Laboratory Study of Accelerated Carbonation With Hydrated Lime for Soil Stabilization

SK Belal Hossen
University of Maine, sk.hossen@maine.edu

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LABORATORY STUDY OF ACCELERATED CARBONATION WITH HYDRATED LIME FOR SOIL STABILIZATION

By
SK Belal Hossen
MS, Hong Kong University of Science and Technology (HKUST), 2015
BS, Military Institute of Science and Technology (MIST), 2009

A DISSERTATION
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Advisory Committee:
Dr. Aaron Gallant, Associate Professor of Civil and Environmental Engineering,
University of Maine, Orono, ME., Co-Advisor

Dr. Warda Ashraf, Associate Professor of Civil Engineering, University of Texas at Arlington, TX., Co-Advisor

Dr. Dana N. Humphrey, Emeritus Dean of Engineering, University of Maine, Orono, ME.

Dr. Eric N. Landis, Professor of Civil and Environmental Engineering, University of Maine, Orono, ME.

Dr. Carlos A. Vega-Posada, Associate Professor of Civil Engineering, Antioquia University, Medellín, Colombia.
Challenging subsurface conditions often dictate the need to augment subgrade soils’ in situ properties via chemical stabilization, a simple method of construction that is widespread globally. Chemical stabilization typically involves the field mixing of calcium-based additives like cement, lime, or fly ash. However, there is increasing awareness of the large carbon footprint associated with typical stabilizing agents. The cement and lime industries currently contribute approximately 10% of all anthropogenic carbon dioxide emissions worldwide each year and are expected to increase. Thus, the development of approaches to chemically stabilize subgrade soils that reduce net carbon emissions would be desirable and align with larger societal initiatives to reduce the rate of global warming.

Accelerated carbonation is a nascent approach to chemically stabilize materials. Soil carbonation describes the process whereby carbon dioxide is introduced into soil mixed with chemical additives and sequestered to generate a carbonate binder. However, aside from small elemental and bench-scale experiments, little has been done to evaluate potential methods that would enable carbonation in the field. Lime is a material that’s readily available in the United States but relatively unexplored with respect to carbonating soil. Hydrated lime in particular is a calcium-based additive with relatively high solubility
in water and high efficiency with respect to absorption of dissolved $CO_2$ to precipitate carbonate minerals. Thus, it is a resource that may be relied on to carbonate soil.

In this study, an elemental testing phase was carried out to evaluate the use of hydrated lime as a chemical stabilizing agent, as well as the state parameters influencing the rate of binder formation and degree of mechanical improvement. This initial study informed experiments evaluating surface carbonation, a method with the potential to be scaled and applied across large areas. The experiments were carried out with highly frost-susceptible silt in a large soil box. The durability of the carbonated material was tested in a large environmental chamber, where the effects of soaking and frost action were examined.

Carbonation with hydrated lime was shown to be a rapid method to stabilize soil, with equivalent mechanical properties as soils stabilized with conventional cement-based additives like cement, and durable under freeze-thaw conditions. It was demonstrated that surface carbonation has the potential to carbonate soil thicknesses typically associated with the stabilization of foundation materials for surface transportation infrastructure. Moreover, carbonation could substantially reduce net carbon dioxide emissions associated with lime production. Recent policy shifts in the United States, most notably the passage of The Inflation Reduction Act, are providing significant incentives for the use of construction materials and products that result in substantially lower levels of embodied greenhouse gas emissions. Thus, soil carbonation technology is ripe for development.
DEDICATION

This dissertation is dedicated to my lovely wife, Rafa Tasnim, for her unconditional support throughout this long journey, not to mention for her great assistance in the laboratory, and data logging during large-scale soil carbonation testing.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Research Motivation and Objectives</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Dissertation Outline</td>
<td>4</td>
</tr>
<tr>
<td>2. CARBONATED NON-PLASTIC SOILS MIXED WITH LIME</td>
<td>7</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>7</td>
</tr>
<tr>
<td>2.2 Soil Carbonation with Lime</td>
<td>9</td>
</tr>
<tr>
<td>2.2.1 Theory</td>
<td>9</td>
</tr>
<tr>
<td>2.2.2 Parameters of Interest</td>
<td>10</td>
</tr>
<tr>
<td>2.3 Materials and Methods</td>
<td>12</td>
</tr>
<tr>
<td>2.4 Experimental Results</td>
<td>18</td>
</tr>
<tr>
<td>2.4.1 Rate of Binder Formation</td>
<td>19</td>
</tr>
<tr>
<td>2.4.2 Mechanical Strength and Stiffness</td>
<td>30</td>
</tr>
<tr>
<td>2.5 Discussion</td>
<td>41</td>
</tr>
<tr>
<td>2.6 Summary and Conclusions</td>
<td>44</td>
</tr>
</tbody>
</table>
3. ACCELERATED SURFACE CARBONATION: SOIL BOX EXPERIMENT ...... 47
   3.1 Introduction ........................................................................ 47
   3.2 Surface Carbonation with Hydrated Lime ......................... 49
       3.2.1 Theory ....................................................................... 49
       3.2.2 Concept of Gas Introduction ..................................... 50
   3.3 Soil Box Assembly and Testing Details ............................... 52
       3.3.1 Tested Materials .................................................... 52
       3.3.2 Soil Box Construction ............................................ 60
       3.3.3 Experimental Arrangement and Instrumentation .......... 62
       3.3.4 Destructive Testing and Sampling ............................. 65
   3.4 Experimental Results ....................................................... 68
       3.4.1 Monitoring of Surface Carbonation ............................ 68
       3.4.2 Binder Content Measurements and CBR Testing .......... 73
   3.5 Discussion ....................................................................... 81
   3.6 Summary and Conclusions .............................................. 83

4. FREEZE-THAW DURABILITY TESTING OF CARBONATED SILT ......... 86
   4.1 Introduction ................................................................. 86
   4.2 Background ................................................................. 89
       4.2.1 Accelerated Surface Carbonation Experiment ............. 89
       4.2.2 Freeze-Thaw Durability of Chemically Stabilized Soils 89
   4.3 Laboratory Methods ....................................................... 90
       4.3.1 Tested Materials .................................................. 90
       4.3.2 Experimental Configuration of Freeze-Thaw (FT) Testing 91
4.3.3 Instrumentation .............................................................. 94
4.3.4 Soaking/Saturation .......................................................... 98
4.3.5 Freeze-Thaw Testing Procedure ............................................ 100
4.3.6 Destructive Testing and Sampling ........................................ 102

4.4 Experimental Results .......................................................... 106
4.4.1 Baseline Conditions and Soaking ....................................... 106
4.4.2 Freeze-Thaw Experiments ............................................... 111
4.4.3 Post Freeze-Thaw CBR Testing and Sampling ......................... 118
4.4.4 CBR Testing and Sampling after Drying Period ....................... 124

4.5 Summary and Conclusions .................................................... 130

5. SUMMARY AND CONCLUSIONS .................................................. 132
5.1 Summary of Laboratory Experiments Conducted ......................... 132
5.2 Primary Findings and Conclusions ........................................ 133
5.3 Recommendations for Future Work ....................................... 136

REFERENCES ........................................................................... 139

BIOGRAPHY OF THE AUTHOR ......................................................... 149
<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of the physical properties of sand and silt.</td>
<td>14</td>
</tr>
<tr>
<td>2.2</td>
<td>Summary of the chemical composition of sand and silt.</td>
<td>14</td>
</tr>
<tr>
<td>2.3</td>
<td>Summary of UCS and TGA tests performed on sand and silt specimens.</td>
<td>18</td>
</tr>
<tr>
<td>3.1</td>
<td>Summary of index properties of tested soil.</td>
<td>55</td>
</tr>
<tr>
<td>3.2</td>
<td>Summary of the chemical composition of tested soil and lime.</td>
<td>56</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

2.1 A conceptual demonstration of accelerated carbonation of lime mixed granular soils for calcium carbonate, $CaCO_3$, binder precipitation on the soil grains ................................................................. 11

2.2 a.) Soil gradation curves for the Ottawa sand and non-plastic silt from the U.S. Silica company; b.) standard proctor compaction curves for the Ottawa sand and non-plastic silt containing 10% lime by dry weight of soil. ............................................................. 13

2.3 Representative thermogravimetric (TG) and derivative thermogravimetric (DTG) plots of lime (10%) mixed sand or silt carbonated for different periods. ................................................................. 16

2.4 Temporal changes in unconfined compressive strength for sand carbonated at different degrees of saturation: a.) $t_c = 3$ hours; b.) $t_c = 24$ hours; c.) $t_c = 72$ hours; d.) $t_c = 120$ hours; e.) $t_c = 168$ hours. ..................................................................................... 20

2.5 Temporal changes in unconfined compressive strength for silt carbonated at different degrees of saturation: a.) $t_c = 3$ hours; b.) $t_c = 24$ hours; c.) $t_c = 72$ hours; d.) $t_c = 168$ hours. ......................... 22

2.6 Unconfined compressive strength vs. gravimetric binder content at the center of: a.) sand specimens reconstituted at $e_o = 0.49$ and b.) silt specimens reconstituted at $e_o = 1.09$. ............................................................. 23
Temporal changes in the gravimetric binder content and degree of carbonation at the center of soil specimens for different degrees of saturation for: a.) sand and b.) silt. The corresponding volumetric air contents and water contents are also shown. 25

Differences in the rate of binder formation in the sand and silt based on the: a.) gravimetric binder content; and b.) the volumetric binder content. 27

Comparison of increases in volumetric binder content for: a.) sand and silt specimens with the same volumetric water content and $S_r$ values associated with gas-phase connectivity throughout the pores; b.) sand and silt specimens with the same volumetric air content and $S_r$ values associated with gas-phase connectivity throughout the pores. 29

Representative stress-strain curves from UCS tests performed on a.) sand and b.) silt specimens at different densities. Specimens were carbonated sufficiently such that the maximum DoC attainable was achieved. 31

Influence of void ratio (i.e. density) on carbonated unconfined compressive strength in: a) sand; and b.) silt. The void ratio ranges considered loose, medium-dense, and dense for each soil type are shown. The top and bottom figures indicate volumetric binder content and the corresponding gravimetric binder content, respectively. Only carbonated specimens with $\theta_B$ greater than 2% were considered due to substantial non-homogeneity of the binder phase in soils with very low binder contents. 33

xi
2.12 Unconfined compressive strength and the adjusted porosity and volumetric binder content ratio ($\nabla = \eta/\theta_B^b$) for: a.) carbonated sand and b.) carbonated silt soils in this study. ......................... 34

2.13 The upper plots show the unconfined compressive strength and the adjusted porosity and volumetric binder content ratio ($\nabla = \eta/\theta_B^{0.28}$) for carbonated sand and silt soils shown against data for cement-stabilized soils: a.) clayey sand data presented by Consoli et al. (2007); b.) fine-grained silt and clay soils presented by Consoli et al. (2016). Note that $\theta_B$ is the volumetric cement content for Consoli et al (2007, 2016) data. The lower plots show: c.) optimized normalized unconfined compressive strength relationship for all carbonated soils sand and silt soils with $\theta_B$ greater than 2%; d.) optimized normalized unconfined compressive strength relationship for all carbonated soils compared with many cement-stabilized soils presented in Consoli et al. (2016). A $\nabla_{ref} = 30$ and $b = 0.28$ was used for both the carbonated and cement-stabilized soils presented by Consoli et al. (2016). ....................................................... 36

2.14 Unconfined compressive strength predicted using the optimized $Q_u$-model developed for: a.) carbonated sand and b.) carbonated silts. ................................................................. 37
2.15 Summary of mechanical strain, strength and stiffness of carbonated soils. a.) relationship between secant Young’s modulus \((E_{50})\) and strain \((\epsilon_{50})\) at 50% of the ultimate strength; Relationship between unconfined compressive strength, UCS \((q_u)\) and: b.) strain at failure, \(\epsilon_f\); c.) secant Young’s modulus at 50% of the ultimate strength, \(E_{50}\); and d.) Young’s modulus normalized by the unconfined compressive strength. Data in part d only considered specimens with strengths greater than 0.3 MPa. .......................................................... 39

2.16 An example to determine the secant Young’s modulus at 50% of the ultimate strength, \(E_{50}\) from the stress-strain plot. ....................... 40

2.17 Influence of porosity and lime content on the predicted unconfined compressive strength (top row) and stiffness (middle row), as well as the influence of water content on the degree of saturation at different porosities, showing the approximate ideal limits to carbonate (bottom row) for: a.) sand and b.) silt. Lime contents refer to the amount of \(Ca(OH)_2\) that has fully reacted to form \(CaCO_3\). ......................... 42

2.18 Flow chart illustrating carbon dioxide emissions during production and sequestration of carbon dioxide during soil carbonation, which is approximately equivalent to process-based emissions. ......................... 43

3.1 a.) A conceptual schematic of surface carbonation on an embankment of soil, where carbon dioxide gas is introduced beneath an impermeable gas barrier (e.g. plastic tarp) and sealed near the perimeter of a targeted area to enforce vertical penetration of carbon dioxide gas into the soil. b.) Large soil box intended to simulate a portion of the embankment near the perimeter where gas escape near the perimeter/slope may occur.......................................................... 51
3.2 Soil preparation. a.) Oven drying of tested soil; b.) soil sieving. ........... 53

3.3 a.) Soil gradation curve of tested soil; b.) standard proctor compaction curves for the tested soil and soil containing approximately 8% lime material by dry weight of soil; the lime material was approximately 80-85% pure calcium hydroxide. ........... 54

3.4 A representative Thermogravimetric Analyses (TGA) of tested silt to verify the presence of carbonate content, and to determine the amount of calcium carbonate, $CaCO_3$ content of the soil.................... 57

3.5 X-ray diffraction (XRD) of tested silt. ........................................ 58

3.6 Thermogravimetric Analyses (TGA) of tested lime–two representative lime samples were tested to verify the purity, and to determine the amount of calcium hydroxide, $Ca(OH)_2$, available in the dry hydrated lime power. ........................................................... 59

3.7 Overview of soil box assembly and installation of instrumentation:

a.) perforated pipes, $CO_2$ gas port, and water sealing on both sides of the box; b.) compaction of soil in 50 mm lifts. Embedment of c.) thermocouples, d.) bender element pairs, and e.) settlement plates (i.e. wooden rod with pedestal) at various depths. View of f.) soil box after filling for sides A ($S_r$ 30%) and B ($S_r$ 40%), g.) plastic tarp seal for surface carbonation and holes on h.) the sloped side of the box. ................................................................. 61
3.8 Overview of setup and equipment used for the large-scale surface carbonation experiment: a.) complete overview of experimental setup highlighting different components; b.) carbon dioxide mass flow meter between the soil box and c.) gas valve located between the flowmeter and the d.) six CO₂ gas cylinders connected through a single manifold to supply uninterrupted flow; e.) data acquisition system connected to thermocouples and bender elements. Note that though pressure at the manifold was 30-40 kPa, at the box opening where the flowmeter was located, the pressure was reduced to ≈ 1 atm (0 gauge).

3.9 Soil box instrumentation plan and dimensions showing the locations of the flowmeter, thermocouples (TC), and bender elements (BE) in a.) plan view and b.) elevation view.

3.10 a.) Overview of field CBR test setup showing the reaction blocks and beam spanning the soil box for testing; b.) field CBR equipment in the soil box; c.) scissor jack being used to penetrate a thin-walled Shelby tube sampler into the soil; d.) extrusion of soil samples from thin-walled sampler; e.) sample collection for drying and storage for thermogravimetric analyses (TGA) later.

3.11 Locations of field California Bearing Ratio (CBR) testing and soil sampling. a.) plan view; b.) elevation view.
3.12 Flowmeter readings at the gas-entry point during the surface carbonation experiment: a.) absolute pressure and temperature readings during the carbonation period; b.) $CO_2$ mass flow rate and total mass of $CO_2$ introduced. Also indicated is the theoretical amount of $CO_2$ required to fully carbonate available $Ca(OH)_2$ at various depth intervals, assuming carbonation progressed vertically from the soil surface downward. ............................................... 69

3.13 Temporal changes in temperature readings and shear wave velocity at various depths in the soil during surface carbonation: a.) temperature readings at 0 and 100 mm (left) and 200, 300, and 400 mm (right); b.) rate of temperature change at 0 and 100 mm (left) and 200, 300, and 400 mm (right); c.) changes in shear wave velocity at 50 mm (left) and 250 mm (right). All plots also indicate the total mass of gas introduced and the theoretical amount of $CO_2$ required to fully carbonate available $Ca(OH)_2$ at various depth intervals, assuming carbonation progressed vertically from the soil surface downward. ............ 72

3.14 Gravimetric $CaCO_3$ binder contents and unreacted hydrated lime contents on a.) side A and b.) side B of the soil box after surface carbonation. ................................................................. 74

3.15 Pre- and post-carbonation CBR values throughout the soil column on a.) side A and b.) side B of the soil box. ................................. 76

3.16 Stress-penetration curves from CBR tests at depths of 0 mm (top), 100 mm (middle), and 150 mm (bottom) on a.) side A and b.) side B of the soil box before and after surface carbonation. ......................... 77
3.17 Unload-reload cycles performed at varying stress levels for depths of 0, 100, and 150 mm for a.) side A and b.) side B of the soil box after surface carbonation. Note that the right figures for (a) and (b) are focused on the stress levels and deformations where unload-reload cycles were performed. ......................................................... 79

3.18 Synthesis of the CBR test results showing: a.) the influence of fully carbonated thickness, $H_c$, underlying the CBR piston of diameter, $B$, on the failure stress, $q_f$; b.) the influence of fully carbonated thickness, $H_c$, underlying the CBR piston of diameter, $B$, on CBR; c.) permanent deformations associated with unload-reload cycles performed at varying stress-levels, $q_{ur}$, at depths of 0, 100, and 150 mm; d.) influence of the unload-reload stress relative to the ultimate capacity of the soil, expressed as a $q_{ur}/q_f$ ratio, on permanent deformations from unload-reload cycles. ........................................... 80

4.1 a.) An overview of the HASTEST environmental chamber (interior dimensions-6.7 m in length and width with a height of 4.3 m) [left] capable to control the temperature (T) between 50 °C and -40 °C and relative humidity (RH) between 5% and 100% including the chamber control station [right]; b.) Overview of setup and equipment used for the large-scale freeze-thaw experiment including field CBR test setup showing the reaction blocks and beam spanning the soil box for testing. ................................................................. 93
4.2 Instrumentation in the soil box during freeze-thaw experiments. a.) Linear Potentiometer Position Sensor (LPPS) mounted on settlement plates to monitor the vertical movement at varying depths (z=0, 100, 200, 300 mm); b.) data acquisition system for shear wave velocity measurement using bender element pairs embedded at z=50 and 250 mm.

4.3 Soil box instrumentation plan and dimensions showing the locations of the thermocouples (TC), bender element pairs (BE), and Linear Potentiometer Position Sensor (LPSS) mounted on settlement plates (wooden rod with a circular pedestal) in a.) plan view and b.) elevation view.

4.4 a.) An overview of bottom-up saturation in the soil box using b.) horizontal and vertical perforated tubes; c.) view of the soil surface after complete saturation, but before applying freeze-thaw cycles.

4.5 a.) Simulation of 1-D (top-down) freezing front to implement field condition; b.) view of the soil surface after complete freezing of the soil column; c.) testing configuration during thawing; d.) view of the soil surface after two freeze-thaw cycles.

4.6 a.) Field CBR equipment in the soil box; b.) scissor jack being used to penetrate a thin-walled Shelby tube sampler into the soil.

4.7 Locations of field California Bearing Ratio (CBR) testing and soil sampling. a.) plan view; b.) elevation view.
4.8 Comparison of BCs measured immediately after accelerated surface carbonation was performed and increases observed in the lightly carbonated region in the seven days between surface carbonation and when the material was fully soaked ...................................................... 108

4.9 CBR testing at the surface in the soil box, but before freeze-thaw testing, compared with measurements immediately after carbonation: a.) stress-penetration curves on Side A (left) and Side B (right); b.) changes in surface CBR and water content after soaking on Side A of the soil box; c.) changes in surface CBR and water content after soaking on Side B of the soil box. ...................................................... 110

4.10 Summary of information continuously monitored during two freeze-thaw cycles on Side A (left) and Side B (right) of the soil box: a.) temperatures monitored in the environmental chamber (room) and at soil depths $z = 0$, 100, 200, 300, and 400 mm; b.) subsurface vertical deformations measured via settlement plate at soil depths $z = 0$, 100, 200, 300, and 400 mm; c.) relative vertical deformations expressed as a percentage of the thickness of soil between settlement plates for the subsurface depth intervals of 0-100, 100-200, 200-300, and 300-450 mm. ............................................................... 114

4.11 Vertical deformations through the subsurface profile at different points in time during the freeze-thaw experiments for: a.) Side A and b.) Side B of the soil box...................................................... 115

4.12 Shear wave velocity measurements on Side B of the soil box at: a.) $z = 50$ mm in fully carbonated silt and b.) $z = 250$ mm in lightly carbonated silt. ................................................................. 117
4.13 CBR values and water contents measured after first freeze-thaw cycles compared with surface measurements after soaking, but before freeze-thaw testing: a.) Side A of the soil box; b.) Side B of the soil box.

4.14 Stress-penetration curves from CBR testing after freeze-thaw cycles were performed: a.) Side A of the soil box; b.) Side B of the soil box.

4.15 CBR values and water contents measured after two freeze-thaw cycles compared with surface measurements after soaking, but before freeze-thaw testing, and before surface carbonation was performed: a.) Side A of the soil box; b.) Side B of the soil box. The frost-susceptibility criteria according to ASTM D5918 is also indicated.

4.16 CBR stress-penetration curves in fully carbonated material at depths $z = 0$ mm, $z = 100$ mm, and $z = 150$ mm after the drying period compared with measurements after surface carbonation, soaking, and two freeze-thaw cycles on: a.) Side A of the soil box; b.) Side B of the soil box.

