Valorization of Industrial Waste by CO₂ Supercritical Curing: Toward Sustainable Building Materials and Circular Economy

by

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FOR MY BELOVED LATE FATHER, WHO WOULD BE PROUD TO SEE HOW I HAVE SHAPED MYSELF

AND,

FOR THOSE WHO SAIL ALONG THE JOURNEY OF

LEARNING AND CHANGING THE WORLD

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ABSTRACT

The cumulative carbon emission from worldwide fossil-fuel-based energy infrastructure is expected to top 850 Gt by mid-century. At this rate, our society will surpass the prescribed carbon budget set to limit the mean global temperature increase below 1.5°C. Current carbon emission levels, and climatic call for the development of new technologies in the capture, storage, and utilization of carbon dioxide. In this context, rapid CO₂ mineralization offers an attractive direction in the immobilization of carbon dioxide (captured from industrial processes) through valorization of industrial waste, and creation of sustainable building materials for construction industry. A significant portion of the solid industrial waste such as slags, cement-kiln dust, fly and incineration ash, demolition concrete, construction gypsum sheetrock, contain natural and synthetic divalent cations, which show strong chemical affinity toward CO₂, and offer a potential for rapid mineralization through carbonation. As a result, calciumbearing building materials can be manufactured for reuse in the construction e.g., concrete aggregates, CO₂-cured structural and non-structural products. Per recent estimates, the volume of construction waste generated worldwide every year is expected to reach 2.2 billion tons by 2025. In case of constructional gypsum and demolition waste, $\approx 90\%$ of bulk waste is directly disposed. In both cases, waste storage represents non-negligible environmental hazard resulting from inadequate waste isolation, or structural stabilization. A lot of alkaline waste carbonation techniques with the use of either gaseous or liquid state of carbon dioxide have been proposed yet they have their shortcomings due to their intrinsic nature.

In this work, the author proposes a novel method of ex-situ mineral carbonation, defined here as super-critical curing of waste materials, and aiming at the extension of the method to different kinds of waste materials along with the plan to bypass the shortcomings associated with the other methods of carbon curing. The proposed technique relies on curing of the waste materials from the municipalities and industries with carbon dioxide (CO₂) in a super critical state which allows the rate and extent of carbonation to exceed the limitations that the curing techniques using gas and liquid state carbon dioxide bear. First, the industrial and municipal waste materials having potential for carbon dioxide sequestration is explored and selected through an extensive literature review. The parametric study targeting packing density, degree of saturation and cement chemistry is designed after analyzing the data from ad-hoc test runs. The experimental outcome is assessed in terms of CO_2 efficiency, which is in fact the weight-increase due to carbon dioxide intake divided by the theoretical weight increase potential, using weight increase method which is cross validated through CO₂ efficiency achieved through results obtained from Thermogravimetric Analysis coupled with Image analysis results. Along the process, the achieved degree of saturation and porosity prior and post carbonation is reported with the error associated with it. It is demonstrated, the porosity has a pronounced inverse effect in the rate and extent of carbonation while the effect of moisture content could not infer any contrasting results. Furthermore, the fly ash sample with same parameters were cured in different conditions: normal curing, hydrothermal curing and super-critical CO₂ curing, and the samples were then tested with the ASTM testing in uniaxial compression. Finally, microstructure of a sample was studied, secondary electron imaging and electron

dispersive x-ray spectroscopy, with the help of Scanning Electron Microscopy. The qualitative analysis for elemental composition is observed and a rough estimate of quantitative elemental composition is also observed.

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CHAPTER 1

Introduction

1.1 Problem statement

The cumulative carbon emission from worldwide fossil-fuel-based energy infrastructure is expected to top 850 Gt by mid-century [1]. At this level, our society will surpass the prescribed carbon budget set to limit the mean global temperature increase below 1.5°C [2][3]. Current carbon emission levels, and experienced changes in the earth climate, call for the development of new technologies in the capture, storage, and utilization of carbon dioxide. In this context, rapid CO₂ mineralization offers an attractive direction in the immobilization of carbon dioxide (captured from industrial processes) through the valorization of industrial waste [4-10] and the creation of sustainable building materials for the construction industry. A significant portion of the solid industrial waste such as slags, cement-kiln dust and other wastes contains natural and synthetic divalent cations, which show substantial chemical affinity toward CO₂, and offer a potential for rapid mineralization [11] through carbonation. As a result, calcium-bearing building materials can be manufactured for reuse in the construction e.g., concrete aggregates, CO2cured structural and non-structural products. Per recent estimates, [4] the volume of construction waste generated worldwide every year is expected to reach 2.2 billion tons by 2025. Moreover, according to the American Coal Association [12], around 40% of the total coal fly ash produced in the US in 2018 only (\approx 100mln ton [13]) was disposed in wet or dry form in landfills or waste ponds. In case of constructional gypsum and demolition

wastes, about 90% of the bulk waste is directly disposed.[14] In both cases, the waste storage represents a non-negligible environmental hazard resulting from inadequate waste isolation or structural stabilization. A 2008 Kingston power plant spill in Tennessee is a prominent example of the intrinsic hazard; more than a billion of gallons of coal ash slurry spilled into local waterways after the six-story earthen containment collapsed [13[15]. Likewise, under compromised storage conditions, the hydrogen sulfide (H2S) gas can be emitted from both construction and demolition (C&D) gypsum debris affecting local communities. Therefore, if successful, the proposed research on accelerated CO₂ mineralization under supercritical conditions, contrary to already existing strategies, may allow for process scalability necessary for large scale implementation, and represents an important contribution to the global (and local) efforts toward sustainable society, circular economy, and clean environment. Finally, the result of the proposed research will be used to qualitatively and quantitatively better understand the kinetics and carbonates crystal growth in the micro-porous Ca-bearing solids under supercritical conditions.

1.2 Proposed approach and objectives

The following hypothesis will be tested in the proposed research: CO₂ mineralization via supercritical curing is the efficient and scalable process for the carbon dioxide immobilization and valorization of solid industrial waste. To test this hypothesis the set of following objectives is put forward: a) waste identification and samples collection, b) mineralization process design, demonstration, and small-scale parametric study of carbonation process, and c) product evaluation and quantification of CO_2 immobilization efficiency with respect to physical and chemical characteristics of the industrial waste, supercritical processing parameters, and textural characteristics of carbonated precast elements. Listed goals are aligned with the growing trends in the construction materials sector, as well as ongoing multidisciplinary research worldwide, and both focused on the mitigation of global warming caused by the anthropogenic CO₂ emissions. Although the potential of the industrial waste, or construction materials based on cement for CO₂ sequestration has been recognized, the culprits of current strategies for CO₂ immobilization are: the low yield of the carbonation process, a slow mineralization kinetics, increased costs and process scalability. Listed deficiencies are present when the mineralization process is carried out using CO₂ in gas or liquid phase, although certain level of increased efficiency has been observed in the latter. Existing limitations originate mainly from the physical and transport properties of CO₂ in both states, as well as the low permeability microstructure of cementitious materials or highly consolidated waste forms. Given the existing limitations, the waste mineralization with the aid of supercritical CO₂ is proposed here and is motivated by the noteworthy transport properties of supercritical fluids which exhibit the intermediate behavior between that of a liquid and a gas. For example, the liquid-like density of supCO₂ allows for higher concentration of CO₂ molecules interacting with the solid material through the water nano-film formed by the water molecules

adsorbed on the solid surface, or through the bulk water present within the micropores of the porous solid. On the other hand, a small linear molecules of CO_2 in supercritical state exhibit gaslike viscosity, low-surface tension, and diffuse more quickly than in bulkier liquid state[9].



