td>
<td>0.82</td>
<td>42</td>
<td>13.24</td>
<td>117</td>
</tr>
</tbody>
</table>
5. To determine how an increment in the flow rate would affect the formation of calcite and the efficiency of CO₂ consumption, two samples of loose and density configuration were tested. The sample with dense configuration has a void ratio of 0.82 with a density of 14.02 kN/m³ while the loose samples have a void ratio of 1.20 and a density of 11.62 kN/m³, these soil properties were obtained with the aid of the phase relationship. To obtain how the carbonation depth evolves with time as the flow rate increases, the samples were tested at different duration and with increasing flowrate. The duration of testing was determined after each sample at desired density state was subjected to a continuous flow of gas for a duration of one hour each to determine the duration at which the reaction ends. The one-hour testing of the loose and dense samples was done at three flow rates namely 2L/minutes, 4L/mins, and 5L/mins which dictated the durations at which the samples were tested for both loose and dense samples. The samples were also tested at different duration with increasing flow-rate to see how the increasing flowrate affects the efficiency of CO₂ consumption. The duration of testing was obtained by conducting a one-hour test for each sample, then the end of the reaction was determined as described in chapter three of this thesis. Samples were retrieved at different locations to see how the carbonation occurs throughout the carbonation front, the height of the samples was 15.6cm and the retrieving of samples was done at depths 0 cm, 3.9 cm, 7.8 cm, 11.7 cm, and 15.6 cm of the sample. These points at which samples will be selected for determination of calcium carbonate content as described in ASTM(D4373, 2021).
Table 3.6: Soil testing matrix to determine the effect of increasing flowrate on the efficiency of CO$_2$ consumption for a loose lime-treated silt

<table>
<thead>
<tr>
<th>$M_{Solids}$ (g)</th>
<th>$M_{silt}$ (g)</th>
<th>$M_{lime}$ (g)</th>
<th>$e$</th>
<th>$S_r$ %</th>
<th>$M_{water}$ (g)</th>
<th>t (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>734</td>
<td>664</td>
<td>70</td>
<td>1.20</td>
<td>35</td>
<td>117</td>
<td>2,5,10,15, 60</td>
</tr>
<tr>
<td>734</td>
<td>664</td>
<td>70</td>
<td>1.20</td>
<td>35</td>
<td>117</td>
<td>2,5,10,60</td>
</tr>
<tr>
<td>734</td>
<td>664</td>
<td>70</td>
<td>1.20</td>
<td>35</td>
<td>117</td>
<td>2,10,60</td>
</tr>
</tbody>
</table>

Table 3.7: Soil testing matrix to determine the effect of increasing flowrate on the efficiency of CO$_2$ consumption for a dense lime-treated silt

<table>
<thead>
<tr>
<th>$M_{Solids}$ (g)</th>
<th>$M_{silt}$ (g)</th>
<th>$M_{lime}$ (g)</th>
<th>$e$</th>
<th>$S_r$ %</th>
<th>$M_{water}$ (g)</th>
<th>t (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>887</td>
<td>817</td>
<td>70</td>
<td>0.82</td>
<td>35</td>
<td>117</td>
<td>2,5,10,15 20,25,30,60</td>
</tr>
<tr>
<td>887</td>
<td>817</td>
<td>70</td>
<td>0.82</td>
<td>35</td>
<td>117</td>
<td>2,5,10,15,20,25,60</td>
</tr>
<tr>
<td>887</td>
<td>817</td>
<td>70</td>
<td>0.82</td>
<td>35</td>
<td>117</td>
<td>2,10,15,20,60</td>
</tr>
</tbody>
</table>
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Introduction

The effects of some soil properties on soil carbonation have been found which brings some answers to the research questions the study aims to answer using the procedures mentioned in the methodologies explained in the previous chapter.

4.2 Limitation of instrumentation used in the study

A limitation of the 5300 series flow meter is that it cannot identify the gas type passing through it. Therefore, the user must know the type of gas being passed through the instrument. This is a limitation because the system cannot be completely saturated with gas. Initially, the cylinder of soil is filled with air, which must ultimately be evacuated through the bottom of the sample and outlet flow meter during the experiment. For the majority of tests the outlet flow meter was set to measure CO$_2$. However, CO$_2$ was not reliably measured until the end of the mineral reaction in the sample was approached, and substantial amounts of CO$_2$ passed through the bottom of the sample. When the flow meter is set to measure CO$_2$, but is filled with air, it provides a non-zero reading that is effectively meaningless. When the flow meter was set to CO$_2$ but filled with air that is not flowing, it was observed that the flow meter indicated a flow rate of approximately 0.6 L/min. As shown in Figure 4.1, the outlet flow meter indicated a measurement of approximately 0.6 STD L/min, when the reaction was occurring. This suggests, almost all CO$_2$ was being consumed and was not passing through the outlet flow meter. To confirm this, an experiment was performed where the outlet flow meter was set to measure air. During the experiment, a flow rate of 0 L/min was observed during the reaction Figure 4.2.
Figure 4.1: Plot showing the results obtained from the flow meter used during soil carbonation with the inlet and outlet flow meter calibrated to capture the CO₂ properties during and after the reaction.
Figure 4.2: Plot showing the results obtained from the flow meter used during soil carbonation with the inlet flow meter calibrated to capture the CO₂ properties during and after the reaction and the outlet flow meter assigned to read the properties of air with the aim of justifying the limitation of instrumentation.
4.2.1 Technique use to deduce what steady state of gas properties indicates using the result from the flowmeter

The end of the formation of calcium carbonate plays an important role in the determination of the efficiency of CO\textsubscript{2} consumption during the carbonation test in this study. Therefore it is so important to know when the consumption of CO\textsubscript{2} which causes the formation of calcite stops during the mineral reaction. To understand what the steady state of gas properties means during testing, samples of similar properties such as void ratio, degree of saturation, and lime content were carbonated at different duration under the same testing conditions to capture the approximate period when the formation of calcite stops and see if there exist an increment in the % calcite formed after the gas properties have attained steady state. In Figure 4.3a, it can be seen that the flow rate of the gas moving into the soil matrix reduces gradually due to the consumption of gas which makes the pressure regulator try to regulate the flowrate as consumption continues, as soon as the formation of calcite ends the gas maintains its flow rate in a steady or quasi-steady state. Also, it can be seen in Figure 4.3a that as soon as the flow rate reaches a steady or quasi-steady state, the temperature of the CO\textsubscript{2} gas both the inlet and outlet temperature attained a steady or quasi-steady state as seen in Figure 4.3b, which is similar for the absolute pressure as shown in Figure 4.3c. To confirm that no formation of calcite takes place after the steady state of gas properties has been attained in this study, Samples of the initial void ratio of 1.30, and degree of saturation of 32% were tested at a carbonation time of 7.5 minutes, 15 minutes, 30 minutes, and 60 minutes. From Figure 4.3d it can be seen that as soon as the carbonation duration reaches approximately 1000 seconds, the amount of calcite remains unchanged throughout for samples carbonated for 1800 seconds and 3600 secs which closely corresponds to the time at which steady state was achieved in Figure 4.3a, Figure 4.3b and Figure 4.3c.
As shown in Figure 4.3a, Figure 4.3b, and Figure 4.3c, the gas flow rate, temperature, and the absolute pressure attained a steady state at 620 sec. In Figure 4.3d, the % calcite remained unchanged after the gas properties reached a steady state at 1000 secs which affirms that as soon as the gas properties attained a steady or quasi-steady state, it indicates that the conversion of lime particles into calcite has stopped, therefore the CO₂ maintains its flow rate as the formation ends (steady state) due to no further reduction of the void space caused calcite formation. This procedure explained was used in the interpretation of flow meter results throughout this study to determine the end of the mineral reaction. The flow meter captures the surge in the temperature of the system due to the exothermic reaction between the Calcium ions and the carbonic acid. The soil matrices used to determine the end of the formation of calcite are presented in Table 3.5 in the methodology section of this thesis.
Figure 4.3: (a) Plot of showing CO₂ flow rate during carbonation against the carbonation time captured by a flow meter during the carbonation test. (b) The plot of the temperature from the inlet and outlet flow rate against the carbonation time, the temperatures from both flow meter attained steady state. (c) The plot of the absolute pressure against the carbonation time showing the absolute pressure approaching steady state. (d) The plot showing the carbonation period against the % binder content approaching steady state indicating formation of calcite stopped as soon as the gas temperature and absolute pressure attained steady state in Figure 4.3a, Figure 4.3b and Figure 4.3c.
4.2.2 Effect of degree of saturation on calcite formation and degree of carbonation