4.17 CBR stress-penetration curves at depths $z = 250$ mm and $z = 350$ mm after the drying period compared with measurements after surface carbonation, soaking, and two freeze-thaw cycles on: a.) Side A of the soil box; b.) Side B of the soil box.
Comparison summary for Side A of the soil box: a.) highlighted the comparison between CBR values observed after two-freeze thaw cycles with values after a 12-week drying period (left); changes in water content (right); b.) highlighted changes in gravimetric binder content (left) and unreacted calcium hydroxide during the drying period. Also shown in (a) and (b) are measurements before carbonation, after accelerated carbonation, and soaking. 128

Comparison summary for Side B of the soil box: a.) highlighted the comparison between CBR values observed after two-freeze thaw cycles with values after a 12-week drying period (left); changes in water content (right); b.) highlighted changes in gravimetric binder content (left) and unreacted calcium hydroxide during the drying period. Also shown in (a) and (b) are measurements before carbonation, after accelerated carbonation, and soaking. 129
CHAPTER 1
INTRODUCTION

1.1 Research Motivation and Objectives

Challenging subsurface conditions often dictate the need to excavate and replace shallow subgrade soils or to modify the native materials’ in-situ properties via soil stabilization methods to support transportation infrastructure. This includes subbase and subgrade layers for roadways, runways, and railways, as well as for foundations, embankments, erosion protection, etc. Depending on the availability and location of borrow sites, the adoption of soil stabilization methods to augment the strength and stiffness of existing subgrade soils may be more suitable than excavation and replacement. Chemical stabilization methods typically involve field mixing of calcium-based additives like cement (Consoli et al., 2007; Yi et al., 2014; Consoli et al., 2016), lime (Sherwood, 1993; Dash & Hussain, 2012; Toohey et al., 2013), or fly ash (Puppala, 2016; Behnood, 2018) with native materials to increase the strength and stiffness. The simplicity associated with this method of construction has resulted in the widespread use of chemical stabilization globally to improve poor subgrade materials.

There is increasing awareness of the relatively large carbon footprint associated with the use of typical stabilizing agents like cement and lime. (Worrell et al., 2001; Yi et al., 2014; Miller et al., 2018; Behnood, 2018). The cement and lime industries alone currently contribute 8% and 2% of all anthropogenic CO₂ emissions worldwide each year, respectively, and are expected to increase (Miller et al., 2018; Reis et al., 2021). Though more cement is produced globally for construction, lime and cement emit similar amounts of CO₂ during production; approximately 0.95 and 1.1 ton of CO₂ is emitted per tonne of cement and lime, respectively UNEP-GEAS (2010); Higgins (2005); Yi et al. (2013b, 2014); Stork et al. (2014); Cai et al. (2015). Thus, the development of approaches to stabilize poor subgrade soils that would reduce net CO₂ emissions associated with the production of
conventional agents would be desirable and align with larger societal initiatives to reduce the rate of global warming.

Soil carbonation is a potentially novel approach to stabilize poor subgrades, whereby carbon dioxide would be introduced in soil mixed with chemical additives (same as conventional methods) and sequestered to generate a carbonate binder. The use of carbonate binders shows potential to be an alternative approach to chemically stabilize soil (Fasihnikoutalab et al., 2017). Initial studies have focused on the use of magnesium-based alkali sources, including reactive magnesia ($MgO$) (Yi et al., 2013b; Cai et al., 2015) and olivine ($Mg_2SiO_4$) (Fasihnikoutalab et al., 2017). However, only 0.35 million tons of magnesium compounds, including reactive magnesia, were produced in the United States in 2020 (Merrill, 2021). This is a small fraction when compared with other minerals in the United States, like quick or hydrated lime (16 million tons) (Apodaca, 2021), which is more likely to be relied on as an alkali source.

It has been shown that soils containing lime will carbonate under natural atmospheric conditions (e.g. Das et al., 2021, 2022; Fan et al., 2023) and this process may be accelerated to chemically stabilize the soil. Hydrated lime ($Ca(OH)_2$) is a calcium-based additive with relatively high solubility in water (Jang et al., 2016) and high efficiency with respect to absorption of dissolved $CO_2$ to precipitate carbonate minerals (Han et al., 2011). Therefore, it could be a good agent to stabilize soil via carbonation. Moreover, conventional lime stabilization, which generates a binder through a long-term pozzolanic reaction, is only effective in “reactive” soils that typically have a high clay content (Little, 1999; Little & Nair, 2009); conventional lime stabilization does not improve the mechanical properties of non-plastic granular soils like sand and silt, where cement would be used today. Thus, carbonation has the potential to expand the applicability of lime with respect to soil stabilization of “non-reactive” soils as well.

Aside from small bench-scale experiments exploring the potential to create carbonated columns of soil (Yi et al., 2013a; Fasihnikoutalab et al., 2016), little has been done to
evaluate potential methods that would enable carbonation in the field (Li et al., 2023). A key difference between conventional chemical stabilization and “accelerated” carbonation is that CO$_2$ gas must be introduced after the soil is mixed with chemical additives. Thus, one of the primary challenges engineers and contractors are faced with is developing scalable processes to introduce CO$_2$ gas in soil that could translate to field settings.

The focus of this research is on the use of hydrated lime to stabilize non-plastic soils. The primary objectives of this work are to:

• Understand if hydrated lime is a chemical additive that can be used to bind non-plastic soils (sand and silt) via carbonation under, and if so, investigate the state parameters influencing the rate of carbonation and degree of mechanical improvement under varying conditions. Additionally, this work aims to understand how the degree of mechanical improvement compares relative to conventional cement-based additives used to stabilize non-plastic soils. Achieving these objectives will help elucidate the parameters of functionality—which will be required to design scaled-processes that enable the extension of soil carbonation to the field.

• Evaluate a “surface carbonation” approach with the potential to be applied over relatively large areas, and which refers to the introduction of CO$_2$ beneath a near-ground-surface seal intended to contain and enforce vertical penetration of CO$_2$ gas into the ground. It is envisioned that surface carbonation could be suitable for situations where there is typically some attempt to control the water content and density of soils mixed with chemical additives; e.g. shallow subgrade stabilization for roadway construction or similar.

• Evaluate the durability and resilience of carbonated soil exposed to soaking and frost action. If it is demonstrated that carbonation with hydrated lime can cement the soil matrix effectively, it is necessary to understand how the binder performs under extreme environmental stressors like frost action.
1.2 Dissertation Outline

This dissertation is comprised of five chapters, including the introduction, three research chapters (2 through 4), and summary and conclusions (Chapter 5). The research chapters are intended to be self-contained, including relevant background information, so that they can be reviewed independently. A summary of each chapter is provided herein.

**Chapter 2 Summary:** The initial phase of this study began at elemental-scales, where non-plastic sand and silt specimens mixed with hydrated lime were carbonated for varying amounts of time at different water contents and densities. Unconfined compressive strength tests and thermogravimetric analyses were performed to evaluate state parameters influencing the rate of carbonation and degree of mechanical improvement. The air content, water content, and associated degree of saturation significantly influence the rate of binder formation. It was found that ensuring continuity of the gas-phase throughout the voids enhances gas mobility which increases the rate of mechanical improvement, while pore water barriers that obstruct the flow of carbon dioxide at high degrees of saturation suppress the binder formation rate. Density and volumetric binder content primarily govern strength and stiffness. Cement is often used to stabilize non-plastic soils and it was demonstrated that carbonated soils: a.) can achieve equivalent strengths as cement-stabilized materials; and b.) have a very similar dependence on soil type, density, and binder content. The potential for carbonation to reduce carbon dioxide emissions associated with lime production by approximately two-thirds is discussed—which is a substantial carbon saving. The findings from this phase elucidated the parameters of functionality that helped inform larger-scale experiments described in Chapter 3.

**Chapter 3 Summary:** In Chapter 2 it was demonstrated that soil carbonation with hydrated lime is a potentially novel approach to chemically stabilize soil, whereby carbon dioxide is introduced in soil mixed with lime, and sequestered to generate a calcium carbonate binder. In Chapter 3, a large soil box experiment of surface carbonation, a potentially scalable method to introduce carbon dioxide, was applied to lime-mixed silt to
evaluate the thickness of carbonated material, rate of carbonation, and degree of mechanical improvement. Real-time monitoring of surface carbonation with a flowmeter and embedded thermocouples and Bender elements, combined with post-carbonation measurements of binder contents and the California Bearing Ratio (CBR), revealed substantial increases in strength and stiffness over a carbonated soil thickness typically targeted for shallow subgrade stabilization applications (e.g. roadway construction) was achieved within 4 to 5 hours. Potential construction and environmental benefits, including current policies incentivizing the use of construction materials and products that result in substantially lower levels of embodied greenhouse gas emissions, are discussed.

**Chapter 4 Summary:** In Chapter 4, environmental testing was carried out on carbonated, highly frost-susceptible silt, from the large soil box experiments described in Chapter 3. The soil box was fully saturated and then exposed to two freeze-thaw cycles in the HASTEST environmental chamber at the Advanced Structures and Composites Center to test the durability of the carbonated soil. The unique experimental setup included insulation and heat provided to the underside of the box to realistically impose a 1D (top-down) freezing front expected in the field. Environmental testing was followed by a 12 weeks drying period to evaluate changes in CBR due to moisture content changes. Upon initial “soaking” of the soil, the CBR values at the surface of the soil decreased, as expected. No change in shear wave velocity was observed at this stage, as expected. A modest drop in the shear wave velocity was observed after the first freeze-thaw cycle but was still significantly elevated relative to pre-carbonation levels, with negligible changes thereafter. Little change in the CBR-levels was observed in carbonated soil after freeze-thaw cycles relative to measurements taken after soaking. Based on shear wave velocity measurements and CBR testing, only the first freeze-thaw cycle had a modest influence on bonding (low damage) and the $CaCO_3$ bonds were generally resistant to frost action. After the drying period, CBR-levels recovered and even exceeded levels prior to soaking. This was
attributed to continued carbonation from atmospheric $CO_2$, as an increase in binder content was observed in soil that was not carbonated during the accelerated process.

**Chapter 5 Summary:** In the final chapter a summary of the work described in Chapters 2 through 4 is provided. The results from elemental and large-scale carbonation experiments are discussed and final conclusions are provided. Aspects of soil carbonation that require further consideration are discussed and recommendations for future work are provided.
CHAPTER 2
CARBONATED NON-PLASTIC SOILS MIXED WITH LIME

2.1 Introduction

Challenging subsurface conditions often dictate the need to excavate and replace shallow subgrade soils or to modify the native materials’ in-situ properties via soil stabilization methods to support infrastructure; this includes subbase and subgrade layers for roadways, runways, and railways, as well as foundations, embankments, erosion protection, etc. Depending on the availability and location of borrow sites, the adoption of soil stabilization methods to augment the strength and stiffness of existing subgrade soils may be more suitable than excavation and replacement.

Chemical stabilization methods typically involve field mixing of calcium-based additives like cement (Consoli et al., 2007; Yi et al., 2014; Consoli et al., 2016), lime (Sherwood, 1993; Dash & Hussain, 2012; Toohey et al., 2013), or fly ash (Puppala, 2016; Behnood, 2018) with native materials to increase the strength and stiffness. The simplicity associated with this method of construction has resulted in the widespread use of chemical stabilization globally to improve poor subgrade materials. However, there is increasing awareness of the relatively large carbon footprint associated with the use of the aforementioned stabilizing agents (Worrell et al., 2001; Yi et al., 2014; Miller et al., 2018; Behnood, 2018). Approximately 1 ton of carbon dioxide ($CO_2$) gas is emitted into the atmosphere per ton of cement UNEP-GEAS (2010) or lime (Stork et al., 2014) production; the cement industry alone currently contributes 8–9% of all anthropogenic $CO_2$ emissions worldwide each year and is expected to increase (Miller et al., 2018; Reis et al., 2021). Thus, the development of approaches to stabilize poor subgrade soils that would reduce net $CO_2$ emissions associated with the production of conventional agents would be desirable and align with larger societal initiatives to reduce the rate of global warming.
The use of carbonate binders (De Silva et al., 2006, 2009; Ashraf, 2016) shows potential to be an alternative approach to chemical stabilization, whereby alkali minerals are mixed with soil (similar to conventional methods) and \( CO_2 \) gas is subsequently introduced. The carbonation reaction consumes \( CO_2 \) and the net carbon footprint is reduced (Fasihnikoutalab et al., 2017). Recent studies have demonstrated that the precipitation of stable carbonate minerals from magnesium-based alkali sources such as reactive magnesia (\( MgO \)) (e.g. Yi et al., 2013b; Cai et al., 2015) or olivine (\( Mg_2SiO_4 \)) (e.g. Fasihnikoutalab et al., 2017) can significantly improve the strength and stiffness of soil. However, only 0.35 million tons of magnesium compounds, including reactive magnesia, were produced in the United States in 2020 (Merrill, 2021). This is a small fraction when compared with other minerals in the United States, like quick or hydrated lime (16 million tons) (Apodaca, 2021), which is more likely to be relied on as an alkali source.

Hydrated lime (\( Ca(OH)_2 \)), referred to herein as lime, is a calcium-based additive with relatively high solubility in water (Jang et al., 2016) and high efficiency with respect to absorption of dissolved \( CO_2 \) to precipitate carbonate minerals (Han et al., 2011). Therefore, it is anticipated that hydrated lime, which is more readily available in the United States than magnesium-based compounds, could be a good agent to stabilize soil via carbonation. Moreover, conventional lime stabilization, which generates a binder through a long-term pozzolanic reaction, is only effective in “reactive” soils that typically have a high clay content; conventional lime stabilization does not improve the mechanical properties of non-plastic granular soils like sand and silt, where cement would be used today. Carbonating soil with lime has the potential to improve “non-reactive” soils as well (Hossen et al., 2020).

The use of lime for chemical stabilization via carbonation has not been investigated extensively. The primary objectives of this study were to: a.) demonstrate the applicability of hydrated lime as a chemical additive that can be used to bind non-plastic soils (sand and silt) via carbonation under low \( CO_2 \) pressures, and b.) investigate the state parameters
influencing the rate of carbonation and degree of mechanical improvement under varying conditions (density and water contents). Achieving these objectives will help elucidate the parameters of functionality—which will be required to design scaled-processes that enable the extension of soil carbonation to the field. The intent of this study is to focus on stabilization applications where there is often some attempt to control the water content and/or density of soils mixed with chemical additives and/or where the soil is not fully saturated (e.g. shallow subgrade stabilization, roadway stabilization, shallow slope stabilization, base of shallow foundations).

### 2.2 Soil Carbonation with Lime

#### 2.2.1 Theory

Soil carbonation with hydrated lime, referred to herein as lime, may be characterized as a two-step process and described by a three-step chemical reaction. After creating a soil-lime-water mixture (first step), which is the same as conventional chemical stabilization methods, the solid lime dissolves in pore water and dissociates into aqueous-phase cations, \( Ca^{2+} \), and anions, \( OH^- \),

\[
Ca(OH)_2[s] + H_2O[l] \leftrightarrow Ca^{2+}(aq) + 2OH^-(aq) \quad (2.1)
\]

Carbon dioxide gas must then be introduced into the soil matrix and dissolve in the pore water (second step), producing a weak carbonic acid \( (H_2CO_3) \) that dissociates into \( H^+ \) and bicarbonate (i.e. \( HCO_3^- \)) or carbonate \( (CO_3^{2-}) \) ions in the pore water solution,

\[
CO_2[g] + H_2O[l] \rightarrow H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3^-(aq) \leftrightarrow 2H^+(aq) + CO_3^{2-}(aq) \quad (2.2)
\]

The \( Ca^{2+} (aq) \) and \( CO_3^{2-} (aq) \) ions combine and calcium carbonate precipitates out of the pore water solution and agglomerates onto the soil grains (\( \downarrow \) signifies precipitation/deposition),
\[ Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3[s] \downarrow \] (2.3)

If enough precipitation occurs, the carbonate minerals will bind the soil matrix. The preceding description of the exothermic carbonation reaction with lime can be summarized as,

\[ Ca(OH)_2[s] + H_2O[l] + CO_2[g] \rightarrow CaCO_3[s] + 2H_2O[l] + Heat \] (2.4)

Note that \( s = \text{solid}, l = \text{liquid}, aq = \text{aqueous-phase} = \text{dissolved}, g = \text{gas-phase}. \)

### 2.2.2 Parameters of Interest

An understanding of how the reaction occurs lends insight into the state parameters expected to influence the rate of binder formation during soil carbonation. One consideration is that a sufficient amount of pore water must be present such that lime must be in contact with, and dissolve into, the pore water (equation 2.1). The pore water is effectively a host medium for dissolved lime and dissolved \( CO_2 \) gas (equation 2.2) that leads to precipitation of binding carbonate minerals (equation 2.3). The more water that’s present, the more lime and \( CO_2 \) can be dissolved at any given moment, which is expected to influence the rate of mineral precipitation and binder formation.

However, a unique feature of soil carbonation is the need to introduce and transport \( CO_2 \) through the soil matrix where lime is present. Soils with a low degree of saturation have a continuous gas-phase and pockets of water. Gas diffusion and mobility through soil increase significantly with air content (Olesen et al., 1996, 1999; Schjønning et al., 1999; Moldrup et al., 2001; Fredlund et al., 2012). Figure 2.1 conceptually illustrates the soil-lime-water mixture and how a continuous gas-phase can facilitate the conveyance of \( CO_2 \) gas. Gas mobility is reduced as the degree of saturation and corresponding air content increase and decrease, respectively. For high degrees of saturation, \( CO_2 \) gas mobility is obstructed by a continuous water phase, and gas mobility is governed, to a large extent, by diffusion of dissolved \( CO_2 \) through pore water. Diffusion of dissolved gas is comparatively
Figure 2.1: A conceptual demonstration of accelerated carbonation of lime mixed granular soils for calcium carbonate, CaCO₃, binder precipitation on the soil grains slow (e.g. Mahmoodi & Gallant, 2020, 2021). Thus, water content and the associated degree of saturation and volumetric air content, is of particular interest. The soil's water content must balance water’s influence on competing mechanisms—gas mobility and the dissolution of chemical constituents that react to generate a binder.

From a mechanical perspective, the relationship between density and gains in strength and stiffness after the formation of a carbonate binder—and how that relationship varies for different non-plastic soil types—has not been explored. This study seeks to link the combinations of densities and binder contents to the degree of mechanical improvement in sand and silt. Additionally, the amount of improvement will be compared with cement, the most widely used additive for chemical stabilization in non-reactive soils.
2.3 Materials and Methods

Ottawa sand and MIN-U-SIL 40 silt (ground silica), referred to herein as sand and silt, from the U.S. Silica Company were used to investigate the influence of carbonation on the mechanical properties of lime-mixed non-plastic soils. The sand and ground silica contained 99.7\% SiO$_2$ with specific gravity, $G_s$, of 2.65, and the sand gradation shown in Figure 2.2a conforms to ASTM C778 (ASTM, 2017c). According to the unified soil classification system (USCS) (ASTM, 2017a), the Ottawa sand is classified as poorly graded sand (SP), and the ground silica is classified as silt (ML). Commercial grade hydrated lime from Acros Organics, USA, where it was determined that the lime was approximately 85-90\% pure calcium hydroxide with a $G_s$ of 2.24. Additionally, compaction tests were carried out on 10\% (by weight) lime mixed sand or silt using the standard compaction effort according to ASTM D698 ASTM (2012). The compaction curves of the 10\% lime mixed soils are shown in Figure 2.2b. The optimum water content ($\omega_{opt}$) and maximum dry density ($\gamma_{d,\text{max}}$) of 10\% lime mixed sand or silt are 9.8 \%, 18.50 kN/m$^3$, and 19.6 \%, 16.10 kN/m$^3$, respectively. Table 2.1 and Table 2.2 summarize the physical properties and chemical composition of sand and silt, respectively.
Figure 2.2: a.) Soil gradation curves for the Ottawa sand and non-plastic silt from the U.S. Silica company; b.) standard proctor compaction curves for the Ottawa sand and non-plastic silt containing 10% lime by dry weight of soil.
Table 2.1: Summary of the physical properties of sand and silt.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity, $G_s$</td>
<td>2.65</td>
</tr>
<tr>
<td>Particle size distribution (%)</td>
<td></td>
</tr>
<tr>
<td>Coarse and medium sand (4.75-0.425 mm)</td>
<td>30</td>
</tr>
<tr>
<td>Fine sand (0.425-0.075 mm)</td>
<td>70</td>
</tr>
<tr>
<td>Silt (0.075-0.002 mm)</td>
<td>-</td>
</tr>
<tr>
<td>Clay (&lt;0.002 mm)</td>
<td>-</td>
</tr>
<tr>
<td>Coefficient of uniformity, $C_u$</td>
<td>2.2</td>
</tr>
<tr>
<td>Coefficient of curvature, $C_c$</td>
<td>1.5</td>
</tr>
<tr>
<td>USCS Soil classification</td>
<td></td>
</tr>
<tr>
<td>Group name</td>
<td>Poorly graded sand</td>
</tr>
<tr>
<td>Group symbol</td>
<td>SP</td>
</tr>
<tr>
<td>Standard proctor test (10% lime mixed soil)</td>
<td></td>
</tr>
<tr>
<td>Optimum water content, $\omega_{opt}$ (%)</td>
<td>9.8</td>
</tr>
<tr>
<td>Maximum dry unit weight, $\gamma_{d,max}$ ($kN/m^3$)</td>
<td>18.50</td>
</tr>
</tbody>
</table>

Table 2.2: Summary of the chemical composition of sand and silt.

<table>
<thead>
<tr>
<th>Composition* (% weight)</th>
<th>Sand</th>
<th>Silt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SiO_2$ (Silicon Dioxide)</td>
<td>99.7</td>
<td>99.7</td>
</tr>
<tr>
<td>$Fe_2O_3$ (Iron Oxide)</td>
<td>0.02</td>
<td>0.018</td>
</tr>
<tr>
<td>$Al_2O_3$ (Aluminum Oxide)</td>
<td>0.06</td>
<td>0.228</td>
</tr>
<tr>
<td>$TiO_2$ (Titanium Dioxide)</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>$CaO$ (Calcium Oxide)</td>
<td>&lt;0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>$MgO$ (Magnesium Oxide)</td>
<td>&lt;0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>$Na_2O$ (Sodium Oxide)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>$K_2O$ (Potassium Oxide)</td>
<td>&lt;0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>LOI (Loss on Ignition)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Based on the product data sheet of US Silica Company

To prepare samples, dry lime, and soil were placed in a mechanical mixer for at least two minutes or until the mixture appeared uniform in color. Deionized water was then added to the mix to achieve a target gravimetric water content, $\omega$, and then mixed again for at least five minutes to achieve uniformity; note that “volumetric air content” is used here generically to signify the void volume containing gas. All soil-lime-water mixtures were immediately transferred to air-tight plastic bags for 24 hours to achieve moisture equalization (ASTM, 2017b). Reconstituted specimens, 50 mm in diameter and 100 mm in
height were prepared to achieve the desired dry density ($\gamma_d$), void ratio and porosity ($e$ and $\eta$), and degree of saturation ($S_r$). Specimens were prepared in four lifts using a two-part split aluminum mold (ASTM, 2009c). Each lift was uniformly compacted with a wooden tamper and soil at the top of each lift was scarified before placing subsequent lifts. Specimens were then placed in a $CO_2$ gas chamber and carbonated under low pressure ($\approx 0$ kPa gauge pressure).