Figure 1: Schematic of the proposed research on accelerated carbonation of solid industrial waste

1.3 Thesis outline

This thesis consists of six chapters, in which a state of art technique to recycle inorganic waste materials is proposed. In Chapter 1, the industrial problem and research context are put forward introducing the motivation for this project. Chapter 2 reviews the literature in extent to identify the potential wastes materials from different sources, different techniques approached to sequester Carbon Dioxide into the waste materials and finally discusses on the state-of-the-art technique of using supercritical carbon dioxide to optimize the carbon sequestration into those waste materials.

In chapter 3, we introduce the materials and experimental methods used to design, process, and analyze the waste materials and the final product after carbonation. The materials are selected according to the availability, their carbon dioxide sequestration potential and hazard potential with information concluded from the literature review. Then, Ad-hoc test runs are performed using the selected materials to design a parametric study encompassing the prescribed temperature, carbon dioxide concentration, curing period, porosity, cement chemistry and saturation levels. At the end of the chapter 3, the methods to determine the carbon sequestration capacity and cross-validate the results along with the error associated with the data analytics are discussed. The different approaches developed to cast and cure the neat fly ash samples are mentioned. The compressive test protocols to determine the compressive strength of the samples complying to the ASTM standards is discussed in this chapter.

In Chapter 4, the experimental results from carbonation of cement and fly ash system, and the neat fly ash system is reported. The carbon sequestration potential is compared in the samples with respect to different parameters. Additionally, the compressive strength of the carbonated neat fly ash class C samples is determined and compared with the comparable system which has not undergone carbon curing. Chapter 5 discusses the error associated with the data analytics. In the last part, Chapter 6, findings of this research are summarized and the extension of the proposed method to develop construction materials from other sources of wastes are discussed.

CHAPTER 2

Literature review

Industrial and municipal wastes have been a major environmental pollutant since the beginning of the industrial age. During the last few decades, extensive actions are taken to manage these wastes around the world. Because of new environmental laws, the industry faces costs associated with the management and disposal of waste material it produces. Similarly, natural disaster debris also challenges cities to find suitable management solutions. The wastes generated from hurricane Harvey (2017) in Texas were dumped in hundreds of landfills. Hence, these wastes need to transform into useful products using carbon dioxide sequestration, which will lead the globe towards the projected carbon goal.

2.1 Carbonation mechanism

Carbonation is when carbon dioxide [CO2] encapsulates into bivalent metal oxides in the presence of water, which can be divided into natural carbonation and accelerated carbonation for convenience. Natural Carbonation includes atmospheric CO₂ absorb into the natural alkaline silicates to form carbonates but has a low rate in doing so [16] [17] [18].

Accelerated carbonation is the process that involves alkaline materials reacting with high-purity CO₂ to accelerate the reaction in the presence of water molecules [19]. Recently, accelerated carbonation processes have been focused on optimizing CO₂ sequestration concerning pressure, temperature, porosity, particle size, and solid pretreatment and more [17][20][21][22] as described in,

$$M^{++} + CO_3^{--}$$
 yields $\rightarrow MCO_{3(aq)} + MCO_{3(s)}$, Eqn. 2.1

where,

MO = Metal Oxides and MCO₃=Metal Carbonates.



Figure 2.1: Alkaline solid waste accelerated carbonation reaction modified schematic.

2.2 Alkaline solid wastes

Table 2.1 summarizes the industrial alkaline wastes that are alternative sources for carbon dioxide sequestration because they are widely available at low cost, provide bivalent metal cations, and are highly reactive compared to natural minerals. Furthermore, as they are close to fixed CO₂ sources, the transportation cost decrease with a possibility of switching their hazardous nature into a value product [24]. The advantage of using

alkaline waste is the achievement of acceptable CO₂ conversion rates with milder reaction conditions [21].

Despite their high potential for carbonation, all waste materials cannot be used for carbonation due to complicated and costly sequestration processes and hence their selection depends on a holistic criteria which includes bivalent metal presence, annual production amount, proper reuse and recycle, distance from CO₂ source, and profitability [23].



Figure 2.2: Accelerated carbonation reaction of alkaline solid wastes [23].

Waste Type	Availability in the North America	CO ₂ (%)	Remarks	Reference
Slag	Abundant in Canada and the United States. Slag has already good use	20-50	High CO ₂ sequestration capacity with associated high cost for operation.	Sanna et. Al [25] Teir et. Al [26] Doucet et. Al [27] Bonenfant et. Al [28]
CKD	15 million metric tons disposed in the United States alone in landfills	10-30	Recycle ratio within the cement plant is high	Huntzinger et. Al [29] Sanna et. Al [25] Gunning et. Al [30]
CBA	4.5 million tons remains unused as of 2018, but with coal industries facing harsh policies, its availability may be limited in the future	N/A	The pH and particle size varies widely with respect to the source and the way it is stored	Gunning et. Al [30]
Coal FA	39.5 million tons of fly ash is disposed into the landfills.	6-30	Fly ash Class F has low CO ₂ sequestration capacity wile Class C has good capacity.	Sanna et. Al [25] Hernandez et. Al [88] Nyambura et. Al [32]
SSA	Available in the United States	25	The particle size varies widely with respect to the source and the way it is stored	Gunning et. Al [30]
FGD gypsum	Roughly, 14 million tons remains unused in the United States as of 2018, but with coal industries facing harsh policies, its availability may be limited in the future	N/A	pH typically exceeds 11.0, and some sources can exceed the Resource Conservation and Recovery Act limit of 12.5 for toxic waste	Lee et. Al [96] Crange [33]
Phosphogypsum	One-billion tons of Phospho-gypsum are stacked in Florida with 30 million tons generated each year because of refining phosphorus	N/A	Ban on use except for agriculture purpose due to radioactivity of phosphor-gypsum (10-26 pCi/gm)	Ding et.Al [34] Strydom et.Al [35] Lu et. Al [36]
Construction Waste Gypsum	Abundant in all states of the United States		Millions of tons of waste dry wall from construction demolition and disaster dumped in the US	Chandara et. Al [37]

 Table 2.1: Waste materials with suitable mineral carbonation properties and their availability in North America.