Silt samples treated with 1%, 5%, and 10% lime by weight of silt were tested at the increasing degree of saturation with a similar void ratio of 1.30 to investigate the effect of degree of saturation on the formation of calcite and degree of carbonation during soil carbonation. The duration of carbonation was one hour (continuous testing) for each sample. The presence of water during soil carbonation helps in the dissolution of the CO₂ gas which leads to the formation of the carbonic acid H₂CO₃ (Cui et al., 2015). The carbonic acid H₂CO₃ formed reacts with the divalent calcium ions Ca²⁺ contributed by the dissolved hydrated lime Ca(OH)₂ to produce calcium carbonate CaCO₃ (Ji et al., 2014) and water, the mass of water produce depends on the lime content as seen in Figure 4.5. From the Figure 4.4a below for samples of silt treated with 5% lime content by weight of silt, it was observed that the percentage average calcium carbonate formed and the average degree of carbonation increases as the degree of saturation increases up to a degree of saturation of 50%. From Figure 4.4a below, the percentage calcite increases from 5.44% to 6.15% as the degree of saturation increases from 12% to 42%. The increasing degree of saturation from 16% to 42% enhances the degree of carbonation from 80% to 91% as shown in Figure 4.4b due to the increased amount of H₂O available for the dissolution of lime and CO₂ gas during the reaction. As the quantity of lime in the mix increases from 5% to 10%, the effect of the increasing degree of saturation on the amount of calcite formed and the degree of carbonation became more obvious. In Figure 4.4a for samples treated with 10% lime content by weight of silt, the average percentage calcite formed at 12% degree of saturation was 9.49% with an average DOC of 69.81%, as the degree of saturation increases to 16%, the average calcite formed and the average DOC increases to 9.63% and 70.84% respectively. Also, at 20% degree of saturation, it was observed that the average percentage calcite formed,
and the average DOC increases to 10.16% and 74.72% respectively. In Figure 4.4a, for samples treated with 10% lime by weight of silt the average calcite equivalent formed increases from 9.49% to 11.04% and the degree of carbonation increases from 69% to 81% as the degree of saturation increases from 12% to 42% as shown in Figure 4.4b. As the degree of saturation increases in the study, the Average DOC and the percentage calcite formed increased. The results from this study are also supported by what Van Balen (2005) obtained in his study stating that the amount of lime particles has been found as one of the controlling factors in carbonation; from the result obtained from this study, as the degree of saturation increases more water will be available for the dissolution of lime particles, hence more lime and CO$_2$ will be dissolved as the degree of saturation increases which plays a vital role in the hydration of calcium and also enhances the formation of more calcium ions Ca$^{2+}$ ions and carbonic acid (H$_2$CO$_3$) leading to the increment in calcite formation and degree of carbonation.

However, as the degree of saturation approaches 50% as shown in the Figure 4.4a and Figure 4.4b for samples tested for 1hr, it was observed that the percentage calcite and the degree of carbonation decrease drastically due to the gas mobility problem caused by the water present in the system which impedes the movement of the gas. At this limit, the CO$_2$ began to witness difficulty to move through the soil matrix causing a lot of the lime particles to be left unconverted to calcite. Through observation during the test at 60% degree of saturation, there wasn’t a spike in the temperature in the mold as seen in Figure A.20b because the gas couldn’t move to pass the soil matrix due to the amount of water present in the voids which impede the gas movement through the sample. Also Deneele et al. (2021) said in his study that the diffusivity of the gas will depend on the amount of water present in the soil. At these degrees of saturation of 50% and 60% where gas mobility problem occurs, if the samples were tested for longer duration, the gas would finally finds it way.
through the soil column and carbonating the lime particles thereby increasing the 
degree of carbonation and % calcite formed.

Based on the results obtained from this study, the implication of carbonating at a 
degree of saturation of 50% and above is that it would elongate the reaction time . 
An increased degree of saturation from this test leads to the dissolution of more lime 
content which enhances the formation of calcite and degree of carbonation. This 
study result confirms that as the degree of saturation is increasing more water will be 
available for the dissolution of lime, as the degree of saturation increases, the number 
of lime particles dissolved will increase leading to more contribution of divalent 
calcium ions $\text{Ca}^{2+}$ and the amount of $\text{CO}_2$ dissolved increases which are good for 
calcite formation.

The positive and negative impact of the degree of saturation based on this study is 
also supported by what (Yi et al., 2013a) obtained in his study, stating water helps 
carbonation but its impact might be negative as it gets to some limit, from the study 
results, there is an elongation of mineral reaction time due to the gas mobility 
problem caused by the volumetric water content. The limit that was referred to by Yi 
et al. (2013a) according to this study where gas mobility problem arises is $S_r=50\%$.
The negative impact of increasing the degree of saturation on carbonation based on 
this study is also supported by what was obtained by Baciocchi et al. (2010), stating 
if the liquid to solid ratio (LS) is increased above a certain point it will affect $\text{CO}_2$ 
absorption.

At a higher degree of saturation of 50% and above based on this study, the gas 
mobility problem witnessed makes it difficult to rely on the result for this region. 
Based on observation from the result, the gas could not flow via the soil column, 
therefore this should create a pressure build up which was not captured by the flow
meter device, hence the pressure relief can be attributed to leakage of CO$_2$ gas which renders the results at these higher degrees of saturation difficult to rely on.

The test results shown in Figure 4.4a and Figure 4.4b indicate the degree of saturation plays a vital role in the dissolution of the Ca(OH)$_2$ and CO$_2$ to form Ca$^{2+}$ ions and H$_2$CO$_3$ which enhances calcite formation. A degree of saturation from 50% and above can constitute a barrier for gas movement which will affect the mineral reaction time therefore elongating the carbonation period.

![Figure 4.4](image)

Figure 4.4: (a) Plot showing the effect of increasing degree of saturation on the average % calcite formed for both samples treated with 5% and 10% lime content by weight of silt. The samples were tested at increasing degrees of saturation for a carbonation period of 1hr with a similar void ratio of 1.30 (b) Plot showing the effect of increasing degree of saturation on the average degree of carbonation for both samples treated with 5% and 10% lime content by weight of silt. The samples were tested at increasing degrees of saturation for a carbonation period of 1hr with a similar void ratio of 1.30.
The additional mass of water formed due mineral carbonation was obtained using stoichiometry which depends on the mass of lime in the soil system.

\[ M_{wr} = \frac{18}{74} \times M_L \tag{4.1} \]

\[ M_{wf} = M_{wo} + M_{wr} \tag{4.2} \]

\[ w_{cf} = \frac{M_{wo} + M_{wr}}{M_{sf}} \times 100 \tag{4.3} \]

The molar mass of water and lime is 18 g/moles and 74 g/moles respectively. The change in other soil properties such as the void ratio and the degree of saturation was obtained based on the concept of stoichiometry coupled with the use of phase equation.

\[ S_{rf} = \frac{V_{wf}}{V_{vf}} \times 100 \tag{4.4} \]
Figure 4.5: (a) Plot showing the change in the water content if all lime particles are converted into calcite due to mineral reaction for samples prepared at similar void ratio of 1.30 at different % lime content. The final water content was obtained using stoichiometry and soil properties as presented in Table. 3.3. (b) Plot showing the change in the degree of saturation if all lime particles are converted into calcite due to mineral reaction for samples prepared at similar void ratio of 1.30 at different % lime content. The final degree of saturation was obtained using stoichiometry and the soil properties presented in Table. 3.3.
4.2.3 Effect of lime content on calcite formation and degree of carbonation