All soil specimens were mixed with a target gravimetric lime content ($\beta_L$), defined as the ratio of the dry mass of lime, $m_L$ by the dry mass of soil, $m_s$. A target value of $\beta_L = 10\%$ was chosen because it is toward the upper-bound of lime contents typically added for shallow subgrade stabilization (Little & Nair, 2009). Varying binder contents (BC) were achieved by varying the amount of time that reconstituted specimens were left in the $CO_2$ gas chamber; i.e. use of a constant lime content was not intended to achieve the same BC across all tests. The gravimetric BC ($\beta_B$) is defined as,

$$\beta_B = \frac{m_B}{m_s} \quad (2.5)$$

where $m_B$ is the mass of the carbonate binder. The volumetric binder content ($\theta_B$) is defined as,

$$\theta_B = \frac{V_B}{V_t} = \frac{m_B/(G_B\rho_w)}{V_t} \quad (2.6)$$

where $V_B$ and $V_t$ are the volume of carbonate binder and total soil volume, respectively. The specific gravity of the $CaCO_3$ binder, $G_B$, and density of water, $\rho_w$, can be used to compute the volume of the binder. The degree of carbonation (DoC) is defined as the ratio of calcium carbonate formed to the maximum amount possible based on the amount of chemical additive mixed in the soil, or,

$$DoC = \frac{\beta_B}{\beta_{B,max}} = \frac{\theta_B}{\theta_{B,max}} \quad (2.7)$$
where $\beta_{B,max}$ and $\theta_{B,max}$ assume all lime has been converted to calcium carbonate via carbonation. The theoretical maximum binder content is,

$$\beta_{B,max} = \frac{m_L}{m_s} \times \frac{100}{74} = \beta_L \times \frac{100}{74}$$

(2.8)

where $100/74$ is the ratio of molecular masses of $CaCO_3$ and $Ca(OH)_2$.

![Diagram](image)

Figure 2.3: Representative thermogravimetric (TG) and derivative thermogravimetric (DTG) plots of lime (10%) mixed sand or silt carbonated for different periods.

To evaluate the influence of initial state parameters on the rate of carbonation and improved mechanical properties of carbonated lime-mixed non-plastic soil, displacement-controlled (0.5 mm/min.) unconfined compression strength (UCS) tests were performed on reconstituted samples of carbonated sand and silt; tests were conducted in accordance with ASTM D5102 (ASTM, 2009c) using an Instron 5900 apparatus. Immediately after UCS testing, a representative sample was collected and dried to prevent any further carbonation. Dried samples were tested afterward via thermogravimetric analyses (TGA) using a TGA 55 from TA instruments to determine the binder content and DoC. Figure 2.3 presents representative TGA analysis consisting of weight loss.
(thermogravimetric, TG) and weight derivative (differential thermogravimetric, DTG) curves of carbonated sand and silt that were mixed with 10% lime at $\omega = 15\%$, and carbonated for 3 or 24 hours. Based on TG and DTG, it is evident that maximum two distinct weight changes were observed in the temperature range between 350-420°C and 550-700°C, respectively. These two temperature ranges correspond to the decomposition of $Ca(OH)_2$ and $CaCO_3$, respectively Scrivener et al. (2016). $Ca(OH)_2$ decomposes into $CaO$ and $H_2O$ while $CaCO_3$ decomposes into $CaO$ and $CO_2$ gas. The weight loss associated with the decomposition of $Ca(OH)_2$ and $CaCO_3$ is due to the formation of $H_2O$ vapor and $CO_2$ gas, respectively. Results revealed that lime (10%) mixed silt had significantly higher weight loss associated with $CaCO_3$ than the carbonated sand mixed with the same amount of lime after 3 or 24 hours of carbonation. On the other hand, weight loss associated with $Ca(OH)_2$ was negligible for carbonated silt whereas carbonated sand had a considerable weight loss. This implied that carbonated sand had a considerable amount of unreacted $Ca(OH)_2$, representing less $CaCO_3$ binder formation for the same carbonation time. The difference in $CaCO_3$ binder formation in carbonated sand and silt for the same amount of lime and carbonation period will be discussed in the following sections. Note that all the lime-mixed carbonated granular soils showed a consistent temperature range between 320-420°C and 450-720°C, considered based on the DTG peaks, for weight loss associated with $Ca(OH)_2$ and $CaCO_3$, respectively Ho et al. (2018). Based on the weight loss percentage ($WL$) from TGA and the known molecular mass of each component, the amount of unreacted $Ca(OH)_2$ (if any) and $CaCO_3$ binder content can be determined as follows (see equations 2.9, 2.10). The amount of $CaCO_3$ and $Ca(OH)_2$ content is expressed herein as a percentage of total mass (i.e. dry soil-lime-$CaCO_3$ binder) after carbonation which can be converted to as a percentage of soil mass only to obtain $\beta_B$ (equation 2.5) and $\beta_{Lf}$ (i.e. unreacted lime content after carbonation).

$$CaCO_3(\%) = \frac{m_{CaCO_3}}{m_{CO_2}} \times WL_{CaCO_3}$$

(2.9)
\[ Ca(OH)_2(\%) = \frac{m_{Ca(OH)_2}}{m_{H_2O}} \times WL_{Ca(OH)_2} \]  

(2.10)

where \( WL_{CaCO_3} \) and \( WL_{Ca(OH)_2} \) are the percent weight loss associated with decomposition of \( CaCO_3 \) and \( Ca(OH)_2 \) respectively, \( m_{CaCO_3} = \) molecular mass of \( CaCO_3 = 100 \ g/mol \), \( m_{CO_2} = \) molecular mass of \( CO_2 = 44 \ g/mol \), \( m_{Ca(OH)_2} = \) molecular mass of \( Ca(OH)_2 = 74 \ g/mol \), \( m_{H_2O} = \) molecular mass of \( H_2O = 18 \ g/mol \).

A total of 132 UCS tests and 88 TGA tests were performed on sand and silt specimens. Table 2.3 summarizes the test conditions.

Table 2.3: Summary of UCS and TGA tests performed on sand and silt specimens.

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Soil Type</th>
<th>( t_c ) (hours)</th>
<th>( e )</th>
<th>( \gamma_d ) (kN/m³)</th>
<th>( \omega ) (%)</th>
<th>( S_r ) (%)</th>
<th>UCS Tests</th>
<th>TGA Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP1</td>
<td>Sand (SP)</td>
<td>3, 24, 72, 120, 168</td>
<td>0.53</td>
<td>16.7</td>
<td>5.0</td>
<td>24.6</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>SP2</td>
<td>Sand (SP)</td>
<td>3, 24, 72, 120, 168</td>
<td>0.49</td>
<td>17.2</td>
<td>7.7</td>
<td>41.0</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>SP3</td>
<td>Sand (SP)</td>
<td>3, 24, 72, 120, 168</td>
<td>0.48</td>
<td>17.3</td>
<td>9.7</td>
<td>52.7</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>SP4</td>
<td>Sand (SP)</td>
<td>3, 24, 72, 120, 168</td>
<td>0.48</td>
<td>17.3</td>
<td>14.1</td>
<td>76.7</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>SP5</td>
<td>Sand (SP)</td>
<td>24, 72</td>
<td>0.65</td>
<td>15.5</td>
<td>7.3</td>
<td>29.4</td>
<td>6</td>
<td>4</td>
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<td>0.64</td>
<td>15.6</td>
<td>13.7</td>
<td>56.2</td>
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<td>0.74</td>
<td>17.7</td>
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<td>SP8</td>
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<td>12.1</td>
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<td>61.4</td>
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Definitions: \( t_c \) = carbonation period; \( e \) = initial void ratio; \( \omega \) = initial gravimetric water content; \( S_r \) = initial degree of saturation; \( \gamma_d \) = dry unit weight; UCS = Unconfined Compression Strength; TGA = Thermogravimetric Analysis

2.4 Experimental Results

Presented herein are results that focus on state parameters influencing i.) the rate of mechanical improvement and binder formation and ii.) degree of mechanical improvement.
2.4.1 Rate of Binder Formation

To explore the relative influence of the degree of saturation and the volumetric air and water content on the rate of carbonation, both sand and silt soils were tested. The use of sand and silt allowed examination of upper- and lower-bound densities, and associated void ratios and porosities, for soils considered in this study; i.e. specimens with the highest and lowest densities could be reconstituted using sand and silt, respectively. The upper-bound density was tested using sand with a target void ratio of $e \approx 0.49$ and the lower-bound density was tested using the silt and a target void ratio of $e \approx 1.09$. The influence of density on mechanical improvement is discussed later.

Figure 2.4 shows the stress-strain curves from UCS tests performed on carbonated sand specimens at degrees of saturation, $S_r = 25, 41, 53, \text{ and } 77\%$. Changes in strength—a proxy for changes in binder content—are illustrated for carbonation times, $t_c = 3, 24, 72, 120, \text{ and } 168\text{ hours}$ (Figure 2.4a-e). Generally, strength gains occurred more rapidly in specimens with lower $S_r$ values (Figure 2.4b), which may be attributed to higher volumetric air contents and a more interconnected gas-phase in the voids. For the sand specimens with $S_r$ less than 53%, similar gains in strength were achieved by $t_c = 72\text{ hours}$ (Figure 2.4c), though strengths didn’t change substantially when carbonated for longer periods (Figure 2.4d-e); i.e. binder contents didn’t change substantially after $t_c = 72\text{ hours}$. However, substantial gains in strength were observed after $t_c = 168\text{ hours}$ for sand specimens with $S_r = 77\%$ (Figure 2.4e). This delayed strength gain is likely attributed to the hindrance of $CO_2$ gas flow caused by the transition from a continuous gas- to water-phase within the voids expected at the higher $S_r = 77\%$. 
Figure 2.4: Temporal changes in unconfined compressive strength for sand carbonated at different degrees of saturation: a.) $t_c = 3$ hours; b.) $t_c = 24$ hours; c.) $t_c = 72$ hours; d.) $t_c = 120$ hours; e.) $t_c = 168$ hours.
Figure 2.5 shows the stress-strain curves from UCS tests performed on carbonated silt specimens at degrees of saturation, $S_r = 27, 40, 49,$ and $61\%$ for different carbonation times. Similar to sand, silt specimens with relatively low $S_r$ values (less than $\approx 50\%$) gain strength relatively quickly; again, a notable delay was observed for the specimen with the highest $S_r$ (Figure 2.5d). The results from the sand and silt tests highlight the role that $S_r$ plays on the rate of strength gain, which is really linked to the rate of binder formation. Figure 2.6 illustrates that strength gains are associated with the amount of binder formed—the rate of which, is governed to a large extent by the degree of saturation and associated intrinsic mobility of gas in the soil matrix—not the carbonation period.
Figure 2.5: Temporal changes in unconfined compressive strength for silt carbonated at different degrees of saturation: a.) $t_c = 3$ hours; b.) $t_c = 24$ hours; c.) $t_c = 72$ hours; d.) $t_c = 168$ hours.
Figure 2.6: Unconfined compressive strength vs. gravimetric binder content at the center of: a.) sand specimens reconstituted at $e_o = 0.49$ and b.) silt specimens reconstituted at $e_o = 1.09$. 
Figure 2.7 shows temporal changes in $\beta_B$ and DoC at the center of sand (Figure 2.7a) and silt (Figure 2.7b) specimens carbonated at different $S_r$. Both soil types ultimately reached similar DoCs and gravimetric binder contents irrespective of the initial $S_r$. The maximum DoCs are not 100% because the lime was not pure $Ca(OH)_2$, which is assumed in Equations 2.7 and 2.8. TGA results indicate lime used in the study was approximately 85% $Ca(OH)_2$, similar to the maximum DoCs achieved.

Though $S_r$ plays a role, it is not the only parameter governing the rate of carbonation. There are notable differences in the carbonation periods required to achieve the maximum strength gains observed in each soil type (at the same $S_r$). Sand specimens reconstituted at $S_r$ values less than 50% reached their maximum BC and DoC within approximately 72 hours, while silt specimens with similar $S_r$ values were near their maximum DoC within 24 hours. Also shown in Figure 2.7 are the corresponding volumetric air contents, $\theta_a$, and volumetric water contents, $\theta_w$ for different $S_r$. Volumetric air contents were greater in the silt specimens than in the denser sand specimens prepared at a similar $S_r$. Thus, volumetric air content, which influences the effective mobility of gas in the soil matrix, can be partly attributed to the greater rate of binder formation in silt, though not entirely (discussed more later).
Figure 2.7: Temporal changes in the gravimetric binder content and degree of carbonation at the center of soil specimens for different degrees of saturation for: a.) sand and b.) silt. The corresponding volumetric air contents and water contents are also shown.
Figure 2.8a compares increases in $\beta_B$ with carbonation time for the sand and silt specimens carbonated at similar $S_r$, but below threshold $S_r$ values where pore water significantly obstructed mobility of $CO_2$ gas. Differences in the time required to reach $\beta_{B,max}$ are due to differences in the soils’ initial state ($\theta_a$ and $\theta_w$), but also differences in the mass of lime that was carbonated. The mass of lime in silt was less than in the sand because the specimens were prepared at different densities, but the same $\beta_L$; i.e. a similar DoC does not imply that the same amount of $CaCO_3$ was precipitated throughout the specimen.

Figure 2.8b shows how the volumetric BC changes with carbonation time, which allows for a direct comparison of the amount of binder formed in sand and silt specimens. The maximum $\theta_B$ for sand is greater than for silt because the mass of soil, and thus lime (Equation 2.6), was greater for the denser sand specimens. A comparison of the state parameters on the carbonation rate can be made by examining the difference in $\theta_B$ at the same carbonation time (e.g. red arrows in Figure 2.8b) or differences in carbonation time required to achieve the same $\theta_B$ (e.g. blue arrows in Figure 2.8b); it can be seen that the rate of increase in $\theta_B$ is greater for the silt when compared with sand specimens at similar $S_r$ values.
Figure 2.8: Differences in the rate of binder formation in the sand and silt based on the: a.) gravimetric binder content; and b.) the volumetric binder content.
Given that finer-grained soils are typically associated with lower fluid conductivities (e.g. water), the higher rate of carbonation in the silt is not readily intuitive. In Figure 2.9, temporal changes in volumetric binder content are compared for sand and silt specimens with the same $\theta_w$ to isolate the influence of $\theta_a$ on gas mobility (Figure 2.9a). Silt specimens, which had a greater $\theta_a$, carbonated more rapidly. The comparisons here demonstrate that the mobility of gas—a non-viscous fluid—is more heavily influenced by the volumetric air content than soil fabric and grain size (assuming gas connectivity in the pores). As discussed previously in the context of the UCS tests (Figures 2.4 and 2.5) and illustrated in Figure 2.7, there is a threshold $S_r$ (greater than 50 to 60%) above which there is continuity of the water-phase throughout the pores that obstruct the mobility of gas and suppresses the rate of carbonation (Moldrup et al., 2000, 2001).

Figure 2.9b compares temporal changes in $\theta_B$ for sand and silt specimens where $\theta_a$ are equal to illustrate the influence of $\theta_w$ (Figure 2.9b). Silt specimens with a greater $\theta_w$ carbonated faster. Also, sand and silt specimens with the highest $\theta_a$ (lowest $S_r$) did not reach their maximum DoC fastest. When $S_r \approx 40\%$, the maximum DoC was achieved in the shortest amount of time (Figure 2.7). This demonstrates that $\theta_w$ and the amount of water serving as a “host medium” to dissolved constituents influences the carbonation rate (recall equations 2.1 and 2.2); i.e. more water permits the dissolution of more $CO_2$ gas and lime that facilities the reaction kinetics during carbonation.
Figure 2.9: Comparison of increases in volumetric binder content for: a.) sand and silt specimens with the same volumetric water content and $S_r$ values associated with gas-phase connectivity throughout the pores; b.) sand and silt specimens with the same volumetric air content and $S_r$ values associated with gas-phase connectivity throughout the pores.
For soils examined here, $S_r$ was seen as a proxy to establish whether there is likely continuity of the water- or gas-phase in the voids. Assuming continuity of the gas-phase, $\theta_a$ is a proxy for gas mobility and the amount of $CO_2$ gas (essential ingredient) that can be conveyed to lime-mixed soil. The state parameter $\theta_w$ is a proxy for the instantaneous amount of lime and $CO_2$ gas that can dissolve and react throughout the carbonation period (i.e. reaction kinetics). There is a balance between $\theta_a$, $\theta_w$, and $S_r$ that can be achieved to optimize the rate of carbonation. However, it may be difficult to control this optimum condition in a field/construction setting. Based on observations from this study, it would be most prudent to ensure continuity of the gas-phase within the pore-network and to avoid potential pore water blockages at higher $S_r$, as the rate of carbonation remains relatively high even at low water contents.

### 2.4.2 Mechanical Strength and Stiffness

The preceding section explored void ratios that approximately bounded the density domain across both soil types to examine the influence of $\theta_a$ and $\theta_w$ on the rate of carbonation. The influence of density across each soil type was explored to evaluate its influence on the degree of mechanical improvement in the sand and silt. Figure 2.10 shows representative stress-strain curves from UCS tests for sand (Figure 2.10a) and silt (Figure 2.10b) specimens carbonated at different initial void ratios. In Figure 2.10, all specimens had a high DoC (i.e. maximum DoC attainable based on available $Ca(OH)_2$ in the lime). Though specimens were prepared at the same $\beta_L = 10\%$, the void ratios associated with similar strengths for the sand and silt differ significantly; silt specimens achieve similar strengths at lower densities (higher void ratios).
Figure 2.10: Representative stress-strain curves from UCS tests performed on a.) sand and b.) silt specimens at different densities. Specimens were carbonated sufficiently such that the maximum DoC attainable was achieved.
Figure 2.11a summarizes the UCS tests performed on sand specimens at different void ratios, which are categorized as “loose,” “medium dense,” and “dense.” The volumetric BCs (top) and corresponding gravimetric BCs (bottom) in each density range are also shown. The comparisons clearly demonstrate the substantial increase in carbonated strength as void ratio decreases and density increases for relatively high DoCs ranging between 68-93%, which are the tan colored symbols where $\theta_B = 5.4-6.8\%$. For the “dense” sands, even subtle changes in void ratio have a significant influence on the UCS when $\theta_B$ was greater than 5.4%; i.e. density has an exponential influence as it increases (and void ratio decreases).

The results in Figure 2.11a also illustrate that the degree of strength improvement is influenced by the BC, though its relative influence is dependent on the density. Though the densities for finer-grained silt specimens differ, Figure 2.11b illustrates that the influence of void ratio on strength improvement is similar to that of sand. To achieve similar strengths as the sand, the density and volumetric binder content in silt are lower.

For cement stabilized soils, Consoli et al. (2007) demonstrated that rates of change in UCS with the voids volume and cement volume are significantly different, but recognized that unifying the influence of each to predict strength improvement was critical to streamlining predictive models. They were the first to develop a relationship between UCS and the influence of density and BC using an adjusted porosity and volumetric BC ratio,

$$\nabla = \frac{\eta}{(\theta_B)^b},$$

where

$$q_u = A \left( \frac{\eta}{(\theta_B)^b} \right)^{-B} = A \cdot \nabla^{-B} \tag{2.11}$$

and where $\eta = 1/(1 + e)$ is porosity expressed as a percentage, and A, B, and b are scalars that relate to the soil type (e.g. coarse vs. fine-grained) and the soil’s critical state condition and strength of the binder phase (Diambra et al., 2017); the latter strength component is by far the most influential and primarily governs in low-stress environments (this study). The use of an adjusted porosity and volumetric BC ratio has been shown to work well to predict the influence of density and BC across many soil types and for several
chemical additives used to generate a binder (e.g. Consoli et al., 2009, 2011a,b, 2016, 2018, 2020, 2021; dos Santos et al., 2022).

Figure 2.11: Influence of void ratio (i.e. density) on carbonated unconfined compressive strength in: a) sand; and b.) silt. The void ratio ranges considered loose, medium-dense, and dense for each soil type are shown. The top and bottom figures indicate volumetric binder content and the corresponding gravimetric binder content, respectively. Only carbonated specimens with $\theta_B$ greater than 2% were considered due to substantial non-homogeneity of the binder phase in soils with very low binder contents.

Diambra et al. (2017) demonstrated a theoretical basis for equation 2.11 and showed that $b = 1/B$, but with the simplifying assumptions that cemented materials are isotropic, contributions of soil and binder strength can be superimposed, and that there is
strain-compatibility of the soil and binder phases in the composite soil material. Enforcing this condition, Figure 2.12 shows the power law relationship between $\nabla$ and UCS. The optimized coefficients were $b = 1/B = 0.34$ for the sand and $b = 1/B = 0.13$ for the silt, with the coefficients of determination, $R^2$, equal to 0.91 and 0.94, respectively. As soils become more fine-grained, the optimized model coefficients $b$ and $A$ are expected to decrease and increase, respectively, which was the case for the carbonated soils in this study (Diambra et al., 2017).

In their original study, Consoli et al. (2007) used a value of $b = 0.28$ acting on the volumetric BC, which has since been used in other studies examining cement-stabilized soils (e.g. Consoli et al., 2016). Figure 2.13a shows the optimized power-law relationship for the sand and silt when $b = 0.28$ so that carbonated soils from this study could be compared with cement-stabilized soils. Changes in $R^2$ for the optimized conditions were negligible, thus optimizing using $b = 0.28$ is reasonable for the carbonated soils. Also shown in Figure 2.13a is the cement-stabilized clayey sand presented by Consoli et al. (2007), which aligns with the data and relationship presented for the carbonated sand. However, the silt...
data is shifted to the right of the carbonated and cement-stabilized sand data, which is expected. The shift in the silt data reflects the lower densities (higher porosities) and lower volumetric binder contents needed to achieve similar strengths as that of sand (recall Figure 2.12). Figure 2.13b shows the power-law relationships for the carbonated sand and silt plotted with data for cement-stabilized fine-grained soils (silts and clays) presented by Consoli et al. (2016), which are also shifted from right from the Consoli et al. (2007) relationship; for reference, note that the blue square symbols in Figure 2.13b are also clayey sand, the same soil type shown in Figure 2.13a. The comparison between the carbonated soils and the cement-stabilized soils investigated independently by others, demonstrates that equivalent strengths can be achieved under similar conditions (i.e. density and binder content) using lime to precipitate $CaCO_3$ via carbonation.