Author's Name	Year	Publication Title	Summary
Sanna et. al	2014	A review of mineral carbonation technologies to sequester CO ₂	Carbonation process types, chemistry and reaction kinetics, material selection and respective CO_2 sequestration capacities, description of recent pilot CO_2 projects, process cost assessment.
Huijgen et. al	2005	Carbon dioxide sequestration by Mineral Carbonation, Literature review update 2003-2004	Estimated global capacity for CO ₂ storage and utilization potential, Material selection, Carbonation Process route description and process efficiency comparison and cost comparison.
Pan et. Al	2012	CO ₂ capture by accelerated carbonation of alkaline wastes: A review on its principles and applications	Guide for material selection, process chemistry and reaction kinetics, Process evaluation of different Mineral Carbonation Techniques and utilization of end products.
Olajire	2013	A review of mineral carbonation technology in sequestration of CO ₂	MCT process routes and their efficiency comparison, commercial pilot plants involving geological CO_2 capture, use and disposal of carbonation product.
Huntzinger	2006	Carbon dioxide sequestration in cement kiln dust through carbonation	Carbonation process mechanism: macro and micro scale process, theoretical carbonation efficiency calculation, post carbonation efficiency assessment.
Greve-Dierfield et. al	2020	Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CC	Carbonation mechanisms in cementitious hydrates, and CO_2 sequestration, factors affecting carbonation rate and extent, intrinsic water generation from portlandite carbonation, connection between C- S-H and Ca(OH) ₂ carbonation, reference for parametric study design.
Tai and Chen	1998	Poly Morphism of CaCO ₃ , precipitated in a constant- composition environment	Stability of the calcite polymorphs with respect to temperature and pH.
Cwik et al	2018	Carbonation of high-calcium fly ashes	Post carbonation assessment guidelines, reference for results comparison, and reference for microstructural assessment.
Gaurav Sant et. al	2018	Clinkering-free cementation by fly ash carbonation	Reference for post carbonation assessment, parametric study design, and CO_2 efficiency.

Table 2.2:	Carbon sequestration research summary.	

Various slag types, which are generated during iron and steel making processes, are good carbon sequestration candidates because they contain calcium, silicate, and a lesser amount of magnesium (Figure 2.3). Moreover, they have particle sizes ranging from 15 μ m to 150 μ m. However, all slags have already a good reuse and recycling potential. They have also a relatively high market value that reduces the possibility of their use for mineral carbonation. On the other hand, construction wastes, such as cement kiln dust and cement waste, that are generated from cement production and structural demolition, have a significant potential for carbon sequestration due to the presence of high calcium and silicon dioxide (Figure 2.4). Moreover, a coal bottom ash has a potential carbon sequestration of around 60% by weight of SiO₂ and iron, calcium, and magnesium content in lesser extent (Figure 2.5). A series of pie charts summarize the chemical composition of the waste material.



Figure 2.3: Relevant physical and chemical properties of different types of slag: Major oxide content comparison between various types of slag, pH and mean diameter. [28] [38] [39] [40] [41] [42] [43] [44] [45].



Figure 2.4: Cement kiln dust average chemical composition [46].



Figure 2.5: Coal bottom ash Average chemical composition [47] [48] [49].



Figure 2.6: Sewage sludge average chemical composition [50].



Figure 2.7: Phospho-gypsum average chemical composition [34] [51].



Figure 2.8: FGD gypsum average chemical composition [35] [37].



Figure 2.9: Fly Ash Class C Average Chemical Composition [32] [39] [99].

2.2.1 Fly Ash Mineral Carbonation

Fly ash is generated as a waste product during coal burning to produce energy [52]. Even though considerable efforts have been made to replace Ordinary Portland Cement (OPC) in concrete with supplementary cementitious materials (SCMs) such as fly ash, the extent of such utilization remains limited 53]. As of 2019, only 15-20% of the produced fly ash in the U.S. has been used to partially replace OPC in concrete [C2.26]. Moreover, according to the American Coal Association, only about 36% of the total coal fly ash produced in the US in 2020 (i.e., about 39.5 million tons) was disposed in landfills or waste ponds [54]. This situation represents a serious non negotiable environmental hazard which comes with an opportunity to valorize the waste and create resources for further use. Since it has high calcium and/or silica, fly ash can be, independently or in conjunction with cement, used for carbon sequestration, which can solve its waste management problem, reduce its carbon footprint, and increase supplementary cementitious use to contribute towards carbon neutrality goal.

2.2.2 Recycled gypsum mineral carbonation

Gypsum is extensively used in dry wall construction and in aesthetic works in United States. Its abundance in the United States did not encourage artificial gypsum recycling [35]. However, the environmental impacts of waste gypsum, such as Flue Gas Desulfurization (FGD Gypsum), Phospho-gypsum and disposed dry walls, are significant [34] [35] [51]. In Houston, the construction debris from Hurricane Harvey, which is still left unattended at hundreds of landfills, presents serious risks for environment pollution [49]. On the other hand, these gypsum wastes can be carbonated and transformed into construction valued products. The carbonation of gypsum wastes generates calcium carbonate, which can be used as cementitious product for construction works and thereby reducing cement use [34] [35]. This subsequently reduces cement production, which helps preserve raw materials and fossil fuels and decrease carbon dioxide emission.

Similarly, most gypsum wastes (Phospho-gypsum (CaSO₄.2H₂O), FGD Gypsum (CaSO₄.2H₂O)) have intrinsic water content, which makes them suitable for carbonation as water is required for dissolution of carbon [34][35].

2.3 Mineral carbonation process routes

Mineral carbonation process routes can be classified under three headings, namely 'ex-situ MCT', 'in-situ MCT' and 'other MCT routes' [16]. Mineral direct carbonation can be conducted using the following approaches:

2.3.1 Ex-situ MCT

The ex-situ MCT route is the process which involves the carbonation of natural mineral and industrial alkaline wastes using controlled conditions [23]. The MCT process routes consist of a combination of different process, majorly pretreatment and sequestration processes, where the pretreatment options include mining, crushing, and milling of the mineral-bearing ores prior to carbonation. The ex-situ MCT process can be divided into direct and indirect methods. The direct methods is a single step process while the indirect methods include a multistep process where extraction of reactive compounds from the mineral matrix occurs followed by the carbon sequestration [16].