To understand the effect of lime content on the degree of carbonation, silt samples were treated with 1%, 5%, and 10% lime by weight of silt with the samples having a similar void ratio of 1.30 at three degrees of saturation of 16%, 24%, and 42%. From Figure 4.6a, it can be observed that the samples with 10% of lime by weight of silt at those three degrees of saturation yielded the highest amount of calcite equivalent of 9.63%, 10.3%, 11.03% at three degrees of saturation of 16%, 24% and 42% respectively, followed by samples treated with 5% lime content by weight of silt with calcite equivalent of 5.44%, 5.51% and 6.15% for the degree of saturation 1%, 24% and 42% respectively while samples treated with 1% lime content by weight of silt has the lowest calcite equivalent. The reason the samples with the highest lime content yielding the highest calcite is because more lime content is available to be dissolved into the water available in the soil matrix, therefore, contributing more Calcium ions $\text{Ca}^{2+}$.The implication of the higher amount of calcite formed as the lime content in the mix increases is seen in the conversion rate of lime into calcite. From Figure 4.6b, it can be seen that samples with the highest calcite formed possess the lowest degree of carbonation for all degrees of saturation. Figure 4.6b, it was observed that the samples with 1% lime content by weight of silt have the highest degree of carbonation followed by samples treated with 5% lime by weight of silt with samples treated with 10% lime by weight of silt having the least degree of carbonation. Samples tested with 1% lime content by weight of silt had a degree of carbonation of 86%, 94% and 98% at degree of saturation of 16%, 24% and 42% respectively, while samples with 5% lime content by weight of silt has degree of carbonation of 80.6%, 82% and 91% at degree of saturation of 16%, 24% and 42% respectively and samples with 10% lime content by weight of silt has the least degree of carbonation of 71%, 76% and 81% at degree of saturation of 16%, 24% and 42% respectively which occurred because in
samples with 10% lime by weight of silt more calcite films were formed due to the
dissolution of larger quantity of lime in water which aid calcite formation as
presented in Figure 4.6a, the calcite formed then precipitates over the unconverted
lime particles which correlates with what Dheilly et al. (2002) stated in his studies
stated, that calcium carbonate precipitates over lime particles during carbonation
reaction, since the calcite produced in samples treated with 1% lime by weight of silt
is lesser than that of samples treated with 5% and 10% lime by weight of lime as seen
in Figure 4.6a, the lime particles covered by the calcite films formed in samples
treated with 1% lime by weight of silt would be lesser which gives room for more lime
particles to be converted into calcite while more lime particles were covered by the
calcite produced in samples treated with 5% and 10% lime content by weight of silt
compared to samples treated with 1% lime by weight of silt. Deneele et al. (2021)
obtained that the carbonate coating formed reduces diffusivity of CO$_2$ gas in the soil
which affects the degree of carbonation, from the Figure 4.6a the calcite formed
increases as the lime content increases, hence sample treated with 10% lime by weight
of silt would produce a higher calcite content which reduces the diffusivity of the CO$_2$
gas. This result affirms that the higher the lime content the lesser the conversion rate
of lime particles into calcite and vice versa. It was observed that the samples with 1%
lime content by weight of silt have the highest degree of carbonation followed by
samples treated with 5% lime by weight of silt with samples treated with 10% lime
by weight of silt having the least degree of carbonation. In Figure 4.6b samples tested
with 1% lime content by weight of silt had a degree of carbonation of 86%, 94%, and
98% for the degree of saturation of 16%, 24%, and 42% respectively, while samples
with 5% lime content by weight of silt has a degree of carbonation of 80.6%, 82%,
and 91% for the degree of saturation of 16%, 24%, and 42% respectively and samples
with 10% lime content by weight of silt has the least degree of carbonation of 71%,
76%, and 81% for the degree of saturation of 16%, 24%, and 42% respectively which
occurred because in samples with 10% lime by weight of silt more calcite films were formed due to the dissolution of a larger quantity of lime in water which aid calcite formation as seen in Figure 4.6a, the calcite formed then precipitates over the unconverted lime particles which correlate which makes it difficult to convert all the lime particles as lime content increases. From the study, we can conclude that the higher the lime content, the lesser the degree of carbonation. According to (Deneele et al., 2021), it was obtained that the morphology of the carbonate and its crystalline state is more critical to strength improvement than the degree of conversion of lime particles (\(\text{Ca(OH)}_2\) into calcite (\(\text{CaCO}_3\)), therefore samples treated with 1% by weight of lime having the highest conversion rate does not connote higher strength when comparing with samples treated with 5% and 10% by weight of silt with higher amount of calcite formed but a lower degree of carbonation.

![Figure 4.6: (a) Plot showing the effect of lime content on the % average calcite formed. Silt samples were treated with 1%, 5%, and 10% by weight of silt at different degrees of saturation with carbonation period of 1hr. (b) Plot showing the effect of lime content on the average degree of carbonation. Silt samples were treated with 1%, 5%, and 10% by weight of silt at different degrees of saturation with carbonation period of 1hr.](image-url)
4.2.4 Effect of density on the degree of carbonation

The effect of increasing density on the formation of calcite and degree of carbonation was determined in this study to show how the reduction in void space affects the amount of calcium carbonate formed during carbonation. The effect of density on the formation of calcite and degree of carbonation was examined in two ways as seen in Table (3.4) and Table (3.5). As seen in Figure 4.7a, the % average calcite formed reduces as the density of the lime-treated samples increases for both series due to the reduction in void spaces which causes a reduction in CO₂ diffusivity which affects the volume of CO₂ dissolved into the available moisture in the system. The reduction in the void ratio reduces the amount of CO₂ dissolved in the system to form Carbonic acid H₂CO₃ which will react with the calcium ions provided by the lime in the mix to form calcite. The increased density lowers the porosity between the particles of the soil causing the infiltration level to be reduced hence affecting the formation of calcite throughout the carbonation front of the sample due to reduced carbon absorption caused by compressed space between particle (Yi et al., 2013a; Song-Yu et al., 2017). In Figure 4.7a, for samples with a constant degree of saturation, as the density increases from 11.65 kN/m³ to 14.02 kN/m³, the average calcite formed reduces from 12.74% to 10.78% and while samples treated with a constant mass of water, the average % calcite formed reduces from 12.65% to 10.76% due to the reduced pore space meant for movement of the CO₂ gas which causes lesser CO₂ absorption and reduces the amount of CO₂ dissolved into the available H₂O to produce carbonic acid (H₂CO₃) which will react with the divalent calcium ions Ca²⁺ contributed by the calcium bearing alkali in the mix (Ca(OH)₂ to form Calcite CaCO₃. Increased density leads to a reduction in the % average calcite formed during soil carbonation.

Another reason there is a reduction in the % calcite formed as density increases are due to the reduction in the lime content as density increases. The sample with the least density has the lowest mass of silt while the densest sample has the highest
mass of silt making the ratio of the divalent calcium ions to the mass of silt in the loose sample more than that of the densest sample due to increased lime content as density reduces causing increased % calcite formation as density reduces as seen in Figure 4.7a.