A benefit of using the same adjusted porosity and volumetric BC ratio, is that it opens up the possibility to develop a unique relationship applicable to several soil types (Consoli et al., 2016). A unique relationship for the carbonated soils can be made by normalizing their UCS at a reference ratio, $\nabla_{\text{ref}}$, that’s common to all soil types. For the sand and silt, this was the case for $\nabla_{\text{ref}} = 30$ when $b = 0.28$. The normalized UCS is then evaluated,

$$Q_u = \frac{q_u}{q_u \text{ at } \nabla_{\text{ref}}} = C \left( \frac{\eta}{(\theta_B)^{0.28}} \right)^{-D} \approx (\nabla_{\text{ref}})^D \cdot (\nabla)^{-D}$$

(2.12)

where $C$ is a scalar dependent on the reference adjusted porosity and volumetric BC ratio, and $D$ is a scalar, similar to $B$ in equation 2.11. For a normalized relationship to work well across multiple soil types, the optimized parameters should result in $\eta/(\theta_B)^{0.28} \approx (\nabla_{\text{ref}})^D$. Figure 2.13c shows $Q_u$ for a $\nabla_{\text{ref}} = 30$, where it can be seen that data for the sand and silt collapse to the same line defined by equation 2.12 $C = 4.05 \times 10^5 \approx (\nabla_{\text{ref}})^D$ and $R^2 = 0.94$. The normalized $Q_u$-relationship for carbonated soils in this study is practically identical to cement-stabilized materials, as illustrated by the comparison with a broad range of cement-stabilized soils shown in Figure 2.13d. This comparison further highlights
that soil carbonation with lime performance that can be achieved by carbonating soils mixed with lime relative to cement-mixed materials.

Figure 2.13: The upper plots show the unconfined compressive strength and the adjusted porosity and volumetric binder content ratio ($\nabla = \eta/(\theta_B)^{0.28}$) for carbonated sand and silt soils shown against data for cement-stabilized soils: a.) clayey sand data presented by Consoli et al. (2007); b.) fine-grained silt and clay soils presented by Consoli et al. (2016). Note that $\theta_B$ is the volumetric cement content for Consoli et al. (2007, 2016) data. The lower plots show: c.) optimized normalized unconfined compressive strength relationship for all carbonated soils sand and silt soils with $\theta_B$ greater than 2%; d.) optimized normalized unconfined compressive strength relationship for all carbonated soils compared with many cement-stabilized soils presented in Consoli et al. (2016). A $\nabla_{ref} = 30$ and $b = 0.28$ was used for both the carbonated and cement-stabilized soils presented by Consoli et al. (2016).
From a practical perspective, a normalized UCS relationship is also useful when it is shown to be applicable to both coarse-grained and fine-grained silt soils, because an understanding of the influence that density and volumetric BC have on any soil type can theoretically be achieved with a limited number of tests. In theory, testing at one value of $\nabla$ would provide an understanding of strength across the entire $\nabla$-domain. Though the relationship shown in Figures 2.13d agrees well with the data, Consoli et al. (2016) stopped short of demonstrating how the normalized $Q_u$-model performed for the individual cement-stabilized soils considered in their study. In some cases, normalization in this manner can be deceptive and provide an unfounded sense of reliability with respect to predictive capabilities. Figure 2.14 shows how the optimized $Q_u$-model predicts strength for the carbonated sand and silt, which provides good agreement with both soil types. A better agreement was observed with the sand, for which there was more data used to optimize the $Q_u$-model parameters. Though this demonstrates the utility of $Q_u$ is promising for carbonated soils, a limited number of soil types were investigated. More soil types will need to be tested to verify the relationship shown in Figure 2.13c is applicable to other materials not investigated in this study.

![Graphs showing predicted strength for carbonated sand and silt](image.png)

Figure 2.14: Unconfined compressive strength predicted using the optimized $Q_u$-model developed for: a.) carbonated sand and b.) carbonated silts.
Figure 2.15 summarized the mechanical strain, strength (i.e. Unconfined compressive strength, $q_u$), and stiffness (i.e. secant Young’s modulus at 50% of the ultimate strength, $E_{50}$) of carbonated soils and their relationship. A typical example to determine the $E_{50}$ from the stress-strain curve is presented in Figure 2.16 considering a correction for the sitting axial strain. Figure 2.15a shows the relationship between $E_{50}$ and strain ($\epsilon_{50}$) at 50% of the $q_u$. It is observed that $E_{50}$ of carbonated soils generally increases with $\epsilon_{50}$ with a significant increase between 0.5-2.0%. Thereafter, the increase is not prominent; the maximum $\epsilon_{50}$ is about 3%. Figure 2.15b shows the relationship between $q_u$ and strain at $q_u$ (i.e. failure), ($\epsilon_f$). It is revealed that $q_u$ increases with $\epsilon_f$, and a linear trend is observed in their relation.

Figure 2.15c illustrates the relationship between $q_u$ and $E_{50}$. The stiffness of carbonated soil increases significantly until $q_u \approx 1$ MPa, and then increases marginally with increasing $q_u$ thereafter. The similarity of the relationship between $E_{50}$ and $q_u$ for both the sand and silt implies that the binder-phase and interparticle bonding is primarily governing the stiffness of the carbonated sands and silts. Recall that similar strengths were achieved in the silt at lower densities (higher void ratios and porosities) than carbonated sand (Figure 2.11); i.e. if the soil matrix and voids volume substantially influenced compressibility, it would be reflected by a difference in stiffness at similar strengths.

Figure 2.15d shows the empirical power law relationship between $q_u$ and $E_{50}/q_u$ for the sand and silt ($R^2 = 0.89$). The strong relationship between $q_u$ and normalized $E_{50}$ is useful, as it expands the utility of the predictive models for strength. The preceding $q_u$ relationships (equations 2.11 or 2.12) can now be applied to predict stiffness as well, with an understanding that more soil types should be investigated to validate the applicability of the “generalized” $Q_u$-model across a broad range of soil types.
Figure 2.15: Summary of mechanical strain, strength and stiffness of carbonated soils. a.) relationship between secant Young’s modulus ($E_{50}$) and strain ($\epsilon_{50}$) at 50% of the ultimate strength; Relationship between unconfined compressive strength, UCS ($q_u$) and: b.) strain at failure, $\epsilon_f$; c.) secant Young’s modulus at 50% of the ultimate strength, $E_{50}$; and d.) Young’s modulus normalized by the unconfined compressive strength. Data in part d only considered specimens with strengths greater than 0.3 MPa.
Steps for $E_{50}$ determination -

a.) Draw a straight line through the linear portion of q-ε curve that intersects the horizontal axis to determine the sitting axial strain, $\varepsilon_s$

b.) Subtract $\varepsilon_s$ from $\varepsilon_{qu}$ and $\varepsilon_{0.5qu}$ to determine the corrected failure strain, $\varepsilon_f$ at $q_u$, and axial strain, $\varepsilon_{50}$ at 0.5$q_u$

c.) $E_{50} = \frac{0.5q_u}{\varepsilon_{50}}$

Figure 2.16: An example to determine the secant Young’s modulus at 50% of the ultimate strength, $E_{50}$ from the stress-strain plot.
2.5 Discussion

Understanding the parameters of the functionality on performance and implementation is essential to extend carbonation from elemental- to field-scales. Development of appropriate specifications will ultimately need to balance the influence of water content on compaction and strength gain with its impact on gas mobility through the soil matrix—which must be understood to efficiently carbonate soil on larger scales. During construction, a contractor is likely to mix soil at specified gravimetric lime and water contents to achieve a desired porosity or density, which is dependent on the compaction energy/equipment. Figure 2.17 synthesizes the predicted strengths (top row) and stiffness (middle row) that can be achieved at different gravimetric lime contents. The gravimetric lime content can be easily related to the final volumetric binder content, and thus predicted strength (Figure 2.13a,b) and stiffness (Figure 2.15) of carbonated non-plastic sands and silts from this study at different densities, where,

\[
\theta_B = \frac{\beta_B/G_B}{(1 + e_f)(1/G_s + \beta_B/G_B + \beta_{LF}/G_L)} \tag{2.13}
\]

and where \(G_s\), \(G_B\), and \(G_L\) are the specific gravity of the soil particles, calcium carbonate binder, and lime, respectively. Any final unreacted lime \(\beta_{LF} = \beta_L - (74/100)\beta_B\) and \(e_f\) is the final void ratio,

\[
e_f = \frac{(1/G_s + \beta_L/G_L)(1 + e_o)}{1/G_s + \beta_{LF}/G_L + \beta_B/G_B} - 1 \tag{2.14}
\]

Note that for typical lime contents, the void volume only decreases from 1% to 3% due to carbonation. Based on the findings from this study, Figure 2.17 also shows the approximate ideal conditions to carbonate sand and silt (bottom row), delimiting limits where the water-phase in the void volume is not expected to obstruct the mobility of gas and significantly suppress the rate of carbonation, but also where the water content should be sufficient to facilitate the carbonation reaction.
Figure 2.17: Influence of porosity and lime content on the predicted unconfined compressive strength (top row) and stiffness (middle row), as well as the influence of water content on the degree of saturation at different porosities, showing the approximate ideal limits to carbonate (bottom row) for: a.) sand and b.) silt. Lime contents refer to the amount of $Ca(OH)_2$ that has fully reacted to form $CaCO_3$. 

Notes: (I) Suppressed carbonation rate anticipated (continuous water-phase in the voids); (II) Transition zone; (III) Efficient carbonation rate (continuous gas-phase in the voids); (IV) Untested
Figure 2.18 illustrates the $CO_2$ emissions associated with hydrated lime production from limestone that is predominantly $CaCO_3$. During production, limestone is calcined and decomposes into quick lime, $CaO$, resulting in “process-based” carbon emissions ($CO_2$ released due to the decomposition of limestone) and “combustion-based” emissions (energy/fuels needed to heat kilns during the calcination process). Process-based emission account for at least two-thirds of $CO_2$ emissions during production (Stork et al., 2014; Campo et al., 2021). After calcination, water is added to quick lime to produce the hydrated (or slaked) lime used in this study, which can then be carbonated, once again resulting in $CaCO_3$ that forms a useful binder to stabilize soils. In this study it was demonstrated that all $Ca(OH)_2$ was effectively carbonated; recall that DoCs were less than 100% (Figure 2.7) simply because pure hydrated lime was not used ($\approx$85-90% $Ca(OH)_2$). Thus, there is the potential to sequester the same amount attributed to process-based emissions, reducing the carbon footprint associated with lime production by more than two-thirds.

![Flow chart illustrating carbon dioxide emissions during production and sequestration of carbon dioxide during soil carbonation, which is approximately equivalent to process-based emissions.](image)

Figure 2.18: Flow chart illustrating carbon dioxide emissions during production and sequestration of carbon dioxide during soil carbonation, which is approximately equivalent to process-based emissions.
For comparison, approximately 0.95 tonne of $CO_2$ is emitted per tonne of Portland cement during production (Yi et al., 2013b, 2014; Higgins, 2005; Cai et al., 2015), while approximately 1.09 tonne/tonne is emitted for lime (Stork et al., 2014). Approximately 0.75 tonne/tonne is process-based emissions for lime; thus, production-based $CO_2$ could reduce to 0.35 tonne/tonne for lime when carbonation is employed—a substantial net reduction in $CO_2$ emissions associated with the use of this chemical additive for soil stabilization relative to Portland cement.

2.6 Summary and Conclusions

The use of hydrated lime to chemically stabilize non-plastic (i.e. non-reactive) soils via carbonation was investigated. Reconstituted specimens of sand and silt mixed with hydrated lime were systematically prepared at different initial densities and degrees of saturation, and then carbonated under low $CO_2$ pressures for varying amounts of time. The influence of initial state parameters on the rate of binder formation and degree of mechanical improvement were evaluated. The relationship between density and binder content on strength for the sand and silt was compared with strengths observed by others for soils stabilized with cement, a conventional additive for chemical stabilization. A relationship between UCS and stiffness for carbonated soils was also developed. The potential benefits of soil carbonation with lime, including reducing the carbon footprint relative to conventional additives for non-plastic soils, were discussed.

It was demonstrated that hydrated lime may be used to rapidly generate a carbonate binder in non-plastic soils by introducing $CO_2$ gas that triggers the carbonation reaction. The rate of binder formation in carbonated soil is highly dependent on gas mobility in the soil matrix, which is governed to a large extent by the degree of saturation and volumetric air content. In soils with degrees of saturation below 50%, a relatively rapid increase in the binder content was observed (all else being equal) compared with higher degrees of saturation. This is attributed to a continuous or near-continuous gas-phase through the
voids. Soils with degrees of saturation greater than 50-60%—threshold values where a
transition from a continuous gas-phase to a continuous water-phase in the void space is
expected—the rate of binder formation decreased substantially because the water-phase
begins to obstruct the movement of gas in the soil matrix. It was also demonstrated that
volumetric air and water contents are also positively correlated to the rate of binder
formation, which is why the volumetric binder content increased more rapidly in silt
prepared at looser densities than sand. A higher gas volume in the soil matrix increases the
mobility of gas, while more water permits the dissolution of more lime and carbon dioxide
gas, which hosts chemical constituents and facilitates the reaction. Attempting to optimize
the air and water contents to achieve the greatest carbonation rate would likely be difficult
(if not impossible) to achieve in a field setting. It would be most prudent to ensure the
continuity of the gas-phase and avoid pore water barriers in the voids at high water
contents, as the rate of carbonation remains relatively high even at low water contents.

The calcium carbonate binder can substantially increase the mechanical attributes of
soil chemically improved via carbonation, thus expanding the applicability of lime as a
chemical additive that can be used to treat non-plastic soils. Like other chemically
stabilized soils, the strength is highly dependent on the density, volumetric binder content,
and soil type. The finer-grained silt soil achieved equivalent strengths as sand at lower
densities and volumetric binder contents. The void volume (density) has a limited influence
on the compressibility of carbonated materials, which is governed primarily by the
binder-phase. It was shown that stiffness correlates well, and in a similar manner, with the
unconfined compression strength of sand and silt.

Comparisons demonstrated that carbonated strengths in this study had a very similar
dependence on soil type, density, and binder content as cement-stabilized soils. Moreover,
equivalent strengths can be achieved in soils carbonated with hydrated lime as conventional
cement-stabilized materials. However, while both soil carbonation and conventional
methods for chemical stabilization require the mixing of chemical additives, carbonation
requires the added step of introducing carbon dioxide. This study helped elucidate the parameters of functionality that can help streamline the discovery of processes that enable the implementation of soil carbonation in the field. If successful, carbonation has the potential to substantially reduce production-based emissions associated with chemical additives. For example, the total carbon dioxide emissions for Portland cement are on average 0.95 tonne per tonne of cement. By employing carbonation, production-based emissions associated with quick lime could be reduced from 1.1 tonne/tonne to 0.35 tonne/tonne—approximately a third of that associated with Portland cement production.
CHAPTER 3
ACCELERATED SURFACE CARBONATION: SOIL BOX EXPERIMENT

3.1 Introduction

Chemical stabilization is a ground modification method, whereby chemical additives (e.g. cement, lime, fly ash) are mixed with soil and react to generate a binder that improves the mechanical properties of targeted materials (Sherwood, 1993; Consoli et al., 2007; Toohey et al., 2013; Yi et al., 2014; Consoli et al., 2016; Puppala, 2016; Behnood, 2018; Dash & Hussain, 2012). This method of construction is often adopted to stabilize soils supporting roadways, runways, railways, erosion protection, shallow slope protection, foundations, etc., and is now widespread globally.

Soil carbonation is a potentially novel approach, whereby carbon dioxide would be introduced in soil mixed with chemical additives (same as conventional methods) and sequestered to generate a carbonate binder. The use of carbonate binders (De Silva et al., 2006, 2009; Ashraf, 2016) shows potential to be an alternative approach to chemical stabilization of soil (Fasihnikoutalab et al., 2017). Initial studies focused on the use of magnesium-based alkali sources, including reactive magnesia ($\text{MgO}$) (Yi et al., 2013b; Cai et al., 2015) and olivine ($\text{Mg}_2\text{SiO}_4$) (Fasihnikoutalab et al., 2017). However, only 0.35 million tons of magnesium compounds, including reactive magnesia, were produced in the United States in 2020 (Merrill, 2021). This is a small fraction when compared with other minerals in the United States, like quick and hydrated lime (16 million tons) (Apodaca, 2021), which is more likely to be relied on as an alkali source. Lime is a chemical additive commonly used with high plasticity, or “reactive,” soils to chemically stabilize and improve subgrade materials and generate a binder via a long-term pozzolanic reaction (Little, 1999; Little & Nair, 2009). However, it has been shown that soils containing lime will carbonate under natural atmospheric conditions (e.g. Das et al., 2021, 2022; Fan et al., 2023) and this...
process can be accelerated to chemically stabilize soil (e.g. Hossen et al., 2020; Xu et al., 2020), and with similar strength gains as conventional additives, like cement (Chapter 2).

Moreover, carbonation has the potential to substantially reduce carbon emissions associated with the production of chemical additives. Production-based \( CO_2 \) emissions for cement and lime are approximately 0.95 and 1.1 tonne per tonne of the chemical additive produced, respectively (Yi et al., 2013b, 2014; Higgins, 2005; Cai et al., 2015; Stork et al., 2014). However, in Chapter 2 it was demonstrated that nearly 100% of process-based emissions can be sequestered when carbonating with hydrated lime, which would reduce the total production-based emissions by nearly two-thirds. The construction industry in the United States and Europe alone uses about 20% of lime produced worldwide (Dowling et al., 2015). Thus, carbonation has the potential to substantially reduce \( CO_2 \) emissions associated with lime.

Aside from small bench-scale experiments exploring the potential to create carbonated columns of soil (Yi et al., 2013a; Fasihnikoutalab et al., 2016), little has been done to evaluate potential methods that would enable carbonation in the field (Li et al., 2023). A key difference between conventional chemical stabilization and “accelerated” carbonation is that \( CO_2 \) gas must be introduced after the soil is mixed with chemical additives. Thus, one of the primary challenges engineers and contractors are faced with is developing scalable processes to introduce \( CO_2 \) gas in soil that could translate to field settings.

This study focuses on the evaluation of a “surface carbonation” approach with the potential to be applied over relatively large areas, which refers to the introduction of \( CO_2 \) beneath a near-ground-surface seal intended to contain and enforce vertical penetration of \( CO_2 \) gas into the ground. It is envisioned that surface carbonation could be suitable for situations where there is typically some attempt to control the water content and density of soils mixed with chemical additives; e.g. shallow subgrade stabilization for roadway construction or similar. Ensuring continuity of a gas-phase in the soil voids has been shown to be a key state parameter that governs the rate of binder formation, as it facilitates the
diffusion of gas in the soil matrix (Moldrup et al., 2000, 2001). Large-scale surface carbonation experiments were carried out to evaluate: a.) the depth of soil carbonation that can be achieved under low $CO_2$ pressures ($\approx 0$ gauge); b.) the rate of carbonation and binder formation in lime-mixed soil; and c.) the degree of mechanical improvement.

3.2 Surface Carbonation with Hydrated Lime

3.2.1 Theory

Surface carbonation with hydrated lime, referred to herein as lime, may be characterized as a two-step process that requires: 1.) the mixing of soil, lime, and water at a desired density (same as conventional chemical stabilization); followed by 2.) the introduction of carbon dioxide gas to accelerate the carbonation reaction, which differs from conventional chemical stabilization. In a soil-lime-water mixture, the solid \([s = \text{solid}]\) lime dissolves in pore water \([l = \text{liquid}]\) and dissociates into aqueous-phase \([aq = \text{dissolved}]\) cations, \(Ca^{2+}\), and anions, \(OH^-\),

\[
Ca(OH)_2[s] + H_2O[l] \leftrightarrow Ca^{2+}(aq) + 2OH^-(aq)
\]  

(3.1)

Carbon dioxide gas \([g = \text{gas}]\) is then introduced into the soil matrix and dissolves in the pore water, producing a weak carbonic acid \((H_2CO_3)\) that dissociates into \(H^+\) and bicarbonate (i.e. \(HCO^-\)) or carbonate \((CO_3^{2-})\) ions in the pore water solution,

\[
CO_2[g] + H_2O[l] \rightarrow H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3^-(aq) \leftrightarrow 2H^+(aq) + CO_3^{2-}(aq)
\]  

(3.2)

The \(Ca^{2+}\) (aq) and \(CO_3^{2-}\) (aq) ions combine and calcium carbonate precipitates out of the pore water solution and agglomerates onto the soil grains (\(\downarrow\) signifies precipitation/deposition),

\[
Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3[s] \downarrow
\]  

(3.3)
If enough precipitation occurs, the carbonate minerals will bind the soil matrix. The preceding description of the exothermic carbonation reaction with lime may be summarized as,

\[
Ca(OH)_2[s] + H_2O[l] + CO_2[g] \rightarrow CaCO_3[s] + 2H_2O[l] + \text{Heat} \quad (3.4)
\]

### 3.2.2 Concept of Gas Introduction

Surface carbonation refers to the method of gas introduction (step 2). Figure 3.1a shows a conceptual schematic of surface carbonation on an embankment of soil. Carbon dioxide gas is introduced beneath an impermeable gas barrier that is sealed near the perimeter of a targeted treatment area to enforce vertical penetration of $CO_2$ into the soil. Figure 3.1 shows the large soil box that was used to simulate a portion of the embankment near the perimeter (see Figure 3.1a), where some gas escape through the perimeter/slope of a treated area may be expected to occur.
Figure 3.1: a.) A conceptual schematic of surface carbonation on an embankment of soil, where carbon dioxide gas is introduced beneath an impermeable gas barrier (e.g. plastic tarp) and sealed near the perimeter of a targeted area to enforce vertical penetration of carbon dioxide gas into the soil. b.) Large soil box intended to simulate a portion of the embankment near the perimeter where gas escape near the perimeter/slope may occur.
3.3 Soil Box Assembly and Testing Details

3.3.1 Tested Materials

The tested soil used in the large-scale surface carbonation experiments was obtained from a local pit in Winterport, Maine. The initial water content ($\omega$) of the soil was measured after bringing it into the laboratory, and it varied between 17.5% and 24.6%, with an average of 20.2% (based on 10 measurements). The average $\omega$ of the collected soils from the pit was significantly higher than the desired or target $\omega$ about 9-12.0% for soil box construction. Also, based on the visual observation, it was found that the fine-grained soils had a trace amount of fine gravel which was not expected. Considering the higher $\omega$ with wide variations in the bulk soil source (about 2000 kg) that contained trace gravel, the soil was oven dried in a large environmental chamber, shown in Figure 3.2a, at a temperature between 60 °C and 70 °C, and relative humidity (RH) between 10% and 15% for 3-5 days until the soil appeared dry. The water content of the dried soils was measured which varied between 0.2 and 0.5 %, with an average of 0.35% (based on 10 measurements). Afterward, the soils were sieved through $\#$ 4 sieve to remove all the trace gravel before mixing as shown in Figure 3.2b.