2.3.1.1 Direct carbonation routes

2.3.1.1.1 Gas solid route

The direct reaction of gaseous CO₂ with solid mineral or alkaline waste is the science behind Gas Solid Route for Mineral Carbonation [55]. However, it suffers from very slow reaction rate and carbonation extent which has made it oblivion [16]. As shown

in Figure 2.9, gaseous CO₂ cannot transport sufficient gas molecules for reaction, which hampers the reaction kinetics of carbon dioxide to form bi-carbonic acid as,

$$M - SiO_2 + CO_2$$
 yields $\rightarrow M - CO_3 + SiO_2$. Eqn. 2.2.a

This can help achieve the carbonation without addition of water from external sources, which eliminates the process to extract the water from the product [16] [23].

2.3.1.1.2 Aqueous carbonation

Direct aqueous carbonation involves mechanism that occurs simultaneously where,

• Carbon dioxide dissolves in the water phase resulting in a mildly acidic environment with HCO3- as the dominant carbonate species,

$$CO_2 + H_2O + yields \rightarrow H_2CO_3 + SiO_2$$
, Eqn. 2.2.b

• following, Alkaline earth metals leaches from the mineral matrix, facilitated by the protons present,

$$M - SiO_2 + 2H^+_{(aq.)} \text{ yields} \rightarrow M^{++}_{(aq.)} + SiO_2 + H_2O,$$
 Eqn. 2.2.c

• Finally, magnesium or calcium carbonate precipitates:

$$M_{(aq.)}^{++} + HCO_{3(aq.)}^{-}$$
 yields $\rightarrow MCO_{3(S)} + SiO_{2} + H_{2}O.$ Eqn. 2.2.d

The aqueous mineral carbonation techniques provide sufficient mass transportation but lacks efficient diffusivity properties. For large samples, aqueous carbonation techniques would require high pressure to get into the pores, which can disturb the pore distribution. The high dissolution rate can be achieved by increasing the specific surface area, removal of the SiO₂ layer, and lowering the bivalent cation activity in solution, thermodynamic input, chemical input, and mechanical input [16].

2.3.1.2 Indirect carbonation routes

The indirect carbonation includes processes that require multiple steps for mineral carbonation. Multi-step gas-solid route and aqueous carbonation are the major sub classes. The indirect aqueous mineral carbonation theoretically shows technical and energetical feasibility but comes with a high processing cost [27] [56] [57] [58].

2.3.1.3 Challenges of ex-situ MCT:

2.3.1.3.1 Scale

USEPA reports 4 million- MWh coal-fired plant emits 4 million tons of CO₂ or 1.1Mt (1.1×10^{-3} Gt) of carbon per year [16]. So, the waste materials along with carbon dioxide are produced in massive scale requiring large scale carbon sequestering facilities with efficient carbonation techniques. On the other hand, this science has not been leveraged for larger sample which can signify different anomalies such as insufficient pore diffusivity of CO₂ and lack of stability of end products in the long run [23] [59].

2.3.1.3.2 Low reaction conversion and slow reaction kinetics

The main barriers for commercializing carbonation are high energy intensity, low reaction conversion, and slow reaction kinetics [60] [61]. Pan et al concludes, "*The solid particle dissolution process is generally controlled by: (1) diffusion through a fluid film surrounding the particle, (2) diffusion through a solid product layer on the particle surface, or (3) chemical reaction at the particle surface*". The detail explanation are explained in the following sub sections.



Figure 2.10: Macro and micro scale processes during mineral carbonation [20].

2.3.1.3.3 Energy costs:

Ex-situ formation of carbonate minerals requires transport of suitable initial material to a carbonation reactor, grind the material, heat the reactor system, and store or dispose of the solid carbonaceous product which comes with a cost [64]. Gerdemann et al. (2007) evaluated the resources, kinetics, process development, and costs for each process step and suggested a total price range of \$54/ton to \$133/ton of sequestered CO₂. [97].

2.3.2 In-situ MCT

In-situ mineral carbonation techniques includes mineral storage in natural rocks by CO₂ injection into silicate rocks containing divalent metal cations (Ca,Mg) such as basalts [65] and peridotites [66]. This route skips the need for mining, mineral transportation and pretreatment, and recovery as experienced in Ex-situ MCT [67]. The CarbFix and Wallula basalt are one of the majors in-situ carbon sequestration projects of such kind. The challenges faced by these techniques are availability of water for CO₂ injection, and the need for impermeable cap rocks over the rocks [54].

There are other types of MCT such as Passive MCT and biomineralization. Figure 10 shows an overview of the different types of existing MCTs. Figure 11 is a flow chart that describes the mineral carbonation of alkaline wastes.



Figure 2.11: MCT process route [16] [69] [70] [71].




2.4 Parameters influencing carbonation rate and extent

2.4.1 Cement chemistry

The available literature data points toward a crucial role of the hydrated cement paste chemistry and the micro texture of the cementitious material on the kinetics of the carbonation process, its degree, and carbonation rate. It is intuitive to think the plain cement samples have one set of hydrated products dominated by the calcium-silicate-hydrate gel and calcium hydroxide. However, the cement paste phase assembly and pore solution do alter to a large extent once the supplementary cementitious materials are incorporated within its microstructure [58]. This fact was confirmed in the carbonation study of cement systems with the fly ash substitution from 30% to 50% by weight of cement at fixed waterto-binder ratio [74]. For example, in concrete with SCM (fly ash replacement up to 30%), the direct comparison with the plain Portland cement concrete revealed only a slight increase in the carbonation depth. Interestingly, the higher rates of cement replacement with the fly ash tend to promote the carbonation process and increase the carbonation rate of concrete to a much higher degree [74]. So, the carbonation resistance is based on more varying parameters including but not limited to the relative humidity, pressure, temperature, and porosity. The correlation mentioned above may not hold when the carbonation efficiency of the system is assessed [58].

2.4.2 Relative humidity

The carbonation process of cement-based materials is much dependent on the diffusion of CO₂ into the pores and dissolution in the pore solution where it interacts with the solid phases across solid-liquid boundary [16] [23] [72]. According to the general theory, the low levels of the RH suppress the carbonation reaction as there is a very limited

volume of the pore solution filling the voids that can continuously provide the necessary amount of dissolved CO₂ for the reaction to progress. On the other hand, the high levels of RH result in the full saturation of the pore domain and this leads to the slower rate of diffusion of mass transfer of dissolved CO₂ across the porous structure of paste [58][74] [75]. It is reported that the highest rate of carbonation in plain cement hydrated pastes is within the approximate range of 50-55% RH; the carbonation coefficient of plain cementitious material is reduced if the relative humidity increases more than 70%. Once the RH drops below 30%, the carbonation coefficient tends to rapidly decline to zero [72]. However, as previously stated this may not necessarily be the general trend for materials containing SCMs, in which the micro-texture characteristics seem to alter the RH range at which the carbonation rate is the highest (Fig. 10,10). Drouet et al. [85][72] [76] found that the most rapid carbonation RH is around 33% for cement pastes with low replacement of slag and fly ash carbonated at a CO₂ concentration of 50% at low temperature, which is a lower RH value than was obtained for the plain Portland cement paste in the same study, which was around 50%. [76]