From Figure 4.7b, the increasing density posses less effect on the degree of carbonation. The degree of carbonation is expressed as the ratio of the amount of calcite formed from the carbonation reaction to the maximum theoretical calcite to be produced, as seen Figure 4.7a the expected theoretical amount of calcite to be formed reduces as the density increases due to the increased mass of silt in the mix as the density increases, samples prepared with void ratio density 11.65 kN/m$^3$, 12.22 kN/m$^3$, 12.66 kN/m$^3$, 13.59 kN/m$^3$, 14.02 kN/m$^3$ has the masses of silt of 817 g, 856 g, 810 g, 770 g, and 734 g respectively which makes the theoretical % calcite to be formed as seen in Figure 4.7b to reduce as density increases. In Figure 4.7a the density increases and the average binder content % moves closer to the expected value which neutralizes the effect of the reduced % calcite as the density increases on the degree of carbonation. The degree of carbonation remains almost similar for all densities in both series as seen in Figure 4.7b which shows the increasing density does not affect the degree of carbonation. The most obvious implication of the increasing density is that, the duration at which the mineral carbonation completes become elongated due to the reduced pore caused by the increased density, as soon as the gas diffuses through the carbonation front, it carbonates the lime particles. This elemental study indicates that during the compaction of sub-grade materials for road construction, the increasing density is not to be worried about when trying to obtain the desired maximum dry density on the field while before introducing CO$_2$ gas if soil carbonation will be used to enhance the engineering properties of such sub-grade materials.
Figure 4.7: Plots showing the effect of increasing density on the average % calcite and average degree of carbonation. Samples with different densities were tested to capture the effect of increasing density on calcite formation. The samples were all tested for a continuous carbonation period of 1hr. The samples were tested having a similar mass of water as density increases. For samples prepared with a constant mass of water, samples with densities of 14.05 kN/m$^3$, 13.61 kN/m$^3$, 12.92 kN/m$^3$, 12.24 kN/m$^3$, 11.62 kN/m$^3$ having degrees of saturation of 42%, 41%, 38%, 36%, 35% respectively with a similar mass of water of 117 g, while samples prepared with a constant degree of saturation has a degree of saturation of 42% with a varying mass of water of 111g, 115g, 123g, 128g, and 134g for densities 14.05 kN/m$^3$, 13.61 kN/m$^3$, 12.92 kN/m$^3$, 12.24 kN/m$^3$ and 11.62kN/m$^3$ respectively,
Presented below is the change in water content and the degree of saturation of tested samples after carbonation. During carbonation that leads to the formation of calcite, an additional mass of water is formed which must be examined to ensure the formed water due to carbonation does not affect the continuous gas flow.

![Graphs](image)

Figure 4.8: Plots showing the change in water content and degree of saturation as density increases due to mineral reaction provided all lime particles are converted to calcite. The final water content and degree of saturation was obtained with the initial soil properties presented in Table 3.5 and stoichiometry for samples prepared with similar mass of water.
4.3 Technique used for the determination of Global efficiency of CO₂ consumption

The efficiency of CO₂ consumption in this study was determined using the method described below. The result presented in Figure 4.9a is the % calcite found throughout the sample depth for varying duration of carbonation. In this approach, the mass of calcium carbonate formed at each carbonation duration was determined based on the area under the curve.

\[
\text{Global Efficiency of CO₂ consumption} = \frac{\text{Mass of CO₂ consumed}}{\text{Mass of CO₂ introduced}} \quad (4.5)
\]

The mass of CO₂ introduced during the test was obtained with the aid of a flow meter. From Figure 4.9b based on flow meter data collected after testing, the volume introduced during the test at 2 mins was 3.52 liters which equals 6.91 grams using the density of CO₂ at STP as 1.964 g/L.

At 2 minutes, the mass of CaCO₃ formed throughout the sample depth was determined using integration by determining the area under the curve. The area under the curve represents the mass of calcite formed.

The mass of CaCO₃ formed after each carbonation period was obtained using the Eqn. (4.6)

\[
m_{\text{CaCO₃}} = \rho_d \frac{\pi d^2}{4} \int_{Z_{\text{bottom}}}^{Z_{\text{top}}} Bc \, dz \quad (4.6)
\]

Where \( \rho_d \) is the dry density of soil, d is the diameter of the sample in the mold, Bc is Binder content obtained from the laboratory test which is a function of the depth Z, \( Z_{\text{top}} = 0 \text{ cm}, \ Z_{\text{bottom}} = 15.6 \text{ cm} \). The integral solutions obtained using Eqn. (4.6) gives the area under the curve in Figure 4.10 representing the mass of calcite formed. The
Eqn. (4.7) gives the total mass of calcite formed throughout a carbonation period in Figure 4.10.

\[ m_{CaCO_3} = \sum_{i=1}^{n} A_i \]  

(4.7)

The mass of calcite formed at 2 mins based on Figure 4.10 is the shaded portion labeled Area$_1$, the mass of calcite formed at 5 mins is Area$_1$ + Area$_2$.

Area$_1$ + Area$_2$ + Area$_3$ represent the mass of calcite formed at 10 mins while Area$_1$ + Area$_2$ + Area$_3$ + Area$_4$ represent the mass of calcite formed at 15 mins which is the total mass of calcite formed in the sample.

The mass of CO$_2$ consumed was obtained based on the mass of Calcite formed using stoichiometry in Eqn. (4.8), where 44 g/moles is the molar mass of CO$_2$ and 100 g/moles is the molar mass of CaCO$_3$.

\[ M_{CO_2} = \frac{44}{100} \times M_{CaCO_3} \]  

(4.8)
Figure 4.9: (a) Plot showing the % binder content formed at different duration through a sample depth of 15.6cm. The duration of testing of 15mins was obtained after a continuous test which indicates the end of the mineral reaction. Samples were tested between 0mins to 15mins to see how the growth of carbonation depth occurs during soil carbonation. The mass of calcite formed at each duration of carbonation was obtained using the integration of the area under the curve method. (b) Plot showing the volume of CO$_2$ introduced during the carbonation test against the time, plot obtained from the flow meter was used in this study; the volume of CO$_2$ introduced was obtained with the aid of the flow meter which was important in computing the efficiency of CO$_2$ consumption.
Figure 4.10: Plot showing the % binder content formed at different duration through a sample depth of 15.6cm. The area under the curve represents the calcite mass formed. The area under each curve was calculated using the integral method. The summation of all areas gives the total calcite mass formed due to soil carbonation. The integration of the area under the curve method helps us obtain the mass of Calcite formed at each shaded region.
The efficiency of CO₂ consumption is expressed as the ratio of the mass of CO₂ consumed due to the mineral reaction to the mass of CO₂ introduced during the mineral reaction. In this study since a method has been established to determine the end, hence the interpretation presented in Figure 4.11 was used to obtain the mass of CO₂ introduced during the mineral reaction. The result presented in Figure 4.11 was obtained using a flow meter, at 460 secs the formation of calcite complete with the flow rate attaining a steady state since there is no further consumption of CO₂. The mass of CO₂ consumed was obtained based on the mass of CaC0₃ formed using Stoichiometry as discussed above.

Figure 4.11: Interpretation using flow meter result to obtain the Mass of CO₂ introduced for efficiency of CO₂ calculations.
4.4 Justification of end of Mineral carbonation with Flow meter result