The specific gravity, $G_s$, determined as per ASTM (2014c), of soil is 2.66. The tested soil was a non-plastic silt that mainly contained 21% fine sand and 71.4 % silt (ASTM, 2009b, 2017d,e) with a plastic limit (PL), liquid limit (LL), and plasticity index (PI) of 25%, 27%, and 2, respectively (ASTM, 2014b). As per USCS soil classification (ASTM, 2017a), the tested soil is classified as silt with sand (ML), referred to herein as “silt”. The high calcium hydrated lime ($G_s$ of 2.24 as per ASTM (2014c)) used in this study was obtained from Graymont Inc. Figure 3.3 shows the gradation curves for the silt and standard compaction curves for the silt with or without lime. The non-plastic silt was mixed with lime at a gravimetric lime content $\beta_L = 8\%$ for the large soil box experiments. A summary of index properties of tested soil is given in Table 3.1.
Chemical analysis was performed on the tested soil and lime using Thermogravimetric Analyses, (TGA) (Hossen et al., 2020) and X-ray fluorescence (XRF) testing. Further testing using X-ray diffraction (XRD) was conducted on the soil. The chemical composition of tested soil and lime determined via XRF are given in Table 3.2. Three TGA were performed on the tested silt to determine any calcium carbonate, $CaCO_3$ content that might be available in the soil. Results showed that the collected soil had a carbonate content between 5.6-6.10% with an average of 5.7%. A representative TGA result of tested soil is presented in Figure 3.4. XRD results, as shown in Figure 3.5, also confirmed that the tested soil contained calcite (i.e. $CaCO_3$). It is noted that the binder contents (i.e. $CaCO_3$) reported here are in addition to the $CaCO_3$ content that was available in the soil inherently and is formed due to carbonation via consumption of $CO_2$ gas. TGA of high calcium hydrated lime as shown in Figure 3.6 revealed that the material was approximately 80-85% pure $Ca(OH)_2$.

![Drying of soils in an environmental chamber](image1.png)

![Sieving of soils through #4 sieve](image2.png)

Figure 3.2: Soil preparation. a.) Oven drying of tested soil; b.) soil sieving.
Figure 3.3: a.) Soil gradation curve of tested soil; b.) standard proctor compaction curves for the tested soil and soil containing approximately 8% lime material by dry weight of soil; the lime material was approximately 80-85% pure calcium hydroxide.
Table 3.1: Summary of index properties of tested soil.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity, $G_s$</td>
<td>2.66</td>
</tr>
<tr>
<td>Particle size distribution (%)</td>
<td></td>
</tr>
<tr>
<td>Coarse and medium sand (4.75-0.425 mm)</td>
<td>1.0</td>
</tr>
<tr>
<td>Fine sand (0.425-0.075 mm)</td>
<td>21.0</td>
</tr>
<tr>
<td>Silt (0.075-0.002 mm)</td>
<td>71.4</td>
</tr>
<tr>
<td>Clay ($&lt;0.002$ mm)</td>
<td>6.6</td>
</tr>
<tr>
<td>Atterberg Limits</td>
<td></td>
</tr>
<tr>
<td>Liquid limit, $\omega_L$ (%)</td>
<td>27</td>
</tr>
<tr>
<td>Plastic limit, $\omega_P$ (%)</td>
<td>25</td>
</tr>
<tr>
<td>Plasticity index, PI</td>
<td>2</td>
</tr>
<tr>
<td>USCS Soil classification</td>
<td></td>
</tr>
<tr>
<td>Group name</td>
<td>Silt with sand</td>
</tr>
<tr>
<td>Group symbol</td>
<td>ML</td>
</tr>
<tr>
<td>Standard proctor test (soil only)</td>
<td></td>
</tr>
<tr>
<td>Optimum water content, $\omega_{opt}$ (%)</td>
<td>15.8</td>
</tr>
<tr>
<td>Maximum dry unit weight, $\gamma_{d,max}$ (kN/m$^3$)</td>
<td>16.39</td>
</tr>
<tr>
<td>Standard proctor test (8% lime mixed soil)</td>
<td></td>
</tr>
<tr>
<td>Optimum water content, $\omega_{opt}$ (%)</td>
<td>16.7</td>
</tr>
<tr>
<td>Maximum dry unit weight, $\gamma_{d,max}$ (kN/m$^3$)</td>
<td>16.40</td>
</tr>
</tbody>
</table>
Table 3.2: Summary of the chemical composition of tested soil and lime.

<table>
<thead>
<tr>
<th>Composition (weight %)</th>
<th>Soil</th>
<th>Lime</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (Silicon dioxide)</td>
<td>69.35</td>
<td>0.85</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (Aluminum oxide)</td>
<td>12.70</td>
<td>0.37</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (Iron oxide)</td>
<td>5.80</td>
<td>0.20</td>
</tr>
<tr>
<td>CaO (Calcium oxide)</td>
<td>4.44</td>
<td>97.55</td>
</tr>
<tr>
<td>K$_2$O (Potassium oxide)</td>
<td>2.11</td>
<td>0.08</td>
</tr>
<tr>
<td>Na$_2$O (Sodium oxide)</td>
<td>2.32</td>
<td>ND$^b$</td>
</tr>
<tr>
<td>MgO (Magnesium oxide)</td>
<td>1.86</td>
<td>0.70</td>
</tr>
<tr>
<td>TiO$_2$ (Titanium dioxide)</td>
<td>0.83</td>
<td>0.01</td>
</tr>
<tr>
<td>P$_2$O$_5$ (Phosphorus pentoxide)</td>
<td>0.25</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO (Manganese oxide)</td>
<td>0.13</td>
<td>0.01</td>
</tr>
<tr>
<td>CuO (Copper oxide)</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>SO$_3$ (Sulfur trioxide)</td>
<td>0.04</td>
<td>0.16</td>
</tr>
<tr>
<td>Other oxides$^c$</td>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$^a$Measured using an X-ray fluorescence (XRF)
$^b$ND-Not detected
$^c$Other oxides consist of BaO, SrO, ZnO, Co$_2$O$_3$, RbO
Figure 3.4: A representative Thermogravimetric Analyses (TGA) of tested silt to verify the presence of carbonate content, and to determine the amount of calcium carbonate, CaCO$_3$ content of the soil.
Figure 3.5: X-ray diffraction (XRD) of tested silt.

Q: Quartz  
M: Mica  
C: Chlorite  
Ct: Calcite  
H: Hematite
Figure 3.6: Thermogravimetric Analyses (TGA) of tested lime- two representative lime samples were tested to verify the purity, and to determine the amount of calcium hydroxide, $\text{Ca(OH)}_2$, available in the dry hydrated lime power.
3.3.2 Soil Box Construction

Figure 3.7 provides an overview of the soil box construction and installation of instrumentation used to monitor the carbonation of the non-plastic silt mixed with lime. The box was sealed at the bottom and jointed connections to prevent gas and water leakage during experiments. Perforated PVC pipes were installed at the base of the box (Figure 3.7a) to allow gas-escape (i.e. flow) at the bottom of the soil. From a gas flow/diffusion perspective, the pipes were intended to simulate a substantially thicker deposit anticipated in the field than the soil column height in the box (i.e. not trap \( CO_2 \) gas in the box). The perforated pipes were later used to introduce groundwater for freeze-thaw durability testing of carbonated soil (not discussed here). The soil was compacted in 50 mm lifts to a modest dry density, \( \gamma_d = 14.2 \) to 14.4 kN/m\(^3\) which is about 87 to 88% of their standard compaction effort, and a target void ratio \( e = 0.8 \) to a final thickness of 450 mm (Figure 3.7b). Thermocouples, bender element pairs, and settlement plate pedestals were embedded in the soil at varying depths during filling (Figures 3.7c-e). The settlement plate pedestals were only used to monitor deformations during freeze-thaw tests (not during surface carbonation; details about this are discussed in Chapter 4). The box was divided into two-halves (Figure 3.7f), sides “A” and “B” to examine the influence of two different degrees of saturation \( (S_r = 30\% \text{ and } 40\%) \) on surface carbonation. To achieve the desired \( S_r = 30\% \) on side “A”, the dry soil and lime-mixed soil were mixed at water content, \( \omega \approx 9.1 \) and 9.2%, respectively. For side “B” \( (S_r = 40\%) \), the dry soil and lime-mixed soil were mixed at water content, \( \omega = 12.1 \) and 12.3%, respectively; note that the optimum water content \( (\omega_{opt}) \) of soil and 8% lime mixed soils are 15.8% and 16.7%, respectively. These degrees of saturation were chosen because there is sufficient air and water to facilitate the reaction, but not so much water that it obstructs the permeation of gas into the soil matrix (Chapter 2). The box was sealed with a plastic covering and sealed around the edges. Holes were drilled through one side of the box (Figure 3.7g) to allow gas flow and simulate the perimeter of an embankment (Figure 3.7h).
Figure 3.7: Overview of soil box assembly and installation of instrumentation: a.) perforated pipes, $CO_2$ gas port, and water sealing on both sides of the box; b.) compaction of soil in 50 mm lifts. Embedment of c.) thermocouples, d.) bender element pairs, and e.) settlement plates (i.e. wooden rod with pedestal) at various depths. View of f.) soil box after filling for sides A ($S_r=30\%$) and B ($S_r=40\%$), g.) plastic tarp seal for surface carbonation and holes on h.) the sloped side of the box.
3.3.3 Experimental Arrangement and Instrumentation

Figure 3.8a provides an overview of the experimental setup, where a mass flowmeter (Figure 3.8b) located between the soil box and gas valve (Figure 3.8c) tracked the standard liters of gas supplied through a single manifold connected to six CO₂ cylinders (Figure 3.8d). The flowmeter provided the gas flow rate, and the total amount of gas supplied in the box during carbonation. The wires for thermocouples were routed through a single opening in the box and connected to a data acquisition system. Bender element cables were routed through the same hole, which was sealed.

Figure 3.9 shows a plan and elevation view of instrumentation locations in the soil box, which was 2 m in length and 1 m wide (each side was 0.5 m wide). Lime-mixed soil was in the upper 300 mm of the 450 mm soil column. The flowmeter, thermocouples, and bender elements allowed for real-time monitoring of the CO₂ gas flow rate, pressure at the box, total gas introduced, the temperature throughout the soil column (a proxy for where the exothermic reaction is occurring), and changes in shear wave velocity during carbonation. Five thermocouples were placed at two locations on each side of the box (20 total) to monitor temperature changes at depths of 0, 100, 200, 300, and 400 mm. Two pairs of bender elements were located on each side of the box at depths of 50 and 250 mm (i.e. 50 mm below the top and above the bottom of the lime-mixed soil). Unfortunately, the upper pair of bender elements on side A of the box did not function during the experiment, which is why they are not shown in Figure 3.9b.
Figure 3.8: Overview of setup and equipment used for the large-scale surface carbonation experiment: a.) complete overview of experimental setup highlighting different components; b.) carbon dioxide mass flow meter between the soil box and c.) gas valve located between the flowmeter and the d.) six CO₂ gas cylinders connected through a single manifold to supply uninterrupted flow; e.) data acquisition system connected to thermocouples and bender elements. Note that though pressure at the manifold was 30-40 kPa, at the box opening where the flowmeter was located, the pressure was reduced to ≈ 1 atm (0 gauge).
All dimensions shown here are in meter, and the measurements of the box represent the inside dimension excluding wall thickness.

Figure 3.9: Soil box instrumentation plan and dimensions showing the locations of the flowmeter, thermocouples (TC), and bender elements (BE) in a.) plan view and b.) elevation view.
3.3.4 Destructive Testing and Sampling

Post-carbonation, destructive testing and sampling were performed to assess changes in mechanical behavior and binder content (BC) and lime content; the gravimetric BC, $\beta_B = \frac{m_b}{m_s}$, is defined as the ratio of the mass of $CaCO_3$ binder and soil. Figure 3.10 illustrates the methods used to perform the field California Bearing Ratio (CBR) test in general accordance with ASTM D4429-09 (ASTM, 2009a) to assess changes in strength and stiffness throughout the soil column inside the box. The field CBR equipment, which consists of a mechanical screw jack and piston that penetrates the ground, reacted off a steel beam spanning the soil the box that was secured by reaction blocks on each side (Figure 3.10a,b). The CBR is a normalized stress defined as,

$$ CBR = \frac{\sigma_\delta}{\sigma_{std}} $$

(3.5)

where $\sigma_\delta$ is the stress after 2.54 or 5.08 mm of piston penetration and $\sigma_{std}$ is a standard stress of 6.9 or 10.3 MPa that corresponds to 2.54 or 5.08 mm deformations, respectively; the CBR is the largest stress-ratio arising from measurements at 2.54 and 5.08 mm. A 75 mm thin-walled shelby tube was used to extract soil samples post-carbonation. Given the stiff nature of the soil post-carbonation, to prevent buckling of the tube, a scissor jack was used to slowly and methodically penetrate the thin-walled sampler by reacting with the steel beam (Figure 3.10c). Samples were immediately extruded, oven dried to prevent any further chemical reactions, and stored in air-tight plastic containers prior to TGA testing to determine the $CaCO_3$ BC and lime content (Figure 3.10d,e).
(a) Field CBR equipment

Steel reaction beam (W 150 x 150 x 37.1) fixed on both ends

(b) Hollow Steel tube across the W-beam

Concrete block (LxWxH=1.4m x 0.6m x 0.7m)

(c) Threaded rod passing through concrete blocks

(d) Ratchet strap to attach mechanical screw jack with reaction beam

(e) Penetration piston

Proving ring with dial gauge

Penetration dial gauge

Wooden tamper to extrude the sample

Zip lock plastic bag to store disturbed soil sample

75 mm dia. shelby tube

Scissor jack to push down the shelby tube for soil sampling

Samples for water content measurement

Dried samples stored for binder content measurement

Figure 3.10: a.) Overview of field CBR test setup showing the reaction blocks and beam spanning the soil box for testing; b.) field CBR equipment in the soil box; c.) scissor jack being used to penetrate a thin-walled shelby tube sampler into the soil; d.) extrusion of soil samples from thin-walled sampler; e.) sample collection for drying and storage for thermogravimetric analyses (TGA) later.
The CBR testing and sampling locations are shown in Figure 3.11. The CBR was performed at five different depths (0, 100, 150, 250, and 350 mm) at 3 locations on each side of the box (6 total locations and 30 total tests); the reaction beam could be repositioned to the centerline of each side of the box. Testing was performed at one location on each side of the box prior to carbonation and at two locations on each side post-carbonation. CBR testing and sampling were performed in tandem; after each CBR test, sampling was performed to collect soil for chemical testing, but also to advance the hole to the next CBR test depth.

Figure 3.11: Locations of field California Bearing Ratio (CBR) testing and soil sampling. a.) plan view; b.) elevation view
3.4 Experimental Results

3.4.1 Monitoring of Surface Carbonation

Figure 3.12 shows the high accuracy flowmeter (TSI 5300 series instrument) data during carbonation, including the absolute gas pressure and temperature where CO$_2$ entered the soil box (Figure 3.12a) and the corresponding flow rate (in standard liters/minute) and total mass of CO$_2$ that entered the box (Figure 3.12b). The accuracy of the mass flow rate and the total mass is ± 2% of the reading (not full scale). Standard liters refer to the mass of gas occupying a volume at a standard pressure $P_{std} = 101.3$ kPa and standard temperature $T_{std} = 21.1$ deg C. Temperature and pressures are accounted for in the readings. The standard liters of CO$_2$ can be converted to mass using the ideal gas law,

$$m_{CO_2} = \frac{P_{std}V_g}{RT_{std}} \times M_{CO_2}$$ \hspace{1cm} (3.6)

where $R$ is the universal gas constant, $V_g$ is the volume of gas, and $M_{CO_2} = 44.01$ g/mol is the molar mass of carbon dioxide. For reference, the corresponding amount of gas that is theoretically required to fully carbonate the available Ca(OH)$_2$ over different depth intervals in the lime-mixed soil, assuming carbonation progresses from the top of the soil column downward, is also shown; e.g. 0-50 mm, 0-100 mm, 0-150 mm, etc. (see Figure 3.12b).

Gas was continuously supplied to the box without making any adjustments to the pressure regulator at the manifold for approximately 10 hours under a low absolute pressure between 101 and 102 kPa ($\approx$ 0 gauge pressure). Flow rate, pressure, and temperature fluctuations after 10 hours reflect user adjustments made to the pressure regulator after 10 hours of continuous flow (see Figure 3.12b). During the period where no adjustments were made during the carbonation period ($t_c < 10$ hours), the flow rate steadily increased for approximately 8 hours and then stabilized. The greatest fluctuations in flow rate were observed at the beginning of the test, presumably due to the influence of an ongoing reaction, which diminished over the course of the first 5 hours when enough gas
had been introduced to carbonate the upper 150 mm of soil (Figure 3.12b). Thereafter, the flow rate steadily increased, but with limited fluctuations.

Figure 3.12: Flowmeter readings at the gas-entry point during the surface carbonation experiment: a.) absolute pressure and temperature readings during the carbonation period; b.) $CO_2$ mass flow rate and total mass of $CO_2$ introduced. Also indicated is the theoretical amount of $CO_2$ required to fully carbonate available $Ca(OH)_2$ at various depth intervals, assuming carbonation progressed vertically from the soil surface downward.
Figure 3.13 shows the temperature readings in the soil at various depths (Figure 3.13a), the rate of temperature change throughout the carbonation period $dT/dt_c$ (Figure 3.13b), and changes in shear wave velocity (Figure 3.13c). Recall that the carbonation reaction with hydrated lime is an exothermic reaction that generates heat (equation 3.4). It can be seen that temperatures first increase rapidly near the ground surface ($z = 0$ mm) followed by a peak in temperature at $z = 100$ mm. The corresponding rate of temperature change is greatest at the beginning of the test at the ground surface, but continuously decreases with time, suggesting that the reaction first occurs at shallow depths (expected) and then progresses vertically downward. The decreased rate of temperature increase at $z = 0$ mm followed by an increase in the temperature (and rate of temperature increase) at $z = 100$ mm (Figure 3.13a, b) supports this hypothesis and indicates that the reaction is progressing to greater depths. The rate of temperature increase also serves as a proxy for when the reaction is occurring in the vicinity of the thermocouple; this is indicated for shallow depths by the light gray and blue shading in Figure 3.13 for thermocouple measurements at $z = 0$ and $100$ mm. Notably, the rate of temperature rise in the vicinity of the $z = 100$ thermocouples is greatest when the theoretical amount of gas needed to fully carbonate to depths approaching 50 to 100 mm has been introduced. Thus, it is likely that the majority of $CO_2$ gas being introduced up to this stage of the test is being sequestered as a result of the reaction.

The temperature also increases at greater depths between $z = 200$ to 400 mm in the soil (shown on the right side of Figure 3.13a). However, the peaks in temperature rise are not as pronounced as at shallower depths, likely signaling that the reaction isn’t occurring as rapidly, if at all, at those locations. This temperature increase at greater depths is undoubtedly due to the diffusion of heat within the soil layer. Although all temperatures increase from $z = 200$ to 400 mm, there is a noticeably higher rate of temperature increase at $z = 200$ mm than the locations at greater depths (Figure 3.13b). It is possible that this
is due to carbonation occurring and/or the proximity of the thermocouples at \( z = 200 \) mm to shallower regions where carbonation has progressed.

At all depths, temperature increases on side A \((S_r = 30\%)\) were higher than side B \((S_r = 40\%)\). However, when temperature changes happen, they occur simultaneously, suggesting that the reactions are occurring simultaneously at similar depths. As water has a high specific heat capacity, lower temperatures on side B can be attributed to a greater volume of water in the soil matrix; i.e. it can absorb a lot of heat energy without significantly increasing in temperature. Thus, thermocouple readings do not indicate that the differences in \( S_r \) on each side of the box had a significant impact on the rate or extent of where carbonation occurred in the soil column.

Shear wave velocities measured at \( z = 50 \) mm increased substantially from approximately \( V_s = 200 \) m/s to 600 m/s, indicating the stiffness of the upper portion of the soil profile is similar to very hard soils or soft rock (NEHRP, 2003; Weil et al., 2012; Loehr et al., 2016). However, the increase was not observed until approximately 3 to 4 hours after it is believed carbonation would have occurred at this depth. Therefore there is a short delay between when the reaction occurs and the \( \text{CaCO}_3 \) binder agglomerating on the grains solidifies and stiffens the soil matrix. Regardless, for most practical construction applications, the improvement after carbonation occurs is effectively “immediate”. No changes in shear wave velocity were observed on either side of the soil box at \( z = 250 \) mm. This confirms that the temperature increases at greater depths (e.g. 300 mm) were due to heat diffusion only and not indicative that carbonation was occurring at those depths.
Figure 3.13: Temporal changes in temperature readings and shear wave velocity at various depths in the soil during surface carbonation: a.) temperature readings at 0 and 100 mm (left) and 200, 300, and 400 mm (right); b.) rate of temperature change at 0 and 100 mm (left) and 200, 300, and 400 mm (right); c.) changes in shear wave velocity at 50 mm (left) and 250 mm (right). All plots also indicate the total mass of gas introduced and the theoretical amount of $CO_2$ required to fully carbonate available $Ca(OH)_2$ at various depth intervals, assuming carbonation progressed vertically from the soil surface downward.

Notes. i) Number in legends shows the depth, $z$ in mm from the soil surface. ii) For $T$ and $V_s$: solid line-Side A ($S_r=30\%$); dash line-Side B ($S_r=40\%$).
3.4.2 Binder Content Measurements and CBR Testing

Figure 3.14 shows the gravimetric $CaCO_3$ binder content and unreacted hydrated lime contents on sides A and B of the soil box after surface carbonation. The binder contents on each side of the box indicate that soil was fully carbonated in the upper 150 mm of the soil column on both sides of the soil box (i.e. all $Ca(OH)_2$ reacted) and was lightly carbonated from 150 to 200 mm. Little to no carbonation occurred from 200-300 mm in the lime-mixed soil. This corresponds well to both the temperature and shear wave velocity measurements. The peaks in temperature and rates of temperature increase were observed at depths where the soil was fully carbonated. The less pronounced peak in temperature and temperature rate increases at $z = 200$ mm was in the vicinity of where the soil was lightly carbonated. The gradual increases in temperature at $z = 300$ and 400 mm, where the rates of temperature increase were approximately zero (Figure 3.13b) were due to diffusion of heat generated in the soil at shallower depths. Also where fluctuations in the flow ceases, and where a steady small increase in pressure at the flowmeter was observed, was when the theoretical amount of gas required to carbonate the upper 150 mm had been introduced after approximately 4.5 hours. Thus, it is believed that the majority of $CO_2$ gas penetrating into the soil during the first 4.5 hours of surface carbonation was consumed. However, it remains unclear why $CO_2$ did not penetrate to greater depths. Water content measurements from soil samples after carbonation remained unchanged, so it is not believed that increases in moisture levels and changes in the degree of saturation that could potentially obstruct the vertical permeation of gas was responsible. It’s more likely that a steady state lateral flow condition developed after carbonation progressed to $z \approx 150 - 200$ mm and gas flowed laterally to the perimeter of the box where the holes in the box and soil slope were located at the end of the box (see Figure 3.7g,h).