2.4.3 Temperature

Temperature is a main external parameter that affects the carbonation of cementitious materials as higher temperature accelerates carbonation rate, as well as the diffusion, is faster. On the contrary, the solubility of portlandite and CO₂ in water decreases with increasing temperature. It has also been found that the temperature affects the stability of the calcium carbonate polymorphs that precipitate during carbonation. [78] have shown that the formation of these polymorphs by precipitation from a CaCl2 /Na2CO3 solution is a function of pH and temperature (Figure 11). At high pH, calcite is the main polymorph

regardless of temperature. At lower pH, the dominant polymorph changes as a function of temperature; for high temperature (58 ⁰C), aragonite will be the main polymorph to precipitate while for ambient temperature (24 ⁰C) vaterite has been observed. Temperature also affects the stability of the calcium carbonate polymorphs that precipitate during carbonation. [76] have found the amount of aragonite and vaterite increased when the relative humidity is decreased with the effect more pronounced at higher temperatures.

2.4.4 Curing time

Another important factor to consider is the curing time. Longer curing leads to increase maturity of the hydrated cement system which is reflected by the higher degree of cement hydration, as well as more refined pore structure. These do influence the mass transport of dissolved species in the pore solution, thus altering the extent to which the carbonation process progressed [58][79] [80] [81]. The curing time effect is less pronounced in plain PC concrete than for concrete with SCMs. In concretes with varying cement replacement levels with fly ash, the shortening of the curing period from 7 days to 1 day enhanced the carbonation process significantly due to more open and coarser pore structure [83] [84] [85]. It was found that 3 days of curing should be enough for replacement levels of less than 30 wt.% for FA [83][84].

2.4.5 Carbon dioxide concentration

According to Lothenbach et al. "the C-S-H carbonation rate increases with the applied CO_2 concentration [86]. The proportion of $CaCO_3$ originating from portlandite and C-S-H carbonation changes significantly from 1% CO_2 onwards, in favor of C-S-H carbonation [112]. A CO_2 concentration above 3% favors the formation of aragonite and vaterite due to pH reduction because of increased amounts of dissolved CO_2 [68].

Researchers have shown that a CO₂ concentration above 10% leads to the incomplete reaction of portlandite which is due to a fast surface reaction causing an overgrowth of portlandite with calcite, which permanently prevents further portlandite carbonation. A high CO₂ concentration also lowers the pH and thus the solubility of CO₂ in water or in solutions containing alkali hydroxides (such as cement pore fluids), leading to the formation of more HCO_3 – and less CO_3 ^{-[87]}. Moreover, for a high CO₂ level, the amount of water produced during carbonation could be more than the porous matrix is capable of expelling in the same time interval that slows down further carbonation [76][88]."

2.4.6 **Porosity and pore size distribution**

As much of the carbonation reaction progress depends on the interaction of dissolved CO₂ with the cement hydration products or incorporated SCMs, the open porosity and the pore size distribution are reported to play a significant role in the carbonation process [95][80]. For example, the amounts of available pore space for saturation with the pore solution, pore network tortuosity, as well as interconnectivity will affect the diffusion of dissolved CO₂ and ultimately control the process [69][70]. Moreover, the precipitation of the carbonation products may alter pore morphology, size, and pore network interconnectivity, which collectively may slow down the carbonation progress. In numerous studies, a pore clogging and formation of dense, carbonated areas within the microstructure was observed and was identified as the main factor responsible for low carbonation rates observed in PC pastes [86][89]. Similar trends were reported for cement-based materials with high FA or SF replacement levels [90][91][92]. In ref [93] a direct suggestion was made that the decrease in micro-pores volume and population is caused by the pore filling and closure by CaCO3 precipitates resulting from C–S–H carbonation. On

the other hand, the observed reduction in the macro-pores volume was mainly attributed to CaCO3 precipitation due to the Ca^{2+} resulting from the portlandite dissolution.

2.5 Super critical carbon dioxide in mineral carbonation

The rate and extent of carbon dioxide are the biggest factors for the feasibility of mineral carbonation technique [16][20][94]. To understand its kinetics, the reaction mechanism must be properly understood [23][68]. One of the dominant precipitations mechanisms is the diffusion of dissolved CO₂ species into bivalent metal hydroxides particles resulting in micropore precipitation and the formation of a carbonate ring that grows inwards and thickens with reaction time as shown in Figure 13. This inhibits further diffusion of CO₂ and stops the core of particles from further carbonation. As the aqueous CO₂ in liquid phase cannot diffuse into narrow spaces, the core remains unreacted which is one of the main reasons for low reaction extent and rate [20][21][69].

Super critical carbon dioxide is a fluid state of carbon dioxide (CO₂ held at or above its critical temperature and critical pressure. CO₂ has a relatively low critical pressure of 74 bars (7.4 MPa) and a critical temperature of 31 ^oC (Figure 13) [95][106]. CO₂ can be directly compressed to supercritical pressure and readily heated to supercritical state before being used for mineral carbonation. At this region, CO₂ is nearly twice as dense as steam, which allows better mass transport that overcomes the deficiency in gas-solid carbonation [106]. On the other hand, super critical CO₂ has viscosity like gas, which enhance pore diffusivity. Thus, it can reach to even the constricted pores to maintain the carbonation efficiency while upscaling the process to a larger dimensional mineral carbonation activity.



Figure 2.13: Macro scale processes during mineral carbonation: Top view of a cylindrical sample undergoing carbonation.



Figure 2.14: Front view of a pore structure: open pore passage, calcite formation starting from the pore wall, Pore clogging due to calcite formation hindering further carbonation.



Figure 2.15: Phase diagram of Carbon dioxide (CO2) (a) showing its different phases (solid, liquid gas and supercritical) with respect to pressure and temperature [95].

2.6 Summary

This chapter initially elaborated the review of literatures explaining the general carbonation process, different carbonation techniques and different kinds of waste materials. Then, it explained the mechanisms taking place during the carbonation in different mineral carbonation techniques and the challenges associated with it. Furthermore, chapter 2 discusses on the major factors influencing the rate and the extent of the carbonation and finally the benefits of supercritical carbondioxide for carbonation.