The results presented in Figure 4.13 were obtained from the carbonation test of samples tested at increasing carbonation time with $q$ of $\text{CO}_2$ shown Figure 4.13 having $\text{Sr}=42\%$ and void ratio of 0.82. The carbonation duration were obtained after subjecting a sample of similar properties with same testing conditions to a continuous testing of 1hr as seen in Figure 4.12. The results presented in Figure 4.12a and Figure 4.12b were obtained using the flow meter shown in Figure 3.3, as the formation of calcite takes place during testing within the mold due to the reaction of the dissolved divalent calcium ions and the Carbonic acid formed from dissolution of $\text{CO}_2$ in $\text{H}_2\text{O}$ due to the consumption of $\text{CO}_2$ during the reaction, the pressure regulator tries to keep the pressure same which leads to the gradual reduction in the flow rate as seen in Figure 4.12a. Based on the continuous testing in Figure 4.12, the formation of calcite ends around 25 mins, therefore to confirm if this is true, a series of samples of similar properties were tested at 2 mins, 5 mins, 10 mins, 15 mins, 20 mins and 25 mins to capture the time at which the growth in the carbonation depth ends. Comparing the calcium carbonate content formed throughout the sample depth based on the mineral reaction as seen in Figure 4.13a with the flow meter results in Figure 4.13b and Figure 4.13c, it shows that the formation of calcite is rapid which increases as carbonation period evolves shown in Figure 4.13c. As carbonation time increases from 2mins to 5mins in Figure 4.13a, the calcium carbonate test result indicated that % calcite formed increases same as in Figure 4.13c where the mass of calcite formed increases from 19 g to 30 g for sample tested at 2mins and 5mins respectively, as the time evolves, at a carbonation time of 25 mins the mass of calcite formed was 62 grams. As seen in Figure 4.13c, there is a slight increase in the mass of calcite formed between the carbonation of time of 20 mins to 25 mins. At 20 mins, 60 grams of calcium carbonate was formed while at 25 mins 62 g of calcite was formed; this happens because there was no more available
lime particles to be the converted into calcite due to the precipitation of the calcite formed on the unconverted lime particles, which also applies to the % calcite formed as seen in Figure 4.13a with little increment in % calcite formed at 20mins and 25mins throughout the depth of the sample. From Figure 4.12, the sample tested at 1hr (continuous) testing indicated that the mineral reaction ends at approximately 23mins which was the reason for carbonating the samples at 2 mins, 5 mins, 10 mins, 15 mins, 20 mins and 25 mins because at the carbonation period of 25 mins based on the result from the continuous testing shown in Fig. (4.13), the mineral reaction would have been completed. From the Figure 4.13, the reduction in the flow rate continues because the pressure regulator keeps regulating the pressure during the consumption of CO$_2$. The carbonation depth is yet to reach full potential for Samples tested for a carbonation duration of 2 mins, 5 mins, 10 mins and 15 mins, more reason the % calcite formed at the sample depth 7.9 cm below for these periods were lesser compared to the maximum % calcite formed at 25 mins when steady state was achieved which marks the end of CO$_2$ consumption and calcite formation. Inability to attain steady state of flowrate and other gas properties at 2 mins to 15 mins means that at these duration of carbonation the formation of calcite still continues just as seen in the flow meter results in Figure 4.13b. In Figure 4.13a as soon as the % calcite formed throughout the sample is about attaining similar value for 20 mins and 25 mins with the mass of calcite formed to be 60 grams and 62 grams respectively in Figure 4.13c symbolizes the completion of mineral reaction with the inlet flow rate at these duration in Figure 4.13b attaining a steady state because there is no change in the pressure gradient as mineral reaction ends.
Figure 4.12: Continuous testing for 1hr of sample tested at target flow rate of 1.25L/mins with degree of saturation of 42% and initial void ratio of 0.82
Figure 4.13: Representative analysis of the samples carbonated at degree of saturation of 42% and initial void ratio of 0.82.
4.4.1 Growth of the carbonation depth with time

In Figure 4.14 shown below, the % calcite or binder content formed during the carbonation of lime-treated silt is plotted against the depth of the sample which shows the revolution or changes in the percentage calcite formed as carbonation time elongates until the formation of calcite stops. As the reaction starts at the top of the sample as shown in Figure 4.14, the CO$_2$ gas gets dissolved into the available water in the soil system to form the Carbonic acid it gets consumed by the lime in the system as it moves through the sample, at time progress, the CO$_2$ initially at the top of the sample finds it’s way down to the bottom of the sample. The mineral reaction that produces calcite ends earlier in the sample with a void ratio of 1.20 than the samples with a denser configuration of e=0.82 due to the reduced void space meant for the passage of the gas as discussed above.

The increasing flow rate of the gas posses some influence on the reaction time and the growth of the carbonation depth or front for both the loose and dense samples as seen in Figure 4.14 and Figure 4.15. In Figure 4.14, samples with a void ratio of 0.82 were tested at an increased flow rate of CO$_2$. In Fig. (4.14a), at 2 mins, the % calcite formed was very low compared to the maximum theoretical % calcite that can be formed at the depth of sample 3.9cm below, indicating the gas is yet to flow to that section of the sample which causes mineral reaction to occur causing the % calcite to increase at that section of the sample, As time evolves, at 5mins there is a huge change in the % calcite formed at the depth of sample at 3.9 cm and 7.9 cm indicating the gas already diffused to that section of the sample, as seen in the Figure 4.14a as time evolves carbonation continues indicating the conversion of lime into calcite continues but as soon as the mineral reaction ends due to the inability of all the lime particles to be converted into calcite because the precipitation of calcite formed on the lime shields them from reacting with the carbonic acid formed from the dissolved CO$_2$, the % calcite formed looks partially uniform throughout the depth
of the carbonated sample which means no further growth in the carbonation depth which marks the end of the mineral reaction. Figure 4.14c show results for the sample tested with the highest CO$_2$ peak flowrate of CO$_2$ indicates that the formation of calcite occurs faster as the peak flow rate increases and also the growth of the carbonation depth occurs faster has peak flow rate increases. At 5 mins and 10 mins, the % calcite formed at depths 3.9 cm and 7.9 cm are greater than the % calcite formed at other reduced flow rates as seen in both Figure 4.14 and Figure 4.15. For both density configuration in Figure 4.14a and Figure 4.14b, the carbonation of depth increases as time evolves during soil carbonation due to the mobility and consumption of CO$_2$ gas as time evolves. As soon as the consumption completes, the carbonation depth remains unchanged due to the conversion of the lime particles into calcite, However, not all lime particles were converted due to the precipitation of the calcite formed on other lime particles because the surface area of the calcite formed is higher than that of the lime particles.

As the flowrate increases in both loose and dense samples shown in Figure 4.14 and Figure 4.15 it possess an effect on the efficiency of CO$_2$ consumption and the mass of calcite formed due to the increased rate at which the calcite formed precipitate over the other lime particles leading to reduced efficiency of CO$_2$ consumption as shown in Figure 4.18 and Figure 4.20 because more CO$_2$ is introduced with being consumed as average flowrate increased. Also, as the flow rate increases, the time needed for the dissolution of lime particles to release Ca$^{2+}$ ions becomes lesser leading to reduced amount of divalent calcium ions in the system which causes the reduction in the calcite formed as the average flowrate increases.
Figure 4.14: Plot of the percentage calcite formed throughout a sample depth of 15.6cm with the CO$_2$ flowrate increasing. The tested samples were prepared at 35% degree of saturation and initial void ratio of 0.82. The samples all possess similar mass of silt and mass of lime.
Figure 4.15: Plot of the percentage calcite formed throughout a sample depth of 15.6cm with the CO$_2$ flowrate increasing with samples prepared at 35% degree of saturation and initial void ratio of 1.20. The samples all posses similar mass of silt and mass of lime.
Figure 4.16: Flowmeter results for samples tested to see the effect of flowrate on the efficiency of CO$_2$ consumption for samples having void ratio of 1.20 and a degree of saturation of 35%
Figure 4.17: Flowmeter results for samples tested to see the effect of flowrate on the efficiency of CO₂ consumption for samples having void ratio of 0.82 and a degree of saturation of 42%.
4.4.2 Effect of increasing flow rate of CO$_2$ gas on Calcite formation and Global efficiency of CO$_2$ consumption

The determination of the relationship between flowrate, the formation of calcite, and how the introduced CO$_2$ used for soil carbonation is efficiently consumed is important to be known for the efficiency of carbonation and to creating a sustainable environment while using this novel chemical stabilization method in enhancing the properties of weak, expansive and frost susceptible subgrade soils. In the study, both dense and loose samples were tested at an increasing flow rate to show the effect of increasing flow rate on the formation of calcite and the efficiency of CO$_2$ consumption in both density configurations. In Figure 4.18b and Figure 4.20b the efficiency of CO$_2$ consumption reduces as the flowrate increases for both density configuration of e=0.82 and e=1.20, also as seen in Figure 4.18a and Figure 4.20b for both the loose configuration and dense configuration. The mass of calcite formed reduces because, as the flow rate increases, the rate of mineral carbonation reaction increases, speeding up the rate at which calcite particles are precipitated. The implication of the increased average flow rate on the reaction kinetics is that, as the flow rate increases it reduces the duration of the reaction due to the increased rate of the precipitation of calcite causing more lime particles to be covered which shortens the mineral reaction time and reduces the number of lime particles to be converted into calcite as shown in Figure 4.18a and Figure 4.20a. As seen in Figure 4.18b and Figure 4.20b, the efficiency of CO$_2$ reduces as the flowrate increases, which indicates that as the flowrate increases more CO$_2$ will be introduced without being consumed due to the rapid shielding of the Un-carbonated lime particles by the calcite formed. When the flow rate of the CO$_2$ increases, more CO$_2$ gas is introduced which can not be efficiently consumed hence shrinking the efficiency of CO$_2$ consumption.