Recall that the experimental design was intended to simulate surface carbonation near the perimeter of a treated area where a permeable surface would exist through an embankment slope or similar; i.e. an attempt to simulate surface carbonation at a critical
Figure 3.14: Gravimetric $CaCO_3$ binder contents and unreacted hydrated lime contents on a.) side A and b.) side B of the soil box after surface carbonation.
location where gas was most likely to escape was made. If surface carbonation was being applied away from the perimeter of a targeted area, it’s possible that \( CO_2 \) would have penetrated deeper into the soil column and carbonated soil at greater depths. Regardless, chemical stabilization typically targets depths ranging from 150 to 300 mm for shallow subgrade stabilization applications for roadways, airports, etc. (Little, 1999; Gross & Adaska, 2020). Thus, it was demonstrated that there is potential to achieve these targets with surface carbonation.

Figure 3.15 shows the pre- and post-carbonation CBR measurements throughout the soil column for both sides of the soil box. For reference, qualitative descriptions provided by Schaefer et al. (2008) for subbase and subgrade soils as part of a pavement system. At the surface, CBR values increased from values considered fair to good for a subgrade material to very good or excellent subbase material, which generally requires much better material. The CBR values at the surface ranged from 60 to 80 at the ground surface, remained elevated through the fully carbonated zone, and decrease with depth to pre-carbonation measurements where no carbonation occurred or where the soil was not mixed with lime. Thus, the CBR values demonstrate that accelerated surface carbonation with hydrated lime can substantially improve the mechanical properties of the soil, as expected (Chapter 2).
Figure 3.15: Pre- and post-carbonation CBR values throughout the soil column on a.) side A and b.) side B of the soil box.

Figure 3.16 shows the stress-penetration curves from CBR tests at depths of 0, 100, and 150 mm in the fully carbonated soil for each side of the box, where the pre-carbonation curves are also shown for reference. The curves demonstrate that there is a substantial increase in stiffness and load-carrying capacity at the surface of the soil, corresponding to the higher CBR values in Figure 3.15. While the load-carrying capacity diminishes with depth, the initial stiffness post-carbonation is much greater, even at the bottom of the fully carbonated layer.

At one location, unload-reload cycles were performed at three stress-levels to demonstrate the plastic deformations that accumulate upon unloading at varying stress levels. Figure 3.17 shows these unload-reload tests at depths of 0, 100, and 150 mm. Generally, tests performed at shallower depths accumulated smaller plastic deformations at the same stress levels because the thickness of fully carbonated material, and their ultimate
Figure 3.16: Stress-penetration curves from CBR tests at depths of 0 mm (top), 100 mm (middle), and 150 mm (bottom) on a.) side A and b.) side B of the soil box before and after surface carbonation.

capacity \(q_f\), is greater. Figure 3.18a illustrates the influence of the thickness of fully carbonated material underlying the piston, \(H_c\), on the ultimate failure stress, which was defined as the stress at a deformation of 12 mm, which clearly illustrates the influence of
$H_c$, which is normalized by the piston diameter, $B$, on the ultimate capacity during the CBR tests. Similarly, Figure 3.18b illustrates the influence $H_c/B$ on CBR values.

Figure 3.18c summarizes the permanent deformations at each unload reload stress (see Figure 3.17), where it can be seen that the permanent deformation is highly dependent on the magnitude of the unloading stress, $q_{ur}$, relative to the ultimate capacity (Figure 3.18d). From a pavement systems perspective, it is well understood that applied stresses near the surface of a roadway (e.g. by vehicles) decay with depth. In all cases, the permanent deformations remain small (less than 1 mm) so long as $q_{ur}/q_f$ is less than approximately 0.5; i.e. the effective modulus of carbonated material remains high, and greater than that of untreated soil, if it does not exceed the aforementioned threshold $q_{ur}/q_f$ ratio and approach its ultimate capacity.
Notes. \(q_u\)-maximum stress and \(\Delta_p\)-permanent deformation in a unloading-reloading (U-R) cycle; \(q_f\)-failure stress i.e. stress at penetration, \(\Delta = 12\) mm.

Figure 3.17: Unload-reload cycles performed at varying stress levels for depths of 0, 100, and 150 mm for a.) side A and b.) side B of the soil box after surface carbonation. Note that the right figures for (a) and (b) are focused on the stress levels and deformations where unload-reload cycles were performed.
Figure 3.18: Synthesis of the CBR test results showing: a.) the influence of fully carbonated thickness, $H_c$, underlying the CBR piston of diameter, $B$, on the failure stress, $q_f$; b.) the influence of fully carbonated thickness, $H_c$, underlying the CBR piston of diameter, $B$, on CBR; c.) permanent deformations associated with unload-reload cycles performed at varying stress-levels, $q_{ur}$, at depths of 0, 100, and 150 mm; d.) influence of the unload-reload stress relative to the ultimate capacity of the soil, expressed as a $q_{ur}/q_f$ ratio, on permanent deformations from unload-reload cycles.
This study has demonstrated that substantial gains in strength and stiffness can be achieved via surface carbonation, but did not consider the durability of the material. As previously discussed, the soil box was designed such that water can be introduced to account for the deleterious effects of “soaking” (Hazirbaba & Gullu, 2010; Leelavathamma et al., 2005) and frost action (Hazirbaba & Gullu, 2010; Zhang et al., 2016, 2019a; Tebaldi et al., 2016). Testing in a large environmental chamber to assess the durability of the carbonated silt under harsh environmental conditions (freeze-thaw cycles) was a separate phase of this larger study (Chapter 4).

3.5 Discussion

A potential drawback of soil carbonation is the required additional step to introduce gas, which is not required with conventional chemical stabilization methods. The large soil box experiment performed to evaluate accelerated surface carbonation, which has the potential to be scaled in the field, demonstrated that a binder is generated rapidly. Based on the interpretation of when carbonation was occurring, the majority of gas was consumed in the first 4 to 5 hours of surface carbonation and sequestered to generate a binder in the upper 150 to 200 mm of soil. Compared with conventional methods, where a chemical additive (e.g. cement or lime) is mixed with soil and then left for days to weeks (sometimes months) prior to binder formation, carbonation could provide a means for “immediate” verification as to a.) the extent of stabilization and b.) adequacy of adopted construction techniques. In a field setting, the ability to efficiently evaluate the efficacy of mixing methods and/or techniques to introduce gas could allow for an adaptive management approach to construction—whereby contractors and engineers can optimize implementation techniques in real-time. In this study, it was demonstrated that temperature is a good indicator of where the reaction is occurring and could be a non-destructive method to immediately verify the extent of carbonation (thermocouples are inexpensive and easy to embed in the soil). Alternatively, the standard test method for
rapid determination of carbonate content of soils (ASTM, 2014a) can be easily deployed in the field and used to determine the binder content of soil samples (e.g. Gomez et al., 2015; Choi et al., 2016; Kim & Youn, 2016; Gomez et al., 2017, 2018; Islam et al., 2020).

In addition to potential construction benefits, soil carbonation sequesters $CO_2$ gas and significantly reduces the carbon footprint associated with lime production. During production, limestone ($CaCO_3$) decomposes into quick lime, $CaO$, resulting in “process-based” carbon emissions ($CO_2$ released due to the decomposition of limestone) and “combustion-based” emissions (energy/fuels needed to heat kilns during the calcination process). Water is simply added to quick lime to form hydrated lime ($Ca(OH)_2$) that was used here. Process-based emissions account for at least two-thirds of $CO_2$ emissions during lime production (Stork et al., 2014; Campo et al., 2021). In this study, it was demonstrated that the carbonated calcium hydroxide once again results in $CaCO_3$ that forms a useful binder to stabilize soils—effectively consuming the equivalent of process-based emissions associated with production. If carbonated, the $CO_2$ footprint associated with the use of lime may be reduced by upwards of two-thirds. The widespread awareness and need to reduce the carbon footprint is already affecting policy. For example, The Inflation Reduction Act recently created the Low-Carbon Transportation Materials Program, which provides US$2 billion in incentives for the use of construction materials and products that result in substantially lower levels of embodied greenhouse gas emissions associated with all stages of production and use in the United States, effective from April 6, 2023 to September 30, 2026. Inflation Reduction Act § 60506, 23 U.S.C. § 179. Thus, there are now explicit financial motives to pursue innovative construction methods like soil carbonation.

The enablement of soil carbonation remains in its infancy. Field-scaling of processes will need to consider techniques to supply large amounts of gas, which are not yet readily available, but soon may be. It will also be necessary to optimize the required thickness of treated material and the lime content to fully exploit the potential environmental benefits. The logistics associated with these challenges will need to be overcome prior to the
widespread adoption of soil carbonation in practice, but it is believed that the
aforementioned incentives will drive continued advancement and discovery of methods to
implement this technology.

3.6 Summary and Conclusions

A large soil box experiment was carried out to evaluate the efficacy of surface
carbonation as a means to chemically stabilize shallow subgrade soils. Motivated by the
need to develop soil carbonation implementation methods that can be applied over large
areas, the technique refers to the introduction of $CO_2$ gas beneath a near-ground-surface
seal intended to contain and enforce vertical penetration of $CO_2$ gas into soil mixed with a
chemical additive (hydrated lime in this study). The soil box experiment was designed to
simulate surface carbonation near the perimeter of an embankment, a critical location
where gas is most likely to escape with this technique. A detailed description of the
experimental design and setup was followed by the presentation of the real-time monitoring
data during surface carbonation and post-carbonation characterization via $CaCO_3$ binder
content measurements and changes in mechanical behavior with CBR testing. Potential
incentives that may drive the continued development of soil carbonation technologies were
discussed.

During surface carbonation, it was demonstrated through subsurface temperature
measurements that carbonation generally progressed from the surface of the soil column
downward. Based on the combined interpretation of flowmeter data, temperature
measurements, and post-carbonation binder content measurements, it was determined that
the upper 150 to 200 mm were carbonated within 4 to 5 hours, during which time most of
the $CO_2$ gas introduced was sequestered to generate a $CaCO_3$ binder. Post-carbonation
binder content measurements revealed that full carbonation was achieved in the upper 150
mm (i.e. all lime was consumed), while at depths from 150 to 200 mm was lightly
carbonated. The differences in the initial degree of saturation on two sides of the box (30
vs. 40%) had no apparent influence on the rate or degree of carbonation that was achieved. Why carbonation did not progress to the maximum depth of lime-mixed soil (300 mm) is unclear. Post-carbonation water content measurements revealed no significant changes (i.e. increases in $S_r$) that would have resulted in water obstructing the permeation of gas vertically. Thus it was speculated that a steady state lateral flow condition developed after carbonation progressed to depths of 150 to 200 mm and gas flowed laterally to the far edge of the box where there was no gas barrier (i.e. the simulated slope of an embankment). It is possible that simulating surface carbonation away from the perimeter of the treated area may have resulted in greater penetration of CO$_2$ gas and carbonation to greater depths.

Regardless, the experiment demonstrated the technique has the potential to carbonate soil thicknesses typically targeted for shallow subgrade stabilization applications (150 to 300 mm).

Shear wave velocity measurements increased from approximately 200 to 600 m/s at a depth of 50 mm, a substantial increase in stiffness akin to very hard soil or soft rock. No increase in shear wave velocity was observed at a depth of 250 mm, consistent with binder content measurements. CBR values improved significantly in the upper portion of the soil column, increasing from approximately 20 to between 60 and 80 at the top of the soil column. The CBR generally decreased with depth, and it was shown that the thickness of fully carbonated soil underlying the test depth influences the ultimate piston stress and CBR. Though the ultimate capacity of carbonated soil decreased with depth, stiffness was substantially elevated in fully carbonated soil based on a comparison of stress-penetration curves with pre-carbonation measurements. Additionally, it was shown that plastic deformations are similar and remain small, regardless of the thickness of fully carbonated material underlying the test depth, so long as the $q_{ur}/q_f$ ratio was less than approximately 0.5.

Two incentives with respect to soil carbonation were discussed: a.) the ability to rapidly generate a binder, allowing for an immediate evaluation of the efficacy of
implementation techniques and opening up the possibility for an adaptive management approach during construction, where contractors and engineers can optimize methods in real-time; and b.) that sequestering $CO_2$ to generate a binder significantly reduces the net carbon footprint associated with lime production, and policies already in place in the United States providing financial motives to use construction materials and products that result in substantially lower levels of embodied greenhouse gas emissions. These incentives will likely drive continued advancement and discovery of methods, like surface carbonation, to implement this technology.
CHAPTER 4
FREEZE-THAW DURABILITY TESTING OF CARBONATED SILT

4.1 Introduction

It is estimated that rising temperatures attributed to climate change will increase repair and maintenance costs of surface transportation infrastructure in the United States by approximately US$ 19 billion annually by 2040 (ASCE, 2021). In cold regions, frost action is one of the most detrimental environmental stressors impacting surface transportation systems (Aldaood et al., 2014; Tebaldi et al., 2016; Zhang et al., 2019a; Uduebor et al., 2022), which includes the foundation soils (e.g. subgrade and subbase materials). In 1999 DiMillio (1999) estimated that US$ 2 billion annually in damage to pavement systems was caused by frost action in the United States, and Doré et al. (2005) reported that seasonal freeze-thaw (FT) cycles contribute up to 75% of the degradation for surface transportation infrastructure. In a warming climate, the number of FT cycles is expected to increase and can be expected to exacerbate the impacts of frost action (Asam et al., 2015; Tonn et al., 2021).

It’s well-known that frost action, particularly in fine-grained soils, is one of the primary contributors leading to degradation of the mechanical properties in foundation soils (e.g. Casagrande, 1931; Chamberlain & Gow, 1979; Johnson et al., 1979; Konrad & Morgenstern, 1980; Loch, 1982; Graham & Au, 1985; Konrad, 1989; Kim & Daniel, 1992; Konrad & Seto, 1994; Lee et al., 1995; Konrad & Roy, 2000; Hohmann-Porebska, 2002; Konrad, 2005; Wang et al., 2007; Qi et al., 2006, 2008; Zhou et al., 2018; Lu et al., 2019, among others). To increase the durability of near-surface foundation materials and combat the impacts of frost-susceptible soils, the native material may be excavated and replaced (Christopher et al., 2006; Schaefer et al., 2016) or modified via chemical stabilization methods with chemical additives such as cement (e.g. Shihata & Baghdadi, 2001; Ding et al., 2018; Zhang et al., 2019b; Lu et al., 2020), lime (e.g. Townsend & Klym, 1966; Dempsey & Thompson,
1972; Thompson, 1973; Little, 1995, 1999; Aldaood et al., 2014; Hotineanu et al., 2015; Tebaldi et al., 2016; Liu et al., 2019; Nguyen et al., 2019; Ismeik & Shaqour, 2020), or fly ash (e.g. Wei et al., 2015; Rosa et al., 2017; Zhang et al., 2019b). Depending on the availability of quality borrow material, the adoption of soil stabilization methods to augment the strength and stiffness of existing foundation soils may be more suitable.

Soil carbonation is a potentially novel approach to chemically stabilize soil, whereby carbon dioxide ($CO_2$) is introduced in soil mixed with chemical additives (same as conventional methods) and sequestered to generate a carbonate binder. Initial elemental studies focused on the use of magnesium-based alkali sources, including reactive magnesia ($MgO$) (Yi et al., 2013b; Cai et al., 2015) and olivine ($Mg_2SiO_4$) (Fasihnikoutalab et al., 2017). Based on the small amounts of magnesium compounds produced in the United States in 2020 (0.35 million tons) (Merrill, 2021), lime is an alkali source more likely to be relied on to carbonate soil in the U.S., which produces approximately 16 million tons annually (Apodaca, 2021).

Lime is a chemical additive commonly used with high plasticity, or “reactive,” soils to chemically stabilize subgrade materials (Little, 1999; Little & Nair, 2009). Chapter 2 examined soil state parameters influencing the rate of carbonation and degree of mechanical improvement in soil mixed with hydrated lime ($Ca(OH)_2$), demonstrating substantial gains in strength and stiffness comparable to conventional cement-based stabilization. It has been shown that soils containing lime will carbonate under natural atmospheric conditions (e.g. Das et al., 2021, 2022; Fan et al., 2023), and this process can be accelerated to stabilize non-plastic, highly frost-susceptible, silt soils as well. Chapter 3 performed a large soil box experiment to evaluate “surface carbonation,” a potential implementation method that could be scaled to carbonate soil over large areas, and which refers to the introduction of $CO_2$ beneath a near-ground-surface seal intended to contain and enforce vertical penetration of $CO_2$ gas into the ground. Their experiments demonstrated this technique (i.e. surface carbonation) can stabilize soil thicknesses
targeted for surface transportation infrastructure. Moreover, carbonated lime has the potential to reduce production-based $CO_2$ emissions by upwards of two-thirds as presented in Chapter 2 and Chapter 3. However, the FT durability of soil stabilized via accelerated carbonation has not been tested.

FT durability testing of chemically stabilized soils has by in large been performed on elemental specimens in open (continuous water supply) or closed systems (no water supply), and typically in general accordance with ASTM D560 or ASTM D5918 (see aforementioned studies). While efforts have been made to overcome some of the limitations of elemental testing, such as efforts to enforce a 1D freezing front during freezing (e.g. Hazirbaba & Gullu, 2010), large FT experiments on carbonated (or chemically stabilized) soils in a controlled setting have not been performed.

This study presents a second-phase of the larger study, which builds upon the large soil box experiment presented in Chapter 3. Environmental testing was carried out on carbonated, highly frost-susceptible silt, where a heavily instrumented soil box was fully saturated (i.e. soaked) and then exposed to multiple FT cycles in the HASTEST environmental chamber at the Advanced Structures and Composites Center at the University of Maine. The unique experimental setup incorporated means to provide a continuous water supply, as well as insulation and heat provided to the underside and sides of the box to simulate a 1D (top-down) freezing front expected in field settings. This was followed by a 12 weeks drying period to determine changes in the California Bearing Ratio (CBR) following moisture content changes. The objective of this study was to evaluate the durability and resilience of a frost-susceptible soil carbonated with hydrated lime in a controlled large-scale FT experiment that replicates the important field conditions influencing post-FT behavior.
4.2 Background

4.2.1 Accelerated Surface Carbonation Experiment

Accelerated surface carbonation with hydrated lime may be characterized as a two-step process. After creating a soil-lime-water mixture in a similar manner as conventional chemical stabilization methods (first step), the solid lime dissolves in pore water and dissociates into aqueous-phase cations, $Ca^{2+}$, and anions, $OH^-$. Carbon dioxide gas was then introduced into the soil matrix via surface carbonation (second step). At this stage the $CO_2$ dissolved in the pore water, producing a weak carbonic acid ($H_2CO_3$) that dissociates into $H^+$ and bicarbonate (i.e. $HCO_3^-$) or carbonate ($CO_3^{2-}$) ions in the pore water solution. The dissolved $Ca^{2+}$ (aq) and $CO_3^{2-}$ (aq) ions combine and calcium carbonate, $CaCO_3$, precipitates out of the pore water solution and agglomerates onto the soil grains. With enough precipitation, the carbonate minerals bind the soil matrix to stabilize the soil. The preceding description of the exothermic carbonation reaction with lime can be summarized as,

$$Ca(OH)_2[s] + H_2O[l] + CO_2[g] \rightarrow CaCO_3[s] + 2H_2O[l] + Heat \quad (4.1)$$

During the accelerated surface carbonation experiment, carbonation occurred in the upper 200 mm; the upper 150 mm was fully carbonated while depths from 150 to 200 mm were lightly carbonated as shown in Chapter 3. This resulted in substantial increases in strength, stiffness, and CBR values in the soil. The CBR values at the surface increased from approximately 20 to between 60 and 80 at the surface while shear wave velocity measurements increased from approximately 215 m/s to greater than 600 m/s. Thus, the stabilized silt exhibited behavior more akin to very dense/hard soil to soft rock.

4.2.2 Freeze-Thaw Durability of Chemically Stabilized Soils

Chemical stabilization increases the resistance to frost action in frost-susceptible soils by cementing (bonding) the soil grains. As a freezing front progresses from the ground
surface downward, ice crystal growth and expansion increase, and a suction gradient can
develop, drawing water from below if the soil is unsaturated. Ice lens segregation increases
the available pore volume in the soil matrix (Konrad & Morgenstern, 1980). At the leading
edge of the freezing front, the formation and expansion of ice crystals can generate excess
pore water pressure and impose a hydraulic gradient, which will dissipate if the
permeability is high. In low permeability frost-susceptible soils, pore volume expansion and
eventual ice lens segregation arise. The adhesive bonds binding the soil grains in chemically
stabilized materials are intended to create a rigid grain-binder skeleton that resists pore
volume expansion due to ice crystal growth and pore water redistribution (Townsend &
Klym, 1966). If the binder is unable to resist the tensile forces imposed by the
aforementioned mechanisms, the adhesion of a binder to the soil grains is lost and its
mechanical benefits degrade. If enough damage to the binder-grain contacts occurs, the soil
may become frost-susceptible again. The large-scale soil box experiments described herein
were performed to test the durability of the $CaCO_3$ binder that forms in lime-mixed soils
as a result of carbonation.

4.3 Laboratory Methods

4.3.1 Tested Materials

The tested soil (specific gravity, $G_s$, 2.66 as per ASTM (2014c)) was a non-plastic silt
that mainly contained 21% fine sand and 71.4 % silt (ASTM, 2009b, 2017d,e) with a
plasticity index (PI) of 2 (ASTM, 2014b). As per USCS soil classification (ASTM, 2017a),
the tested soil is classified as silt with sand (ML), referred to herein as “silt”. The silt is
considered to have a “very high” degree of frost susceptibility (frost category F4)
(Christopher et al., 2006). The high calcium hydrated lime ( $G_s$ 2.24 as per ASTM
(2014c)) used in this study was obtained from Graymont Inc. and Thermogravimetric
Analyses, TGA (Hossen et al., 2020) showed that the hydrated lime was approximately
80-85% pure $Ca(OH)_2$. To prepare a lime-mixed subgrade soil layer for a large soil box
experiment, a gravimetric lime content, $\beta_L = 8\%$, by dry weight of soil, was considered. The soil gradation curves for the silt and standard compaction curves for the silt with and without lime can be found in Chapter 3.