CHAPTER 3 MATERIALS AND METHODS

This chapter presents the work focused on the development and adaptation of the experimental setup, developing the mix designs for three mixture variants, tailoring the experimental methodology, and establishing the sample preparation procedures, and testing protocols. This includes the calibration and operation of the pressure cell system used for creating super critical carbon dioxide curing, use of dry ice to generate super critical carbon dioxide. Sample preparation and preconditioning are presented along with the test associated with the efficacy of carbonation. The parametric study diagram and mix design table are presented to give the reader an overview on the series of experiments designed to test the postulated hypothesis

3.1 Materials

3.1.1 Coal fly ash

Fly Ash is a heterogeneous by-product material produced in the combustion process of coal used in power stations. The chemical composition of fly ash depends upon the type of coal used and the methods used for the combustion of the coal [98]. Class C Fly Ash provides unique self-hardening characteristics and reduces permeability. It is particularly useful in pre-stressed concrete and other applications where high early strengths are required [98]. Moreover, Class C Fly Ash is useful in soil stabilization. In this study, Class C type fly ash (Boral Resources, Texas) was used in the preparation of the cementstabilized and neat consolidated fly ash samples. Fly ash chemical and physical properties are presented in the Table 1.

3.1.2 Portland cement

Type G cement manufactured by Lafarge; Canada was used as a fly ash stabilizing agent in the proposed experiments. Class G cement is commonly used as oil well cement, with a special hydraulic binding material [99]. The cement chemical and physical properties are reported in Table 3.1.

3.1.3 Master glenium 7920

Master Glenium 7920 is used as a plasticizer and high range water reducing admixture. It has a recommended dosage range of 130 to 780 milliliters per 100 kg of cementitious materials. Master Glenium 7920 admixture can be added to the mix with the initial batch water or later. It was used for Mix II design, specifically for Solid Volume Fractions (SVF) of 0.65 and 0.55 with water to solid ratios of 0.18 and 0.29, respectively, to increase the mix workability during casting [101].

3.1.4 Dry ice

Dry ice pellets, which were obtained from the research store at the University of Houston, was used as the source of carbon dioxide. Dry ice pellets are manufactured by taking Liquid CO_2 and depressurizing it in a chamber of a dry ice pelletizer from a pressure ranging from 13 to 25 bar to 1 bar [102].

3.1.5 Theoretical potential of materials for carbon sequestration:

Fly ash Class C and Class G cement, serve as the sources of divalent cations (e.g., Ca^{2+} , Ma^{2+}), that take active role in the CO₂ mineralization process. Therefore, it was important to estimate the theoretical limit for the CO₂ uptake, which is called herein a theoretical potential of material for carbon sequestration.

Compound	Percentage by solid weight (%)						
	Fly Ash	Cement					
Silicon Dioxide (SiO ₂)	35.36	21.00					
Aluminum Oxide (AL ₂ O ₃)	17.41	3.60					
Iron Oxide (Fe ₂ O ₃)	5.97	4.50					
Sum (SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃)	58.74	-					
Sulfur Trioxide (SO ₃)	1.94	2.70					
Calcium Oxide (CaO)	27.83	61.80					
Magnesium Oxide (MgO)	5.54	4.30					
Sodium Oxide (Na ₂ O)	1.68	1.68					
Potassium Oxide (K ₂ O)	0.51	0.51					
Sodium Oxide Equivalent (Na ₂ O + 0.65 K ₂ O)	2.02	2.02					
Calcium Sulfate (CaSO ₄)	-	-					
Limestone (CaCO ₃) or Dolomite (CaMg(CO ₃) ₂)	-	-					
Moisture	0.11	-					
Loss on ignition	0.39	0.39					
Physical Analysis							
Fineness, % retained on 45 µm sieve	17.03	5.3					
Density	2.73	3.15					
Theoretical Capacity based on Stenouir's Equation							
Theoretical Capacity (Stenoiur's equation)	28.26g CO ₂ /100g	47.02g CO ₂ /100g					

Table 3.1. Chemical and Physical analysis of Fly ash and Cement and calculation of carbon sequestration capacity of carbon dioxide sequestration in fly ash and cement using Stenouir's equation

Chemical Analysis

The theoretical potential was estimated based on the model proposed by Stenoiur and Huntzinger [103] [104] [105] and according to equation Eq. 3.1.a where,

$$\% ThCO_2 = 0.785(\% CaO - 0.56\% CaCO_3) - 0.7\% SO_3) +$$

1.091\% MgO + 0.71\% Na_2O + 0.468(\% K_2O - 0.63\% KCl), Eq. 3.1.a

Where, %XX refers to the weight percent of compound independently measured in the chemical analysis of each material reported in Table 3.1. The estimated values of the theoretical CO_2 uptake for each material are reported in Table 3.1.

A simple alternative method, which considers only the effect the bivalent metal ions (Ca^{2+}, Mg^{2+}) is also applied. The ideal capacity of the given fly ash material to sequester carbon dioxide can be calculated according to stoichiometric equations Eq. 3.1.b and 3.1.c, given the measured concentrations reported in Table 3.1 as,

$$CaO + CO_2 \text{ yields} \rightarrow CaCO_3$$
 Eq. 3.1.b

and,

$$MgO + CO_2$$
 yields $\rightarrow MgCO_3$. Eq. 3.1.c

 Table 3.2. Molar weight of calcium dioxide, magnesium oxide, calcium carbonate, magnesium carbonate and carbon dioxide

	CaO	MgO	CaCO ₃	MgCO ₃	CO ₂
Molar Weight	56	40.3	100	84.3	44

Accordingly, 56 grams of CaO combines with 44 grams of CO₂, and 40.3 grams of MgO combines with 44 grams of CO₂ to form 100g of Ca-bearing or Mg-bearing carbonate compounds. Therefore, 100 grams of Class C fly ash investigated are capable of

cement at the ration of 60:40 (at this ration the fly ash is stabilized with cement) is capable of mineralizing 38 grams of CO₂ per 100 grams of the dry blend.

3.2 Methods

3.2.4 Supercritical CO₂ curing sequence and reactor

All samples are cured with carbon dioxide in the supercritical state achieved at the temperature of 75°C, and at the initial CO₂ concentration inside the pressure cell fixed at 5.23 moles. The pressure inside the pressure cell is the resultant of the prescribed temperature and prescribed concentration of CO₂. For all the tests, the initial pressure at the first time point of the stable temperature was approximately in the range of about 1900 to 2000 psi. The process schematic of the supercritical (sup. CO₂) curing operation in presented in Figure 3.1.



Figure 3.1: Flow chart for super-critical CO₂ curing of the cementitious samples

The Curing Chamber (see Figure 3.2) is a COL-INT TECH non-stirred HiP reactor 25-500 ml which is made of Steel alloy, designed to work under a pressure of 20 MPa and

at a temperature of up to 350 degrees Celsius. The temperature inside the curing chamber is strictly controlled via an internal thermocouple connected to the digital control system. Moreover, the heating element is installed on the lower part of the curing cell to provide the heating schedule according to the pre-programmed protocol (i.e., 75°C in 2 hours with some settling time for the temperature inside the chamber to align with the temperature prescribed by the heater). The pressure inside the cell is monitored with an externally installed pressure gauge.