Another reason why the efficiency of CO$_2$ consumption reduces as the flow rate increases is the amount of CO$_2$ dissolved which plays an important role in the
formation of Carbonic acid \( \text{H}_2\text{CO}_3 \) needed to react with the divalent calcium ions \( \text{Ca}^{2+} \) provided by the \( \text{Ca(OH)}_2 \) in the mix. As the flow rate increases, the rate at which the \( \text{CO}_2 \) gas moves into the soil matrix will reduce the efficiency of \( \text{CO}_2 \) gas consumption and the degree of carbonation because, during the reaction, the \( \text{CO}_2 \) gas moves into the soil matrix and dissolves into the available solution, as the flow rate increases, the gas moves faster during the test it was observed that the \( \text{CO}_2 \) travels faster through the sample depth making the formation of calcite to be rapid as the flow rate increases and causing more lime to be covered leading an early completion of the reaction with more gas introduced without been consumed. The increased flow rate makes the \( \text{CO}_2 \) gas diffuse faster in the soil matrix leaving less quantity of \( \text{CO}_2 \) gas to be dissolved in the solution in the soil system, it gives the gas more energy to egress the system easily via the unclogged pores before calcite formation will occur. As the flow rate of the \( \text{CO}_2 \) gas increases, the quantity of \( \text{CO}_2 \) gas dissolved in the \( \text{H}_2\text{O} \) will be reduced hence reducing the amount of calcite formed as shown in Figure 4.18a and Figure 4.20a and the efficiency of \( \text{CO}_2 \) consumption as presented in Figure 4.18b and Figure 4.20b.

In Figure 4.18a and Figure 4.20a the increasing flowrate has a negative influence on the mass of calcite formed, as the flow rate increases the amount of \( \text{CO}_2 \) consumed reduces due to the increased rate at which the calcite formed precipitate over lime particles, which causes the reduction in the mass of calcite formed. Also, the increasing flow rate causes a reduction in the mass of \( \text{CO}_2 \) dissolved in the system leading to a reduction in the mass of calcite formed as the flow rate increases. For samples tested at the highest flow rate in Figure 4.18a, the mass of calcite formed was 20 grams, as the flow rate reduces, 50 grams of calcite was formed, which is similar to the dense configuration where 45 grams of calcite was formed at the least average flowrate and as it reduces, more \( \text{CO}_2 \) was consumed which yielded 60 grams.
of calcite while the sample tested with the least flow rate yields the highest mass of calcite i.e 70 grams of calcite as seen in Figure 4.20a.

The reduction in efficiency of CO$_2$ consumption and the mass of calcite formed based on the results obtained from this study may also occur due to the number of divalent calcium ions available when the CO$_2$ is being introduced, as the flow rate increases it does not give enough time for lime particles to be dissolved to form divalent calcium ions which would react with the carbonic acid to form calcite, while a reduction in the flow rate gives more time for lime particles to be dissolved in into the water in the soil mix leading to more availability of more divalent calcium ions Ca$^{2+}$ which is one of the controlling factors during soil carbonation as stated by (Van Balen, 2005). These results ascertain the hypothesis that increasing the flow rate would possess a negative effect on the efficiency of CO$_2$ consumption and the amount of calcite formed.

\[
\text{Average flowrate } q = \frac{Q_t}{t_c} \quad (4.9)
\]

where $Q_t$ is the total volume of CO$_2$ introduced at the end of carbonation (if carbonation ends or the total volume of CO$_2$ introduced for a carbonation duration if carbonation does not end), while $t_c$ is the carbonation time.
Figure 4.18: (a) Plot showing the effect of increasing flow rate on the formation of calcite in a lime-treated silt in loose configuration. The increased flow rate leads to the reduction in the mass of calcite formed. All samples possess same mass of lime of 70g and mass of silt (734g) with similar degree of saturation of 35%. (b) Plot showing the effect of the increasing flow rate on the efficiency of CO$_2$ consumption in a Loose configuration, the increased flow rate cause a reduction in the efficiency of CO$_2$ consumption.
Figure 4.19: Plot of the mass of CO$_2$ introduced during carbonation against mass of CO$_2$ consumed for samples with initial void ratio of 1.20.
Figure 4.20: (a) Plot showing the effect of increasing flow rate on the efficiency of CO$_2$ consumption in lime treated silt in a dense configuration. The increased flow rate posses a negative impact on calcite formation, an increased flow rate leads to reduction in the mass of calcite formed. All samples possess same mass of lime of 70g and mass of silt (817g) with similar degree of saturation of 42%. (b) Plot showing the effect of increasing flow rate on the efficiency of CO$_2$ consumption, the increased flow rate leads to a reduction in the efficiency of CO$_2$ consumption.
Figure 4.21: Plot of the mass of CO$_2$ introduced during carbonation against mass of CO$_2$ consumed for samples with initial void ratio of 0.82.
4.4.3 Efficiency of CO\textsubscript{2} consumption with increasing degree of saturation

The degree of saturation has a huge influence on the formation of binder leading to increment in the degree of carbonation as degree of saturation increases, then the question of how much did we consume the introduced CO\textsubscript{2} gas arises. The degree of saturation influences the efficiency of CO\textsubscript{2} Consumption as shown in Figure 4.22a and Figure 4.22b for samples treated with 5\% and 10\% lime content by weight of silt respectively. As the amount of water or degree of saturation in the mix increases, more Ca\textsuperscript{2+} will be released by the lime and more CO\textsubscript{2} will be dissolved leading to an increment in the Consumption of CO\textsubscript{2} and degree of Carbonation due to increased degree of saturation as seen in Figure 4.22a and Figure 4.22b. However, as the degree of saturation attained 50\% for samples carbonated for one hour, there is a drastic reduction in the degree of carbonation due to the inability of the gas to move through the samples because of the reduction in the volumetric air space meant for gas mobility similar to what was reported by (Yi \textit{et al.}, 2013a) stating water has pros and cons during soil carbonation. At a degree of saturation of 60\% as shown in Figure 4.22a and Figure 4.22b during the carbonation test which lasted for one hour, based on observation, there was not a surge in the temperature of the mold housing the lime-treated silt which supports the reason there was a very low \% calcite formed. However, if the gas is allowed to flow for a longer period, it will carbonate the lime particles. As seen in Figure 4.22a and Figure 4.22b, it was impossible to obtain the efficiency of CO\textsubscript{2} consumption for samples carbonated for one hour at degree of saturation of 50\% and above due the volumetric water content which impedes the flow of gas. At this degrees of saturation, the confidence on the result becomes low due to potential gas leakages that might have happened.
Figure 4.22: (a) Plot showing the effect of increasing degree of saturation on degree of carbonation and efficiency of CO₂ consumption for samples of void ratio $e_o = 1.30$ treated with 5% Lime content by weight of silt tested for a duration of 1hr (b) Plot showing the effect of increasing degree of saturation on degree of carbonation and efficiency of CO₂ consumption for samples of void ratio $e_o = 1.30$ treated with 10% Lime content by weight of silt tested for a duration of 1hr,
4.4.3.1 Global Efficiency of CO₂ Consumption and the Local efficiency of CO₂ consumption during soil carbonation

The result presented below in Figure 4.23) is for lime-treated silt carbonated for a duration of 25mins. The Global efficiency of CO₂ consumption and the Local efficiency of CO₂ consumption in this study is expressed in Eqn. (4.10) and Eqn. (4.11) respectively. From the result obtained from the study, the result in Figure (4.23a) is the representative % calcite formed throughout the sample depth from a carbonation duration of 2mins to 25mins. From the result shown in Figure (4.23c) it can be observed that the Global efficiency of CO₂ consumption reduces as carbonation time increases, the reduction in the Global efficiency of CO₂ consumption occurs due to the increased amount of CO₂ introduced as the duration of carbonation increases with the consumption ability of the system reduces with time due to the reduction in the mass of lime available for conversion as time evolves during soil carbonation. At the end of the test in Figure (4.23b) the total mass of CO₂ introduced was 47g with a Global efficiency of 57% at the end of the formation of calcite, this would decline further if the flow of gas is not interrupted without the formation of calcite with more gas been introduced. For this method of chemical stabilization to be environmentally friendly, hence it is important to interrupt the flow of gas as soon as the lime particles available for carbonation have been converted.