4.3.2 Experimental Configuration of Freeze-Thaw (FT) Testing

A large-scale freeze-thaw experiment was conducted in an environmental chamber (interior dimensions-6.7 m in length and width with a height of 4.3 m) that is capable to control the temperature (T) between $+50^\circ$C and $-40^\circ$C, and relative humidity (RH) between 5% and 100% to evaluate the durability of carbonated soils against frost action (i.e. freezing-thawing cycles). An overview of the environmental chamber is shown in Figure 4.1a with the chamber control station that is located separately in the instrumentation monitoring room. A large soil box was constructed to evaluate the potential of surface carbonation to stabilize highly frost susceptible silt (previously discussed in Chapter 3). The methodology presented herein mainly focuses on durability testing to simulate frost action that commonly exists in a field scenario for the cold regions of the USA (e.g. in Maine). The mechanism of frost action- generally consisting of frost heave and thaw weakening- has been studied extensively Konrad (1999); Konrad & Roy (2000); Konrad (2005). Frost heave is attributed to the uptake of groundwater via capillary action and formation of ice lenses which in turn causes segregation within the subgrade layer when the freezing front penetrates (top-down) into the ground (Sheng et al., 2014; Carter & Bentley, 2016). Thaw weakening, on the other hand, causes loss of bearing capacity or strength weakening of subgrade soils resulting from soil saturation as ice within the soils melts during and after thawing (Konrad & Seto, 1994; Zhang et al., 2016; Aldaood et al., 2014). In summary, the formation of ice lenses (i.e. frost heave) below a pavement system requires three essential factors, including i.) subfreezing temperature to penetrate below the pavement surface and into the subbase and subgrade soils (i.e. 1-D freezing front); ii.) a frost-susceptible soil that is lying within the freezing zone; and iii.) a
continuous groundwater source into the freezing zone (Konrad, 1999). The freeze-thaw experiment was designed by taking into account the aforementioned factors and mechanisms. After post-carbonation testing (Chapter 3), the large soil box was moved into the environmental chamber to investigate the FT effects on carbonated soils. Figure 4.1b shows the FT experimental setup inside the chamber, where an insulation system consisting of thermal insulation covered by a plastic tarp fixed at the top of the subgrade layer with a wooden beam, and at the bottom of the box with surcharge weights all round—was provided to enforce a 1-D (top-down) freezing front. During freezing, relatively hot (compared to freezing room temperature) air, temperature varied between 5-10°C approximately, was supplied from a heating system via an insulated flex duct to the bottom of the soil box. This ensured to maintain a warm (i.e. slightly above zero °C) temperature at the bottom of the subgrade soils inside the box as compared to the soil surface, and a thermal differential between the top and bottom of the subgrade layer that exists in a field scenario when frost penetrates into the ground. This soil box was designed and built with horizontal perforated conduits installed at the bottom of the box (see Figure 4.4b) to supply groundwater during freezing as an open system for water uptake. Figure 4.1b shows also shows the reaction blocks and beam spanning the soil box to perform the field California Bearing Ratio (CBR) test in general accordance with ASTM D4429-09 (ASTM, 2009a) to assess changes in strength and stiffness after subjected to FT cycles throughout the soil column inside the box. The field CBR testing setup details are discussed later in section 4.3.6 (i.e. Destructive Testing and Sampling).
Figure 4.1: a.) An overview of the HASTEST environmental chamber (interior dimensions-6.7 m in length and width with a height of 4.3 m) [left] capable to control the temperature (T) between 50 °C and -40 °C and relative humidity (RH) between 5% and 100% including the chamber control station [right]; b.) Overview of setup and equipment used for the large-scale freeze-thaw experiment including field CBR test setup showing the reaction blocks and beam spanning the soil box for testing.
4.3.3 Instrumentation

During the construction of the soil box (presented in Chapter 3), thermocouples, TC (thermocouple probe wire-20 wire gauge, K calibration from Thermo Electric Company), bender element pairs, BE (GDS encapsulated bender element and insert from GDS instruments, UK), and settlement plate pedestals (wooden, in-house built) were embedded in the soil at varying depths. The thermocouples and bender element pairs were used to monitor the real-time carbonation progress, whereas the settlement plate pedestals were installed to mount the Linear Potentiometer Position Sensor (LPPS); note that these spring-loaded LPPS are from the LPPS-SL series that was manufactured by Harold G. Schaevitz Industries LLC, MI, USA. The mounting of LPPS on settlements plates using a wooden beam across the box is presented in Figure 4.2a, whereas Figure 4.2b shows GDS bender element system, GDS BES (i.e. data acquisition) to measure the shear wave velocity, $V_s$ during FT cycles. The TC and LPPS wires were connected to a USB data acquisition system, (i.e. USB -2416 series from Measurement Computing) with a real-time monitoring system in the instrumentation monitoring room beside the environmental chamber. A detailed instrumentation plan and dimensions showing the locations of each instrumentation (i.e. TC, BE, LPPS) in the soil box during FT experiments are shown in Figure 4.3. The length, width, and height of the soil box (inside dimensions) were 2 m, 1 m, and 0.75 m, respectively. The box was divided into two sides-Side A and Side B with an initial degree of saturation, $S_r$, of 30% and 40%, respectively during surface carbonation (discussed in Chapter 3), and each side was approximately 0.5 m wide. Lime-mixed soil was in the upper 300 mm of the 450 mm soil column. Five thermocouples were placed at two locations on each side of the box (20 total) to monitor temperature changes at depths of 0, 100, 200, 300, and 400 mm whereas, two pairs of bender elements were located on each side of the box at depths of 50 and 250 mm (i.e. 50 mm below the top and above the bottom of the lime-mixed soil) to monitor the changes in temperature, $T$ and shear wave velocity, $V_s$, respectively during freeze-thaw cycles. Unfortunately, the upper pair of bender
elements on side A of the box did not function during the experiment, which is why they are not shown in Figure 4.3. Four LPPS were placed for each side (8 total) on top of the settlement plates that were installed at depths 0, 100, 200, and 300 mm to monitor the vertical movement (i.e. heave or settlement) during freeze-thaw cycles.
Settlement plates (wooden rod with pedestal) installed at different depths ($z=0, 100, 200, 300$ mm) [total 8 for side A and side B]

Thermocouples installed at depths $z=0, 100, 200, 300, 400$ mm

Shear wave velocity measurement using bender element pairs installed at depths $z=0$ and 250 mm

Figure 4.2: Instrumentation in the soil box during freeze-thaw experiments. a.) Linear Potentiometer Position Sensor (LPPS) mounted on settlement plates to monitor the vertical movement at varying depths ($z=0, 100, 200, 300$ mm); b.) data acquisition system for shear wave velocity measurement using bender element pairs embedded at $z=50$ and 250 mm.
All dimensions shown here are in meter, and the measurements of the box represent the inside dimension excluding wall thickness.

Figure 4.3: Soil box instrumentation plan and dimensions showing the locations of the thermocouples (TC), bender element pairs (BE), and Linear Potentiometer Position Sensor (LPSS) mounted on settlement plates (wooden rod with a circular pedestal) in a.) plan view and b.) elevation view.
4.3.4 Soaking/Saturation

Before applying freeze-thaw cycles, the post-carbonated soil column inside the box was saturated (soaked); recall side A and side B had $S_r$ of approximately 30% and 40%, respectively. An overview of bottom-up saturation for Side A and Side B of the box is shown in Figure 4.4a where water (additional theoretical amount needed to achieve $S_r$ of 100% for each side) was introduced from the water buckets to the bottom of the box using tubes and pre-installed groundwater conduits (see Figure 4.4b). These conduits were approximately 25 mm in diameter (inside) and the horizontal conduits shown inside the box are perforated whereas, the bottom 150 mm of the vertical conduits were perforated (2 on each side, 4 total- see Figure 4.4b and 4.4c together). This plumbing arrangement was made to ensure bottom-up saturation and to supply water during freezing through horizontal perforated conduits on both sides of the box. The water buckets were placed at a higher elevation to flow water due to the total head difference between the water bucket and the bottom of the box. After saturation, the soil surface appeared completely wet with surface moisture observed at different locations as shown in Figure 4.4c. After the saturation, a field CBR test was performed on the carbonated soil surface for each side (total 2) to understand the relative influence of soaking on the mechanical strength and stiffness of the carbonated soils.
Figure 4.4: a.) An overview of bottom-up saturation in the soil box using b.) horizontal and vertical perforated tubes; c.) view of the soil surface after complete saturation, but before applying freeze-thaw cycles.
4.3.5 Freeze-Thaw Testing Procedure

After post-soaking CBR testing, the soil box was subjected to two FT cycles. During FT cycles, the temperatures at various depths of the soil column on each side of the box (as per the instrumentation plan shown in Figure 4.3) were monitored in real-time using the embedded thermocouples to control the FT cycles. The temperature monitoring data are presented and discussed in the results section (see Figure 4.10). During FT cycle 1, the temperature in the environmental chamber was set to -23 °C to impose a 1-D freezing front through the top of the soil surface by providing an insulation system all around the soil box and supplying relatively hot air at the bottom of the box from a heating system as shown in Figure 4.5a. The freezing temperature (i.e. approximately -23 °C) in the chamber was continued until the soil column (depths between 0 to 400 mm) on each side of the box achieved at least -10 °C. A view of the frozen soil surface is shown in Figure 4.5b when the freezing front penetrates the bottom of the soil layer. Afterward, the insulation system was removed to expose the soil box completely to ambient room temperature for thawing of the soil column on each side of the box. The temperature of the chamber was set to +23 °C with relative humidity (RH) of approximately 85% at the beginning, and then the temperature was increased to +33 °C to accelerate the thawing process of the soil column inside the box. The testing configuration during thawing is shown in Figure 4.5c. Thawing of the soil column continued until the temperature attained at least +10 °C along the depth between 0 to 400 mm for both sides. The freezing and thawing duration during FT cycle 1 was 125.4 and 91.2 hours, respectively and the soil column in the box experienced a -10 °C to +10 °C cycle during FT 1. After FT cycle 1, soil samples were collected from both sides of the box to measure the water content, and CaCO$_3$ binder and Ca(OH)$_2$ content along the depth. During FT cycle 2, initially, the chamber temperature was set to -23 °C which was reduced further down to -40 °C to accelerate the freezing in the soil column; note that the water was supplied through the bottom perforated conduits (as an open system in the field) by continuous monitoring of the water level/head in the extended
vertical part of the horizontal perforated conduits as shown in Figure 4.4b, and having insulation system all around similar to freezing during cycle 1. Also, a similar criterion (i.e. at least -10 °C along the depths between 0 to 400 mm) was considered to complete the freezing and begin the thawing process. At the beginning of the thawing, the chamber temperature was set to +23 °C and RH of approximately 85%, and then the temperature was subsequently increased to +33 °C and continued until the soil column between 0 to 400 mm on each side of the box reached to approximately +20 °C. Afterward, the temperature of the chamber was reduced to ambient temperature and prolonged to achieve a complete thermal equilibrium that concluded the second FT cycle. The freezing and thawing duration during FT cycle 2 was 115.8 and 142.8 hours, respectively. Note that during FT cycle-2, the soil box was covered by the plastic tarp to avoid possible moisture changes on the soil surface due to freezing/thawing in the environmental chamber. \( V_s \) measurements were taken periodically during both FT cycles using the embedded bender element pair at different depths on both sides of the box and GDS BES, whereas the vertical movement (i.e. heave/settlement) data during FT cycles was logged continuously and monitored in real-time. Field CBR tests and sampling were performed after two FT cycles on both sides of the box. After post-FT 2 CBR testing and sampling, the soil box was removed from the environmental chamber and kept in the laboratory for approximately 12 weeks by covering the soil box with a plastic tarp. Note that these 12 weeks of drying following the saturation and FT cycles represent the Spring field condition after the harsh winter. After 12 weeks of post FT-2 drying, field CBR tests were performed on both sides of the soil box to investigate the long-term performance in terms of mechanical strength/stiffness of the carbonated soils that were subjected to saturation and two FT cycles. In addition, soil sampling was performed to evaluate any possible chemical reaction via \( CaCO_3 \) binder formation or lime, \( Ca(OH)_2 \), consumption.
4.3.6 Destructive Testing and Sampling

Destructive testing (i.e. CBR) and sampling were performed to assess changes in mechanical behavior and CaCO$_3$ binder and Ca(OH)$_2$ content after post-carbonation saturation, and freeze-thaw cycles. The gravimetric BC, $\beta_B = m_b/m_s$, is defined as the ratio of the mass of CaCO$_3$ binder and soil. Figure 4.6 illustrates the methods used to perform the field California Bearing Ratio (CBR) test in general accordance with ASTM D4429-09 (ASTM, 2009a) to assess changes in strength and stiffness throughout the soil.
column inside the box. The field CBR equipment, which consists of a mechanical screw jack and piston that penetrates the ground, reacted off a steel beam spanning the soil the box that was secured by reaction blocks on each side (see Figure 4.1b). The CBR is a normalized stress defined as,

\[
CBR = \frac{\sigma_\delta}{\sigma_{std}}
\]  

(4.2)

where \(\sigma_\delta\) is the stress after 2.54 or 5.08 mm of piston penetration and \(\sigma_{std}\) is a standard stress of 6.9 or 10.3 MPa that corresponds to 2.54 or 5.08 mm deformations, respectively; the CBR is the largest stress-ratio arising from measurements at 2.54 and 5.08 mm. A 75 mm thin-walled Shelby tube was used to extract soil samples. To prevent buckling of the tube, a scissor jack was used to slowly and methodically penetrate the thin-walled sampler by reacting with the steel beam (Figure 4.6b). Samples were immediately extruded and oven-dried to measure the water content of the extruded samples, and to prevent any further chemical reactions. The dried sample was stored in air-tight plastic containers prior to TGA testing to determine the \(CaCO_3\) BC and lime content.

The CBR testing and sampling locations are shown in Figure 4.7. The CBR was performed on the surface (i.e. 0) on each side after carbonation and saturation, but before freeze-thaw cycles. After 2-FT cycles, and after post-FT 2 drying for 12 weeks, CBR tests were performed at five different depths (0, 100, 150, 250, and 350 mm) at 2 locations on each side of the box (total 4 locations). A total of 52 field CBR tests were conducted on the soil box at different testing conditions. The reaction beam, as shown in Figure 4.1, could be repositioned to the centerline of each side of the box. CBR testing and sampling were performed in tandem; after each CBR test, sampling was performed to collect soil for water content measurements and TGA but also to advance the hole to the next CBR test depth.
Ratchet strap to attach mechanical screw jack with reaction beam

Proving ring with dial gauge

Penetration piston

Penetration dial gauge

Figure 4.6: a.) Field CBR equipment in the soil box; b.) scissor jack being used to penetrate a thin-walled shelby tube sampler into the soil.
Figure 4.7: Locations of field California Bearing Ratio (CBR) testing and soil sampling. a.) plan view; b.) elevation view.
4.4 Experimental Results

4.4.1 Baseline Conditions and Soaking

After the surface carbonation was conducted (Chapter 3), seven days elapsed prior to soaking the silt (i.e. fully saturating the soil box) for FT experiments. During the period between surface carbonation and soaking, the water contents were relatively low with degrees of saturation (30% and 40%) that would have created a continuous interconnected gas-phase in the voids. Thus, any remaining lime had the potential to react with atmospheric $CO_2$ between the end of surface carbonation and soaking. Once the box was soaked, diffusion of $CO_2$ into the voids would no longer have been able to occur as diffusion would have ceased because water obstructs the mobility of gas (Moldrup et al., 2000, 2001; Mahmoodi & Gallant, 2020, 2021).

TGA testing on soil samples collected after soaking and FT cycles were performed when the box was fully saturated revealed that there was some additional carbonation at depths where lime had not fully reacted during the accelerated surface carbonation experiment. Figure 4.8 shows the gravimetric binder contents (BC) and unreacted $Ca(OH)_2$ after accelerated carbonation was performed and after soaking and during the FT experiments; percentages shown are the ratio of the masses of $CaCO_3$ and $Ca(OH)_2$ divided by the dry mass of soil. Based on TGA testing, there was an increase in the BC and the corresponding decrease in the $Ca(OH)_2$ content that took place where lime had not fully reacted in the lightly carbonated zone during that time period. Thus, the BC measurements shown in Figure 4.8 are representative of the conditions during FT testing. This finding was viewed positively because: a.) it demonstrates that regions where surface carbonation did generate a binder “immediately” will continue to carbonate if water contents are low enough; b.) it extended the lightly carbonated region deeper (bottom of lime mixed soils) and presented the opportunity to assess the FT durability of fully carbonated soil with BCs of approximately 8.5% and lightly carbonated regions with BCs ranging from approximately 2% to 4%. Aside from marginal differences in BC measurements observed in the lightly
carbonated zone, there were no significant differences in the testing conditions on each side of the box during soaking, FT experiments, and the drying period reported herein.
Figure 4.8: Comparison of BCs measured immediately after accelerated surface carbonation was performed and increases observed in the lightly carbonated region in the seven days between surface carbonation and when the material was fully soaked.
Figure 4.9 shows the stress-penetration curves from CBR testing (Figure 4.9a) and the decrease in surface CBR measurements and increased water content observed after fully saturating the silt in the soil box (Figure 4.9b,c), which was expected. It’s widely understood that soaking subgrade materials results in reduced bearing capacity and CBR measurements after soaking (e.g. Leelavathamma et al., 2005; Hazirbaba & Gullu, 2010; Feng et al., 2020). Thus, the durability of carbonated material after FT cycles were conducted is compared with the baseline measurement after soaking. However, the reduced CBR values at the surface are indicative of very good quality subgrade material or good subbase materials for roadway foundation materials according to Schaefer et al. (2008).
Figure 4.9: CBR testing at the surface in the soil box, but before freeze-thaw testing, compared with measurements immediately after carbonation: a.) stress-penetration curves on Side A (left) and Side B (right); b.) changes in surface CBR and water content after soaking on Side A of the soil box; c.) changes in surface CBR and water content after soaking on Side B of the soil box.
4.4.2 Freeze-Thaw Experiments

Figure 4.10 summarizes the temperature and vertical deformation data with time, \( t_{FT} \), monitored throughout the duration of FT testing. The combination of cold temperatures provided by the environmental chamber and heat provided to the underside of the soil box successfully enforced the intended 1-D (top-down) freezing front in the soil on both sides of the box (Figure 4.10a). The soil generally thawed in a top-down manner as well, especially through fully carbonated soil; though soil at depths of 200, 300, and 400 mm typically reached zero deg. C horizon at the same time and the \( z = 300 \) mm depth was the last to rise above zero deg. threshold during thaw cycles (Figure 4.10a). This was due to the warmer temperatures on the bottom of the box, which were exposed to the warmer temperatures during thaw cycles, and the associated thermodynamics of heat exchange occurring within the box—which is not an unrealistic scenario in the subgrade; i.e. there are typically two thaw fronts (Konrad & Roy, 2000).

During both freezing phases, there was limited vertical movement (Figure 4.10b) and associated compression or expansion (Figure 4.10c) observed at different depth intervals within the soil column. Note that relative vertical deformations are expressed as a percentage of the thickness of soil between settlement plates for the subsurface depth intervals of 0 to 100, 100 to 200, 200 to 300, and 300 to 450 mm; i.e. expansion or compression indicates overall changes in layer thickness as a whole, but do not necessarily represent the compression or expansive strains of the entire depth interval. Notably, the greatest amount of upward vertical movement was observed at the start of a thaw cycle followed by downward vertical movement of the settlement plates embedded in the soil layers (Figure 4.10b).

As the top-down freezing front advanced in saturated soil, there was likely some adhesion between the side walls of the box and frozen water. Any adhesion would effectively impose a higher overburden stress on soils below the freezing front, which decreases the segregation potential and amount of heave where ice lens formation occurs.
during freezing (Konrad & Morgenstern, 1984). Thus, the sidewall adhesive forces may have restricted the amount of movement at greater depths in the soil box as the frost front advanced; i.e. ice lens segregation and heave in unstabilized material at the bottom may have been greater otherwise, and this could have led to more degradation to the carbonated soil in the upper layer.

During a thaw period, there are typically two thaw fronts—one that progresses from the top of the soil column and the other one that progresses from beneath the depth of frost penetration—which was simulated in these experiments. As summarized by Konrad & Roy (2000), the lower thaw front advances upward, and melted ice water under the weight of overburden material cannot escape (i.e. drain) upward due to the existence of an overlying impervious ice barrier. A hydraulic gradient can develop under the weight of overburden, driving downward groundwater flow and redistribution of pore water that results in the “swelling” of unfrozen soils below the thaw front, a mechanism that contributes to the weakening of subgrade soils. After the complete thaw, consolidation is typically observed (Konrad & Roy, 2000). Both swelling and consolidation were observed during each thaw cycle based on deformations shown in Figure 4.10b. However, it can be seen that the settlement plates generally move together, signaling that the greatest amount of expansion due to swelling was observed in the untreated layer from z = 300-450 mm (see Figure 4.10c). Figure 4.11 shows the subsurface deformations at different stages of the freeze-thaw experiments, where it can be observed that vertical deformations are primarily due to the expansion of untreated layers and that the overlying carbonated soil generally moves coherently.

Though there was little difference in the amount of deformations observed at all depths through the first FT cycle, there was substantially more swelling/expansion observed from 0 to 100 mm during the second thaw cycle on both sides of the box (Figure 4.10c). At the upper thaw front, an impermeable ice boundary below forces upward flow of groundwater when excess pore water pressures exist, which can contribute to the redistribution of pore
water and increases in water content to overlying soils, similar to unfrozen soils underlying
the lower thaw front (Konrad & Roy, 2000). There was also compression from 100 to 200
mm during the second thaw cycle (Figure 4.10c), which may have arisen due to the
combination of pore water redistribution to the soil above and swelling of the underlying
soil below (also reflected in Figure 4.11); notably some of the material through this depth
interval is lightly carbonated. The least amount of relative movement was observed from
200 to 300 mm, which was sandwiched between the two thaw fronts (Figure 4.10c).
Figure 4.10: Summary of information continuously monitored during two freeze-thaw cycles on Side A (left) and Side B (right) of the soil box: a.) temperatures monitored in the environmental chamber (room) and at soil depths $z = 0, 100, 200, 300,$ and $400 \text{ mm}$; b.) subsurface vertical deformations measured via settlement plate at soil depths $z = 0, 100, 200, 300,$ and $400 \text{ mm}$; c.) relative vertical deformations expressed as a percentage of the thickness of soil between settlement plates for the subsurface depth intervals of $0$-$100$, $100$-$200$, $200$-$300$, and $300$-$450 \text{ mm}$. 

114
Note. number in legend reflects the time during freeze-thaw experiments. For thawing, "swell" indicates the approximate time peak swelling was observed and "end" indicates at the end of a freeze or thaw period.

Figure 4.11: Vertical deformations through the subsurface profile at different points in time during the freeze-thaw experiments for: a.) Side A and b.) Side B of the soil box.