Figure 3.2: Pressure cell for carbonation of cementitious materials

3.2.2 Supercritical CO₂ generation

The dry ice was used in all experiments to generate supercritical CO₂ for the carbonation of the samples (Figure 3.3). It was placed over a tared container and weighed on a weighing machine. After quickly transferring the dry ice to the pressure cell, the system was sealed as fast as possible by setting up the nut and bolt into it. Next, all the

valves and seams of the pressure cell were checked for any leakage. The dry ice was allowed to melt and expand as it absorbed heat from the surrounding environment (room temperature). The temperature was monitored using internal thermocouple. As the temperature exceeded zero degree Celsius, the heater was turned on to provide heat source at the prescribed rate. The heater followed a prescribed protocol. The pressure buildup was monitored using an externally mounted pressure gauge.



Figure 3.3 Phase diagram of Carbon dioxide (CO2) (a) showing its different phases (solid, liquid gas and supercritical) with respect to pressure and temperature (b)in the density-pressure plane [95].

• CO₂ load correction

To preserve the consistency of the experiment and CO₂ dosage, it was necessary to account for the possible CO₂ losses due to its sublimation during cell loading, assembly, and sealing. This was accomplished by assessing the CO₂ weight loss during an average assembly time of around 5 minutes (Figure 3.4). A prescribed amount of dry ice was weighed in the pan and the mass loss was calculated. It was found that the weight loss was 3% of total initial weight per minute. So, the sublimation weight correction of the dry ice was estimated to be 15%. In the initial series of experiments, the dry ice, which was purchased from an external dry ice retailer, was used.



Figure 3.4: Dry ice being weighed on a OHAUS NAVIGATOR weighing balance.

3.2.3 Supercritical CO₂ curing cycle

Batches of fly ash and fly ash-cement pastes were cured. Each batch included three samples of the same mix, preconditioned in the same way. Prior to their insertion, the linear dimensions and weights of the samples were determined. A dry ice sample of 230 grams, which corresponds to an actual weight of 213 grams after accounting for sublimation losses, was placed in the pressure cell. It took approximately two hours and thirty minutes to reach the stabilized cell pressure of 1900 PSI (Figure 3.5). The pressure drop due to carbon dioxide intake by the samples was recorded during the carbonation process in equal time intervals for 72 hours.



Figure 3.5: Carbon dioxide pressure variation versus time inside pressure cell.

The heater was stopped after 72 hours, and the chamber was let to naturally cool down to room temperature. The residual pressure was released gradually to reach atmospheric pressure. The samples were then extracted, wiped with the towel to SSD state, and weighed. Post-carbonated samples were subjected to other experimental tests to assess CO₂ sequestration efficiency.

3.2.4 Post curing characterization

Post curing characterization was used to assess the carbonation efficiency of the samples using various techniques for result validation and cross-checking. A combination of qualitative and quantitative methods was used. The general schematic of the characterization process flow is presented in Figure 3.7.



Figure 3.6: Schematic characterization process flow

3.2.4.1 Dry weight change – carbonation metric

The weight changes of the samples before and after the carbonation was the first step in assessing their carbonation efficiency. The pre- and post-cured samples were dried at 105 degrees Celsius in the convective oven until their weight change between two successive measurements in 6 hours was below second decimal. Ohaus Balance was used to weigh the samples (room conditions). The measurements of the three samples were taken after carbon dioxide curing at different saturation levels (i.e., ranging from completely dry to saturated surface dry conditions). The carbon dioxide weight was calculated as the difference between sample dry weights prior and post carbonation where,

$$\Delta W = W_{post-carbonation}^{dry} - W_{pre-carbonation}^{dry}$$
 Eqn. 3.2.a

The relative weight increase was calculated with reference to the original weight and expressed in terms of weight gain percentage due to carbon dioxide curing where,

Relative Wt. gain (%) =
$$\frac{\Delta W}{W_{pre-carbonation}^{dry}} \times 100\%$$
. Eqn. 3.2.b

3.2.4.2 Porosity measurement

The porosity of the sample-post carbonation was measured using standard fluid displacement method [113]. For this purpose, the dried post-cured samples were cut to extract discs from four different locations. Sample discs with a height of 5 mm to 15 mm and a regular diameter of 22 mm were taken from the top, bottom, and two intermediate locations and placed in plastic separate cups (Figure 3.5). Next, the dry discs were degassed for 60 minutes, together with tap water, under the vacuum range of 500 to 710 mmHg. After that, the degassed water was slowly poured into the container with the sample, allowing for pore space re-saturation. The samples were left submerged in water for approximately 2 hours before taking weight measurements in SSD state. Based on dry and SSD sample weights and estimated sample volume, the open porosity was estimated using Eq. 2.3d. where,

$$\Phi = \frac{V_{Pores}}{V_{SSD}} x \ 100\%, \qquad \text{Eqn. 3.2.c}$$

$$\Phi = \frac{M_{Water}}{\rho_{water} x V_{SSD}} x \ 100\% , \qquad \qquad \text{Eqn. 3.2.d}$$

where,

 Φ = Porosity of the sample

 $V_{pores} = Volume of pores$

 V_{SSD} = Volumr of the sample at surface saturated dry state

 $M_{water} = Mass of the water$

 $\rho_{water} = Density of the water.$





Figure 3.7: Schematic diagram showing post carbonation porosity measurement of the samples(a) completely dried samples with known volume for water penetration under vacuum (b) Buheler Cast N Vac chamber (c) Water pouring into the sample in the vacuum state (d) Surface saturated carbonated sample discs ready for measurements.

3.2.4.3 Calculation of sample post-carbonation saturation

The sample saturation levels prior and post carbonation can change mainly due to two factors, namely, escaping of water molecules from the sample to the cell due to temperature change on heating and generation of intrinsic water molecules in the carbonation process (e.g., hydrated cement). Similarly, the dry ice used to generate carbon dioxide may contain some water as impurities that may alter the sample saturation level post carbonation. To assess possible moisture content changes, the sample weights prior and after carbonation and after the carbonation was monitored. The carbonated sample weight is taken after extracting it from the carbonation chamber and wiping the excess water from its surface with a paper towel as mentioned in the introduction of the section 1.3 and the equation states:

$$MC^{post-carb} = \frac{W_{surface dry}^{post-carb} - W_{complete dry}^{post-carb}}{W_{dry}^{post-carb}} \times 100\%$$
 3.2.e

and,

Saturation =
$$\frac{MC}{[MC]max} \times 100\%$$
. 3.2.f

3.2.4.4 Phenolphthalein test for carbonation front assessment

The depth or degree of carbonation can be determined by petrographic techniques (ASTM C856) through the observation of calcium carbonate, which is the primary chemical carbonation product. In addition, a pH stain (phenolphthalein) can be used to estimate the depth of carbonation by testing the concrete pH (Figure 3.8). For example, upon application of a phenolphthalein solution to a freshly cut concrete surface, non-carbonated areas turn red or purple while carbonated ones remain colorless. When observed against hardened paste, the phenolphthalein indicator color changes at a pH value of 9.0 to 9.5. The pH of a good quality non-carbonated concrete without admixtures is usually in between 12.5 and 13 [114].