The Local efficiency of CO₂ consumption obtained from this study as presented in Figure 4.23a, indicated that the mass of CO₂ consumed between two carbonation periods increase, between 0-2mins the mass of CO₂ consumed was 5.99g which increases between 2-5mins to 6.52g while the peak mass of CO₂ consumed was attained between 10-15 mins. The local efficiency of CO₂ consumption reduces as seen in Figure 4.23b from 97% to 7% due to the reduction in the lime particles available as the conversion of Ca(OH)₂ particles into CaCO₃ occur from 0-2 mins, 2-5 mins, 5-10 mins, 10-15 mins, 15-20 mins, and 20-25 mins. The Local efficiency of CO₂
consumption reduces drastically at 15-20mins and 20-25mins due to the limited amount of Ca(OH)$_2$ left to be carbonated due to the precipitation of the calcite formed on other unconverted lime particles (Dheilly et al., 2002). Figure 4.23a, it can be seen that more calcite is formed compared to other carbonation period, which means the rate of the production of calcite and consumption of CO$_2$ rate is not always similar during carbonation.

\[
Global \ Eff. \ of \ CO_2 \ consumption = \frac{\text{Mass of CO}_2 \ consumed}{\text{Mass of CO}_2 \ introduced} \quad (4.10)
\]

\[
Incremental \ Eff. \ of \ CO_2 \ consumption = \frac{\Delta \text{ in } M_{CO_2} \ consumed \ between \ t_i \ and \ t_{i+1}}{\Delta \text{ in } M_{CO_2} \ introduced \ between \ t_i \ and \ t_{i+1}} \quad (4.11)
\]
Figure 4.23: (a) % Calcite formed throughout a sample tested at a gas flowrate presented above with samples having initial void ratio of $e=0.82$ and $S_r=42\%$, The sample was tested for different duration which were deduced from a continuous test (b) Local efficiency of CO$_2$ consumption between two carbonation periods during the carbonation of a lime-treated silt having a void ratio of 0.82 and a degree of saturation of 42\% (c) Global efficiency of CO$_2$ consumption throughout a carbonation period of 25mins of a lime-treated silt having a void ratio of 0.82 and a degree of saturation of 42\%, tested at a gas peak flow rate which ranges between
CHAPTER 5
SUMMARY AND CONCLUSIONS

This chapter presents the summary of the major findings from this study which were obtained based on the methodologies described in the third chapter of this thesis. The amount of calcite formed was obtained using the procedures in ASTM(D4373, 2021) and the experimental setup utilized in this study is presented in Chapter 3 of this thesis.

5.1 Major Findings

(a) The degree of carbonation decreases as lime content in the mix increases, because as the lime content in the mix increases more calcium carbonate particles are formed which precipitate over other lime particles yet to be converted. The lesser the lime content, the lesser the amount of divalent Calcium ions to be released into the system which leads to less amount of calcite formed, the reduced amount of calcite formed would lower the number of lime particles to be covered by the calcite formed, hence giving more chances for more lime to be converted into calcite.

(b) The Average % calcite formed during carbonation and the degree of carbonation increases as the degree of saturation increases due to the increased quantity of CO₂ dissolved to form carbonic acid H₂CO₃ and the increased amount of dissolved lime to form more divalent Calcium ions Ca²⁺ due to the increased volumetric water content or degree of saturation in the soil system which enhances the formation of calcite and increases the degree of carbonation.

(c) The increasing volumetric water content or degree of saturation possess a negative effect carbonation period due to the gas mobility problem caused by the amount of volumetric water content which impedes gas movement, at these
degrees of saturation more time is required for the gas to move via the soil column due to the reduced gas diffusivity.

(d) The increasing density affects the amount of calcite formed, as the density increases the total mass of the solid increases and the void ratio reduces causing a reduction in the average % calcite formed due to the reduction in pore space in the soil. The increased density also elongated the mineral carbonation time due to the lowered gas movement in the system. However, the increasing density from this study shows a minor effect on the degree of carbonation due to the reduced theoretical % calcite to be formed as the density increases caused by increasing mass of silt increases, so as the density increases it becomes easier for its capacity to be easily reached because of the lowered expected % calcite to be formed.

(e) The degree of saturation and the flowrate of CO$_2$ has a huge influence on the efficiency of CO$_2$ consumption.

(f) The increasing flow rate possesses an effect on both the efficiency of CO$_2$ consumption and the mass of calcite formed. The increased flow rate will make the reaction end abruptly due to the rapid formation of calcite which causes rapid shielding of other lime particles yet to be carbonated, as soon as the lime particles yet to be converted are fully covered by the calcite, the reaction ends which shortens the % calcite to be formed. Also, has the flowrate increases, less time will be available for the dissolution of the lime particles which will affects the % calcite formed.

(g) Based on the result obtained from this study, this study shows that 60 % to 98% of the process-related CO$_2$ can be consumed via soil carbonation which relies on the soil condition during soil carbonation especially the degree of saturation can have a massive influence on the efficiency of CO$_2$ consumption.
(h) It is difficult to convert all lime particles into calcite during soil carbonation and mineral reaction occurs rapidly and the top of the soil sample is always more carbonated because it is the first point of contact of the CO₂ gas with the treated sample, by this time the CO₂ gas hasn’t lost some of its intrinsic properties such as flow rate and diffusivity.
5.2 Conclusions

Soil carbonation is a novel and promising method of chemical stabilization which offers the opportunity to reduce the carbon footprint associated with the production of calcium and magnesium-bearing minerals used for soil stabilization via carbon sequestration and also enhances the strength development in weak soils due to the formation of calcite. This study has helped me understand more about the kinetics of carbonation and how some factors influence the formation of calcite and the degree of carbonation. As promising as this novel method of chemical stabilization might be, it is pertinent to check if the method is environmentally friendly, based on this research work it was discovered that 60 % to 98 % of the process-related CO$_2$ emission can be consumed via soil carbonation at optimum gas flow condition, which will play a huge role in the reduction in the carbon footprint associated with the production of calcium and magnesium bearing materials. The results obtained from this study as showing that some soil conditions enhance and affect the formation of calcite, degree of carbonation, and efficiency of CO$_2$ consumption. The degree of saturation, density, and lime content all possess an influence on the calcite formation during soil carbonation, this result would play a huge role as we proceed in transferring the knowledge from the elemental testing research into fully understanding the kinetics and the mechanism of soil carbonation in a field scenario or large scale.
5.3 Limitation of study

One of the limitations of this study includes the inability of the flow meter used to test samples at the target flow rate. This makes testing of samples at desired CO$_2$ flow rate difficult during the study. A Flowmeter of improved capability should be used in this type of one-dimensional gas flow test.