Shear wave velocity measurements for Side B of the box, where bender elements were located at both z = 50 mm (fully carbonated soil) and 250 mm (lightly carbonated soil), are shown in Figure 4.12. Shear wave velocity measurements in the fully carbonated material were initially 659 m/s prior to beginning the FT experiments. The shear wave velocity decreased to 461 m/s after the first FT cycle, but effectively remained unchanged thereafter (Figure 4.12a). Thus, there was a modest drop due to weathering imposed by frost action after the first FT cycle in the carbonated silt, but remained substantially elevated from pre-carbonation levels ($V_s = 228 \text{ m/s}$). Prior to the FT experiments at z = 250 mm (Figure 4.12b), the shear wave velocities were marginally greater than what was observed immediately after accelerated surface carbonation was performed, presumably due to the additional $CaCO_3$ precipitation attributed to the introduction of atmospheric $CO_2$. 
in the seven days between when accelerated surface carbonation was conducted and when the box was fully-saturated; which would have inhibited any further carbonation during that time period. A decrease to $V_s = 165 \text{m/s}$ was observed after the first FT cycle, but remained unchanged after the second FT cycle, similar to the shallower measurement. Recall that only one bender element pair was located on Side A of the box at $z = 250 \text{ mm}$ in lightly carbonated silt, with negligible differences compared with Side B.
Notes. i) Number in legends shows the depth, z in mm from the soil surface. ii) Temperatures were recorded at location B1.

Figure 4.12: Shear wave velocity measurements on Side B of the soil box at: a.) z = 50 mm in fully carbonated silt and b.) z = 250 mm in lightly carbonated silt.
4.4.3 Post Freeze-Thaw CBR Testing and Sampling

Figure 4.13 shows the CBR values and water contents measured after the first freeze-thaw (FT) cycle, which are compared with surface measurements after soaking, but before freeze-thaw testing. It is found that after the first FT cycle, CBR at the surface is increased for side A of the box and gradually decreased with depth within the fully-carbonated zone. A similar observation was found for side B of the box except for the CBR value at the surface did not increase as much as side A. Below the fully-carbonated soil, CBR values decreased significantly with depth being the lowest CBR value at the soil layer (i.e. untreated) which is expected. The higher CBR value after the FT 1 on the surface especially for side A could be attributed to the moisture loss (i.e. drying effect on the strength of the carbonated soils). Based on the water content measurements along the soil column on both sides of the box clearly showed that the water content decreased approximately between 5-10% with the highest water loss at the top and lower bottom of the soil column. This water loss was associated with evapotranspiration due to the significant wind currents in the HASTEST environmental chamber. To avoid this moisture loss and to ensure the material remained saturated, a plastic tarp was placed over the box during the second FT cycle, and water was supplied to the bottom of the box during freezing (discussed previously). These measures demonstrated a fully saturated soil column during FT 2 (refer to Figure 4.15).
Figure 4.13: CBR values and water contents measured after first freeze-thaw cycles compared with surface measurements after soaking, but before freeze-thaw testing: a.) Side A of the soil box; b.) Side B of the soil box.
Figure 4.14 shows the stress-penetration curves throughout the soil column after the two freeze-thaw cycles were performed. As expected, the strength and stiffness of fully-carbonated silt had the greatest strength and stiffness, and generally decreased in the lightly carbonated and uncarbonated soil below. Notably, the stress-penetration curves for lightly carbonated soils generally exhibited a substantially greater initial stiffness than uncarbonated soil below. This suggests that the lower BCs at these depths: a.) influenced the mechanical behavior; b.) had some resistance to the environmental stressors imposed by frost action during FT testing.
Figure 4.14: Stress-penetration curves from CBR testing after freeze-thaw cycles were performed: a.) Side A of the soil box; b.) Side B of the soil box.
Figure 4.15 shows the CBR values and water contents measured after two freeze-thaw cycles, which are compared with surface measurements after soaking, but before freeze-thaw testing, and before surface carbonation was performed (i.e. at low water contents). According to CBR-based frost susceptibility criteria (ASTM, 2013), measurements indicate fully carbonated silt had a very low susceptibility to frost action. Below the fully-carbonated soil, CBR values generally decreased with depth and the frost-susceptibility rating ranged from medium to high. Decreasing CBR values with depth can be attributed to the decreasing thickness of carbonated soil below the depth where CBR testing was conducted. CBR values in the untreated silt were very low with a high to very high frost-susceptibility rating, as expected. The results from deeper tests, where loading likely resulted in some interaction with the untreated material, are also compared with CBR values before carbonation when water contents were lower. This further highlights: i.) the substantial impact that environmental stressors can have on the strength and bearing resistance of frost-susceptible soils; and ii.) that CBR values based on compaction alone should not be relied on as an indicator of the quality of subgrade material supporting surface transportation infrastructure where frost action occurs. CBR values based on compaction only would be considered a “very good” subgrade material (Schaefer et al., 2008) (see criteria presented in Figure 4.9).
Figure 4.15: CBR values and water contents measured after two freeze-thaw cycles compared with surface measurements after soaking, but before freeze-thaw testing, and before surface carbonation was performed: a.) Side A of the soil box; b.) Side B of the soil box. The frost-susceptibility criteria according to ASTM D5918 is also indicated.
4.4.4 CBR Testing and Sampling after Drying Period

After the 12-week drying period of the soil column to allow moisture contents to decrease, which is expected for roadway foundation materials after seasonal periods where frost action occurs, CBR testing and sampling were performed to assess the resilience of carbonated material and potential changes in the BC. Figure 4.16 shows the stress-penetration curves from CBR testing in fully carbonated material after the drying period compared with results immediately after surface carbonation, soaking, and two freeze-thaw cycles at depths of \( z = 0, 100, \) and \( 150 \text{ mm} \). The strength and stiffness of fully carbonated silt not only recovered, but exceeded bearing resistances observed immediately after carbonation before FT testing was performed. Figure 4.17 shows the same information at depths \( z = 250 \) and \( 350 \text{ mm} \), where a significant increase in bearing resistance was also observed in the carbonated material. The uncarbonated material recovered and also exceeded pre-FT bearing resistances, but to a lesser extent.
Figure 4.16: CBR stress-penetration curves in fully carbonated material at depths z = 0 mm, z = 100 mm, and z = 150 mm after the drying period compared with measurements after surface carbonation, soaking, and two freeze-thaw cycles on: a.) Side A of the soil box; b.) Side B of the soil box.
Figure 4.17: CBR stress-penetration curves at depths $z = 250$ mm and $z = 350$ mm after the drying period compared with measurements after surface carbonation, soaking, and two freeze-thaw cycles on: a.) Side A of the soil box; b.) Side B of the soil box.
Figures 4.18a and 4.19a illustrate the changes in CBR and water content observed throughout the drying period. CBR values fully recovered, and in most cases, exceeded values observed after carbonation, but prior to soaking and FT testing. The notable increases in CBR, especially in the lightly carbonated soil, was not expected. Sampling and TGA results revealed a continued increase in the BC and associated decrease in unreacted $Ca(OH)_2$ from depths $z = 150$ to $300$ mm (Figures 4.18b and 4.19b). It is believed that as the water content in the soil decreased, it opened pathways for atmospheric $CO_2$ to diffuse into the soil and react with the remaining lime in the previously lightly carbonated soil.

Based on the increase in BC observed between accelerated surface carbonation and soaking, as well as increases observed during the drying period, substantial amounts of binder can form so long the water content does not obstruct the mobility of gas. This observation opens up the possibility of carbonating soil in a reasonable time frame without introducing the $CO_2$ directly (i.e. via surface carbonation). If so, implementation methods may not be necessary, so long as it is ensured that lime-mixed soil is prepared (mixed and compacted) at water contents that permit the diffusion of $CO_2$ gas. Thus, aside from demonstrating that carbonated material is durable when exposed to frost action, this study has revealed that carbonation can occur relatively rapidly under natural atmospheric conditions if water does not obstruct the mobility of gas within the pore volume. This would greatly simplify the implementation of this soil stabilization approach.
Figure 4.18: Comparison summary for Side A of the soil box: a.) highlighted the comparison between CBR values observed after two-freeze thaw cycles with values after a 12-week drying period (left); changes in water content (right); b.) highlighted changes in gravimetric binder content (left) and unreacted calcium hydroxide during the drying period. Also shown in (a) and (b) are measurements before carbonation, after accelerated carbonation, and soaking.
Figure 4.19: Comparison summary for Side B of the soil box: a.) highlighted the comparison between CBR values observed after two-freeze thaw cycles with values after a 12-week drying period (left); changes in water content (right); b.) highlighted changes in gravimetric binder content (left) and unreacted calcium hydroxide during the drying period. Also shown in (a) and (b) are measurements before carbonation, after accelerated carbonation, and soaking.
4.5 Summary and Conclusions

This study was built on a prior experiment where an accelerated surface carbonation technique was employed to rapidly stabilize subgrade soils mixed with hydrated lime in a large soil box. The objective of this study was to evaluate the durability of a frost-susceptible soil carbonated with hydrated lime in a controlled large-scale FT experiment that replicates the important field conditions influencing post-FT behavior. Environmental testing was carried out on the carbonated, highly frost-susceptible silt, which was first soaked and then exposed to two FT cycles in an environmental chamber. The FT experimental was heavily instrumented and intended to replicate field conditions by providing a continuous water supply and enforcing a 1D (top-down) freezing front. FT testing was followed by a 12 weeks drying period to determine changes in CBR following moisture content changes. Sampling and TGA were also performed to evaluate changes in water content and binder content—which revealed interesting results.

The experimental setup was able to replicate field conditions in several important ways: a.) a top-down freezing front was enforced; and b.) two thaw fronts formed in the soil box (i.e. top-down and bottom-up) during warming periods, which is expected in the field. The latter resulted in substantial swelling of uncarbonated soil at the bottom of the box. However, limited movement was observed throughout the soil column was observed during freezing. It was speculated that the adhesion of ice to the sidewalls of the box may have restricted movement and unintentionally applied a higher effective overburden stress, which could have suppressed ice lens segregation and heave during freeze cycles at greater depths in the box. Future large-scale FT experiments should attempt to limit any adhesion or boundary effects (e.g. using grease or similar).

In the fully carbonated soil, shear wave velocities decreased during the first freeze-thaw cycle and remained unchanged after the second cycle. Though shear wave velocities decreased, they remained significantly elevated relative to measurements prior to carbonation. This signaled that any damage to the binder-grain contacts likely only
occurred during the first FT cycle. This is consistent with observations from several other studies, where it has been observed that the majority of degradation of soils’ mechanical properties occurs during the first cycle of FT and moderates thereafter.

CBR testing revealed that fully carbonated material was durable and generally resistant to frost action. The lightly carbonated soils exhibited higher CBR values than untreated soil, and were likely moderately resistant to the effects of frost action. Thus, it can be concluded that carbonation with hydrated lime is a stabilization method that is durable against extreme environmental stressors—which is not dissimilar from conventional methods. However, carbonation sequesters $CO_2$ to generate the $CaCO_3$ binder, which substantially reduces the net carbon emissions associated with the production of lime.

A notable finding from this study was temporal changes in the binder content observed. This was attributed to atmospheric $CO_2$ reacting with unreacted $Ca(OH)_2$ that was not converted to $CaCO_3$ during accelerated carbonation that was performed prior to soaking and FT testing. It appears that if water contents are low enough such that water does not obstruct the mobility of gas, atmospheric $CO_2$ can diffuse through the soil matrix and generate a binder relatively quickly. This unexpected finding has the potential to simplify the implementation of soil carbonation and eliminate the additional step of introducing $CO_2$. However, this requires further research.
CHAPTER 5
SUMMARY AND CONCLUSIONS

5.1 Summary of Laboratory Experiments Conducted

This study of soil carbonation with hydrated lime was generally broken into three phases, which included: i.) elemental testing; ii.) a large soil box experiment examining a surface carbonation method; and iii.) freeze-thaw durability testing of carbonated silt stabilized during the surface carbonation experiment.

The initial phase sought to understand if hydrated lime may be used as a chemical additive to bind non-plastic soils (sand and silt) via carbonation and demonstrate the state parameters influencing the rate of carbonation and degree of mechanical improvement under varying conditions. Mechanical strength and stiffness were evaluated through unconfined compression tests and thermogravimetric analyses were performed to assess the binder content of carbonated soils. The degree of mechanical improvement was compared with soils stabilized using conventional cement-based additives. The results from this phase informed the testing conditions considered in the follow-up surface carbonation experiment performed in a large soil box.

The second phase was aimed at evaluating the efficacy of surface carbonation as a means to chemically stabilize shallow subgrade soils, which refers to the introduction of \( CO_2 \) gas beneath a near-ground-surface seal intended to contain and enforce vertical penetration of \( CO_2 \) gas into soil mixed with a chemical additive. This experiment was motivated by a need to develop implementation methods that can potentially be applied over large areas. The soil box experiment was designed to simulate surface carbonation near the perimeter of an embankment, which was deemed a critical location where gas is most likely to escape with this technique. Real-time monitoring of gas flow, temperature changes, and shear wave velocities, combined with post-carbonation characterization via \( CaCO_3 \) binder content measurements and CBR testing, were used to assess: a.)
carbonated thicknesses that could be achieved when carbonating under low \( CO_2 \) pressures; b.) the rate of carbonation and binder formation; and c.) the degree of mechanical improvement. Potential incentives that may drive the continued development of soil carbonation technologies were also discussed.

The third phase was aimed at understanding the durability of carbonated silt exposed to harsh environmental stressors (soaking and frost action). The soil box was fully saturated and then exposed to two freeze-thaw cycles in the HASTEST environmental chamber. The unique experimental setup included insulation and heat provided to the underside of the box to realistically impose a 1D (top-down) freezing front expected in the field. Environmental testing was followed by a 12 weeks drying period to evaluate changes in CBR due to moisture content changes. Temperature, shear wave velocities, and heave were monitored in the soil during freeze-thaw testing. CBR testing was performed to assess changes in mechanical behavior due to soaking, frost action, and moisture changes during the drying period.

5.2 Primary Findings and Conclusions

It was demonstrated that hydrated lime may be used to generate a carbonate binder in non-plastic soils by introducing \( CO_2 \) gas that triggers the carbonation reaction. The rate of binder formation in carbonated soil is highly dependent on gas mobility in the soil matrix, which is governed to a large extent by the degree of saturation and associated volumetric air content. In soils with degrees of saturation below 50%, a relatively rapid increase in the binder content was observed (all else being equal) compared with higher degrees of saturation. This is attributed to a continuous or near-continuous gas-phase through the voids. Soils with degrees of saturation greater than 50-60%—threshold values where a transition from a continuous gas-phase to a continuous water-phase in the void space is expected—the rate of binder formation decreased substantially because the water-phase begins to obstruct the diffusion of gas in the soil matrix. A higher gas volume in the soil
matrix increases the mobility of gas, while more water permits the dissolution of more lime and carbon dioxide gas, which hosts chemical constituents and facilities the reaction. Attempting to optimize the air and water contents to achieve the greatest carbonation rate would likely be difficult (if not impossible) to achieve in a field setting. Thus, it is most prudent to ensure the continuity of the gas-phase and avoid pore water barriers in the voids at high water contents, as the rate of carbonation remains relatively high even at low water contents.

A calcium carbonate binder can substantially increase the mechanical attributes of soil chemically improved via carbonation, thus expanding the applicability of lime as a chemical additive that can be used to treat non-plastic soils. Like other chemically stabilized soils, the strength is highly dependent on the density, volumetric binder content, and soil type. Fine-grained soils achieve equivalent strengths as coarser-grained materials at lower densities and volumetric binder contents. Density has a limited influence on the compressibility of carbonated materials, which is governed primarily by the binder-phase. It was shown that stiffness correlates well, and in a similar manner, with the unconfined compression strength for both fine and coarse-grained non-plastic soils.

Comparisons of strength with cement-stabilized soils demonstrated that soil carbonated with hydrated lime has a very similar dependence on soil type, density, and binder content. Moreover, equivalent strengths can be achieved in soils carbonated with hydrated lime as in soils stabilized with conventional cement additives.

A substantial increase in strength and stiffness akin to very hard soil or soft rock was observed in carbonated silt from the surface carbonation experiment. During surface carbonation, carbonation generally progresses from the surface of the soil column downward. Based on the combined interpretation of flowmeter data, temperature measurements, and post-carbonation binder content measurements, it was determined that typical thicknesses typically stabilized for roadway applications could occur in a matter of hours (4 to 5 hours in this study). Differences in the initial degree of saturation on two
sides of the box (30 vs. 40 %) had no apparent influence on the rate or degree of carbonation that was achieved. Why carbonation did not progress to depths greater than 200 mm in this study remains unclear. Post-carbonation water content measurements revealed no significant changes (i.e. increases in $S_r$) that would have resulted in water obstructing the permeation of gas vertically. Thus it was speculated that a steady state lateral flow condition developed after carbonation progressed to depths of 150 to 200 mm and gas flowed laterally to the far edge of the box where there was no gas barrier (i.e. the simulated slope of an embankment). It is possible that surface carbonation occurring away from the perimeter of the treated area may have resulted in greater penetration of $CO_2$ gas and carbonation to greater depths, but was not demonstrated or evaluated here.

A potential drawback of soil carbonation is the required additional step to introduce gas, which is not required with conventional chemical stabilization methods. Compared with conventional methods, where a chemical additive (e.g. cement or lime) is mixed with soil and then left for days to weeks (sometimes months) prior to binder formation, carbonation could provide a means for “immediate” verification as to a.) the extent of stabilization and b.) adequacy of adopted construction techniques. In a field setting, the ability to efficiently evaluate the efficacy of mixing methods and/or techniques to introduce gas allows for an adaptive management approach to construction—whereby contractors and engineers could optimize implementation techniques in real-time (and techniques not yet explored).

Soaking of carbonated soil results in a decrease in the CBR, which is expected generally true for all chemically stabilized soils. However, no changes in shear wave velocity were observed, which indicates soaking did not influence bonding. Relatively small changes in shear wave velocity and CBR values were observed in carbonated soil after two freeze-thaw cycles relative to measurements taken after soaking. Thus, the $CaCO_3$ bonds were generally resistant, and soil carbonated with hydrated lime appeared to be durable after being subjected to two freeze-thaw cycles. After a drying period, CBR-levels recovered and
even exceeded levels prior to soaking. This was attributed to continued carbonation from atmospheric $CO_2$, as an increase in binder content was observed in soil that was not carbonated during the accelerated process. Thus, even in areas not fully carbonated would be expected to increase with time.

If successful, carbonation has the potential to substantially reduce carbon dioxide associated with production-based emissions of hydrated lime. For example, the total carbon dioxide emissions for Portland cement are on average 0.95 tonne per tonne of cement. By employing carbonation, production-based emissions associated with quicklime could be reduced from 1.1 tonne/tonne to 0.35 tonne/tonne—approximately a third of that associated with Portland cement production. The widespread awareness and need to reduce the carbon footprint is already affecting policy. For example, The Inflation Reduction Act recently created the Low-Carbon Transportation Materials Program, which provides US$2 billion in incentives for the use of construction materials and products that result in substantially lower levels of embodied greenhouse gas emissions associated with all stages of production and use in the United States, effective from April 6, 2023 to September 30, 2026. Inflation Reduction Act § 60506, 23 U.S.C. § 179. Thus, there are now explicit financial motives to pursue innovative construction methods like soil carbonation.

5.3 Recommendations for Future Work

The findings from this study have provided many important insights regarding soil carbonation. However, a substantial amount of work remains before this chemical stabilization will be considered a proven technology. An unexhausted list of future activities to consider are:

- A broader range of soil types should be considered moving forward. Relationships for strength and stiffness presented in Chapter 2 were only for two non-plastic sand and silt. Additionally, more sophisticated mechanical laboratory tests (e.g. triaxial)
should be performed to address the cyclic resistance to loading and degradation of
strength and stiffness under varying load amplitudes.

• Surface carbonation was conducted under low $CO_2$ pressures (1 atm $\approx 0$ kPa gauge
pressure), where it was demonstrated that the upper 150+ mm of soil could be
carbonated within 4 to 5 hours. It’s entirely conceivable that high flow rates could be
generated such that a greater build-up of pressure beneath a surface seal would
facilitate the penetration of $CO_2$ gas, and carbonation, at greater depths. The
influence of surface pressure on the depth and rate of carbonation should be
investigated further.

• Future experiments, including the surface carbonation technique, should be
investigated in a field. These methods should incorporate a rapidly deployable seal
(or pseudo-seal) that entraps $CO_2$ gas and enforces vertical penetration into the
ground. The experiments should be able to evaluate the seal’s ability to contain $CO_2$
gas (i.e. limit losses at the perimeter or otherwise) and depths of carbonation. It will
also be important to assess differences in carbonated soil thicknesses achieved at
different locations (e.g. near and away from the perimeter of the sealed area).

• Future experiments should also consider the rate of carbonation with hydrated lime
when no attempt is made to accelerate the process relative to atmospheric conditions.
Binder contents measured showed an increase in previously uncarbonated soil after
the accelerated surface carbonation experiments. It is believed atmospheric $CO_2$ was
responsible. If so, and the process can occur at a reasonable rate under certain
conditions, there may be scenarios where carbonation could be a technique without
the need to introduce gas, which would eliminate a step from the process.

• Future work should consider the physics of gas flow and reaction kinetics, which is
linked to gas concentrations, gas pressures, and the dissolution of dissolved
constituents (chemical additive and $CO_2$), on the binder formation rate. The ability
to numerically simulate the aforementioned items would allow numerical studies that
could investigate implementation schemes that would better inform future large-scale
or field-scale experiments, which are resource intensive.

- The large-scale freeze-thaw tests demonstrated that, when carbonated, soils highly
  susceptible to frost action exhibit substantial resistance to environmental stressors
  and durable after being subjected to two freeze-thaw cycles. A reduction in shear
  wave velocity in carbonated soil, presumably due to particle-scale damage to bonds,
  was only observed after the first freeze-thaw cycle and then remained constant
  thereafter. However, only two freeze-thaw cycles were performed due to the
  availability of the HASTEST environmental chamber at the University of Maine.
  Future testing (lab or field) should evaluate the durability of carbonated subgrades
  exposed to environmental stressors for longer periods of time. Additionally, it is
  imperative that the durability of carbonated soils be tested under realistic traffic
  loading conditions for the stabilization of subgrade (or subbase) materials for
  transportation applications. An appraisal of the performance of carbonated soils
  under these conditions will be needed prior to the widespread adoption of this ground
  stabilization method in practice.
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145


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BIOGRAPHY OF THE AUTHOR

SK Belal Hossen completed his BS in Civil Engineering from the Military Institute of Science and Technology (MIST), Dhaka-Bangladesh in December 2009, and his MS in Civil and Geotechnical Engineering from the Hong Kong University of Science and Technology (HKUST) in 2015. He started his PhD in Civil Engineering (majoring in Geotechnical Engineering) at the University of Maine in September 2018. Before pursuing his PhD, he worked in academics and engineering consultancy firms. He was a lecturer in the civil engineering department at MIST for 4 years. He also worked as a geotechnical engineer for engineering consulting firms (Maurice Lee and Associates and ARUP) in Hong Kong for 3 years. His geotechnical engineering experience includes the design and construction observation of slope stabilization, ground investigation, deep foundations, and support of excavation. He is a candidate for the Doctor of Philosophy degree in Civil Engineering from the University of Maine in May 2023.