Instead of using the flow meter result to capture the surge in temperature due to mineral reaction, which was also used as a proxy to determine the end of the reaction coupled with observations during testing to see the movement of gas throughout the soil column, a device should be attached to the mold to capture the increase and decrease in the temperature as the reaction starts and end, with this approach we would be able to know the exact period mineral reaction ends and also it will make the determination of the carbonation depth easier as CO$_2$ moves down the soil column during carbonation. The % binder was determined using the ASTM standard method of rapid determination of calcite content in soil, the Thermo-gravimetric analysis can be used which is regarded as one of the most efficient way of measuring carbonate content of soil.

5.4 Recommendations for Future Work

Numerical modeling that can mimic or replicate elemental testing results of soil carbonation should be developed which will enable Geo-technical engineers to efficiently consume the CO$_2$ introduced and also predict the performance of carbonated sub-grade materials when used in large-scale or field scenarios.
REFERENCES


*Construction and Building Materials* **22**, No. 8, 1789–1797.


APPENDIX A

RESULTS FROM FLOW METER TS 5300 USED DURING THE ELEMENTAL TESTING

This appendix contains the results from the Flow meter device used during the elemental testing which captures the flow rate of the CO$_2$ gas, absolute pressure and its temperature at entry and exit.
Figure A.1: Flow meter results for the determination of the end of mineral reaction with testing duration of 7.5 minutes. Testing condition is presented in Table.3.1. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.2: Flow meter results for the determination of the end of mineral reaction with testing duration of 15 minutes. Testing condition is presented in Table.3.1. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.3: Flow meter results for the determination of the end of mineral reaction with testing duration of 30 minutes. Testing condition is presented in Table 3.1. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.4: Flow meter results for the determination of the end of mineral reaction with testing duration of 60 minutes. Testing condition is presented in Table 3.1. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
(b) Determination of the effect of degree of saturation on the degree of carbonation.

Figure A.5: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=12%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.6: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=16%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.7: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=20%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.8: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=24%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.9: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=28%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.10: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=42%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.11: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 5% Lime content at Sr=50%. Testing condition is presented in Table.3.2. Testing condition is presented in Table.3.2.
Figure A.12: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=12%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.13: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=16%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.14: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=20%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.15: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=24%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.16: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=28%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.17: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=42%. Testing condition is presented in Table 3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.18: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=50%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.19: Flow meter results for the determination of effect of degree of saturation on degree of carbonation for sample treated with 10% Lime content at Sr=60%. Testing condition is presented in Table.3.2. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
(c) Determination of the effect of Lime content on the formation of calcite and degree of carbonation.

Figure A.20: Flow meter results for the determination of effect of Lime content on degree of carbonation for sample treated with 1% Lime content at Sr=16%. Testing condition is presented in Table.3.3. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.21: Flow meter results for the determination of effect of Lime content on degree of carbonation for sample treated with 1% Lime content at Sr=24%. Testing condition is presented in Table.3.3. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.22: Flow meter results for the determination of effect of Lime content on degree of carbonation for sample treated with 1% Lime content at Sr=42%. Testing condition is presented in Table 3.3. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
(d) Determination of the effect of density on the formation of calcite and degree of carbonation.

Figure A.23: Flow meter results for the determination of effect of density on degree of carbonation for sample with e=0.82 at Sr=40% (varying mass of water). Testing condition is presented in Table.3.4. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.24: Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.88$. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.25: Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.98$ at $Sr=40\%$ (varying mass of water). Testing condition is presented in Table.3.4. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.26: Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=1.09$ at $Sr=40\%$ (varying mass of water). Testing condition is presented in Table 3.4. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.27: Flow meter results for the determination of effect of density on degree of carbonation for sample with e=1.20 at Sr=40% (varying mass of water). Testing condition is presented in Table.3.4. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.28: Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.82$ at Sr=42% (Constant mass of water). Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.29: Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.88$ at Sr=40% (Constant mass of water). Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.30: Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=0.98$ at $Sr=38\%$ (Constant mass of water). Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.31: Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=1.09$ at $Sr=36\%$ (Constant mass of water). Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.32: Flow meter results for the determination of effect of density on degree of carbonation for sample with $e=1.20$ at $Sr=35\%$ (Constant mass of water). Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
(e) Determination of the effect of flowrate on the formation of calcite and efficiency of CO$_2$ consumption

Figure A.33: Flowmeter results for the sample with $e=0.82$ tested at a gas flowrate of 1.44 L/mins for 2mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.34: Flowmeter results for the sample with $e=0.82$ tested at a gas flowrate of 0.98 L/mins for 10mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.35: Flowmeter results for the sample with $e=1.30$ tested at a gas flowrate of 1.02L/mins for 15mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.36: Flowmeter results for the sample with $e=0.82$ tested at a gas flowrate of 0.98L/mins for 20mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.37: Flowmeter results for the sample with $e=0.82$ tested at a gas flow rate of 1.81L/mins for 25mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.38: Fl owmeter results for the sample with e=0.82 tested at a gas flow rate of 1.77 L/mins for 30mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.39: Flowmeter results for the sample with $e=0.82$ tested at a gas flowrate of 1.5 L/mins for continuous testing. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.40: Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.55L/mins for 2mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.41: Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.37L/mins for 5mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.42: Flowmeter results for the sample with $e=0.82$ tested at a gas flow rate of 1.15L/mins for 10mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.43: Flowmeter results for the sample with $e=0.82$ tested at a gas flow rate of 1.22L/mins for 15 mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.44: Flowmeter results for the sample with $e=0.82$ tested at a gas flow rate of 1.10 L/mins for 20 mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.45: Flowmeter results for the sample with e=0.82 tested at a gas flow rate of 1.61L/mins for 25mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.46: Flowmeter results for the sample with $e=0.82$ tested at a gas flowrate of 2L/mins for 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.47: Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 1.98L/mins for 2 mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.48: Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 1.87L/mins for 5 mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.49: Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 1.56L/mins for 10 mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.50: Flow meter results for the sample with $e=0.82$ tested at a gas flow rate of 1.25L/mins for 15mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.51: Flow meter results for the sample with e=0.82 tested at a gas flow rate of 2.08L/mins for 20mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.52: Flow meter results for the sample with \( e=0.82 \) tested at a gas flow rate of 2L/mins for 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.53: Flow meter results for the sample with $e = 1.20$ tested at a gas flow rate of 1.74L/mins for 2mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.54: Flow meter results for the sample with $e=1.20$ tested at a gas flow rate of 1.56L/mins for 5mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.55: Flow meter results for the sample with e=1.20 tested at a gas flow rate of 1.23L/mins for 10mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.56: Flow meter results for the sample with $e=1.20$ tested at a gas flow rate of 1.53 L/mins for 15 mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.57: Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2L/mins for 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.58: Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2.78 L/mins for 2mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.59: Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2.58L/mins for 5mins. Testing condition is presented in Table 3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.60: Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2.44L/mins for 10mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.61: Flow meter results for the sample with $e=1.20$ tested at target flowrate of 4l/mins 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.62: Flow meter results for the sample with $e=1.20$ tested at a gas flow rate of 3.13L/mins for 2mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.63: Flow meter results for the sample with e=1.20 tested at a gas flow rate of 2.70L/mins for 5mins. Testing condition is presented in Table.3.5. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
Figure A.64: Flow meter results for the sample with $e=1.20$ tested at a gas target flow rate of 5L/mins for 1hr. The measurement from the outlet flow meter is invalid until the end of mineral reaction.
BIOGRAPHY OF THE AUTHOR

Temitope Babatunde Omokinde was born in the southwestern part of Nigeria in Africa. He completed his primary school education in 2006 at Faithfulness of God foundation school in a town in Alade-Idanre Ondo state. Temitope started his High school education at Ebun Ogunyimika Comprehensive college Atosin-Idanre and completed it at Bafeds High school Odode-Idanre. After the completion of his High school education, In 2012, he was admitted into the Federal polytechnic Ado-Ekiti, where he bagged a National diploma degree in Civil engineering technology. In 2019, he bagged a Bachelor of Engineering degree in Civil Engineering at the Federal university of technology Akure, Ondo state Nigeria. Temitope is a candidate of Master of Science degree in Civil Engineering from the university of Maine in May 2023.