Figure 3.8: Schematic showing phenolphthalein indicator test color change with change in pH [KJK, 2021].

One-third of the carbonated samples were cut from the top for this test using Buehler Isomet Low-Speed Saw and discarded. 5 mm discs were cut from the remaining carbonate samples (Figure 3.10). The samples were polished using Silicon Carbide abrasive paper starting from P1200 (coarse) to P4000 (fine) until the desired finish is achieved.



Figure 3.9: Sample Extraction for Phenolphthalein test (a) Carbonated sample (b) Sample discs being extracted in Buehler Isomet Low-Speed Saw (c) Sample discs ready for Phenolphthalein test.

The phenolphthalein (0.5%) was sprayed on such prepared surfaces until saturation with the indicator solution. The sample discs were let to dry and the corresponding colors to emerge and stabilize. The sample discs saturated with the indicator solution were placed in a contrasting background for imaging as shown in Figure 3.11.



Figure 3.10: Sample preparation for Phenolphthalein test (a) sample discs before phenolphthalein test (b) dressed sample discs after phenolphthalein test with indicator effect.

3.2.4.5 Image Analysis of the Carbonation Front

The carbonation front extent can be approximately analyzed using image analysis tools (Image J). This method is a qualitative approach that facilitates proper sampling for subsequent approaches, namely, Thermogravimetric Analysis and Scanning Electron Microscopy. The carbonation front and surface area fraction are the two parameters that are assessed using image J. The carbonation front essentially gives the depth of the carbon dioxide penetration within the sample interior while the surface fraction gives an "approximate" value of the carbonated zone area. User judgment is used to assess the image analysis parameters (Figure 3.12) and the area is given by,

$$A_{carbonated} = A_{total} - A_{non-carbonated core}$$
 3.2.g

and,

$$S.A.R = \frac{A_{prescribed region}}{A_{Total}},$$
 3.2.h

where,

A_{carbonated} = Carbonated sample disc surface-area



Anon-carbonated = Non-carbonated sample disc surface area

S.A.R = Surface area ratio.



Figure 3.11: Image analyis using Image J analysis (a) Analyzed image showing non-carbonated core region and carbonated peripheral region (b) Sketch of visualized sample discs with a carbonation front.

3.2.4.6 Thermo-Gravimetric Analysis

Through this technique weight changes events can be observed which highlights the presence of certain compounds which complies with the results from other analyses [105]. Thermogravimetric analysis (TG) was performed on small quantities of powdered samples. Carbonated powdered samples tests were carried out in Discovery TGA 550 Advanced (TA instruments) at the temperature rate of 200 ^oC/min up to the maximum temperature of 1000 ^oC and under the N2 atmosphere. A minimum of 3 samples were tested for each specimen inside the Pt TGA pan. The average sample weight was approximately 20 +/- 5 mg.

• Sampling from the carbonated materials and analytical protocol

A segment was extracted from the sample disc after the Phenolphthalein test using Buehler Isomet Low-Speed Saw. A fragment from the peripheral region was then polished thoroughly using Silicon Carbide abrasive paper starting from P1200 (coarse) to P4000 (fine) until the fragment looked homogenous in color. After that, the sample tray was cleaned inside the dusting room using a brush and a duster. The tray was burned with a torch for 5-6 seconds to evaporate all the impurities inside it. The sample discs after the phenolphthalein tests were grinded to form a homogenous fine powder. Approximately 20 grams of the sample was carefully placed into a tared pan using a designated spatula. The powdered sample was spread into the pan to cover all of the pan contact area and heated up.





(e)(f)(g)(h)Figure 3.12: Method for sample extraction and process run for DT/TGA (a) Fragmented sample disc (b)
Thorough beam (c) non-carbonated core and carbonated rim (d) sample being polished for

TGA instrument (h) Completed test setup.

homogeneity (e) Sample grinding for TGA test (f) Sample loading into pan (g)pan loaded into

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• TGA data analysis approach

The weight loss curve obtained from the TG test represented the weight decrease amount associated with continuous, or discrete, decomposition events taking place in the sample at different temperatures. Based on the literature review, the weight loss occurring at the temperatures between 400 to 750 degrees Celsius is the weight loss due to decomposition of carbon dioxide bearing phases present in the sample [107] [108] [109] [110] [111]. On the other side, it is considered that, the weight loss occurring at the temperatures until 400 degrees Celsius is associated with the gradual loss of water from hydrated phases e.g. C-S-H, ettringite, silica gel etc. To eliminate the possible effect of the variable initial moisture content (free water) of the samples in TGA analysis, a correction step is applied [111] (see Figure 3.14).



Figure 3.13: TG graph values correction for moisture. Hypothetical curve displaying two main events of weight loss associated with free water escape (at Tw=105C) and decompositon of CO₂-bearing phases (marked at Tc). Normalization step w.r.t. to sample wt% after dehydration at 105°C allows for elimination of the bias cause by possible variations in the moisture content of samples prior to TGA experiment.

Figure 3.14 represents the general schematic of the TGA outcome with two discrete events of the weight loss: a) first step at 105°C corresponding to loss of free water from the sample, and b) weight loss caused by the decomposition of CO₂-bearing phase. For samples which contain different amounts of free water (moisture content), the first event will be reflected by different intensity. This will result with biased estimates of the carbonates content depending on the free water amount. Therefore, the data normalization step with respect to the initial point considering at 105 degrees Celsius is performed, and the experimental data is recalculated the accordingly. The effect of normalization is demonstrated on the example of the experimental data in Figure 3.15, The weight percentage loss (Δ_c) is increased from 17.1% to (Δ^2_c) a 17.8% i.e; an increase of 4.2% after normalizing the values with respect to weight at 105 degree Celsius considered as dry state.



Figure 3.14: Graph showing TG graph correction for moisture. Δ_c represents weight loss percentage from 400C to 700C for the initial system which has not been normalized and $\Delta_{c'}$ represents the weight loss percentage from 400C to 700C after the system has been normalized with respect to the weight percentage at 105C.

3.2.4.7 Scanning electron microscopy

Scanning Electron Microscopy (SEM) coupled with Electron Dispersive Spectroscopy (EDS) has many applications in cementitious materials. For example, it can be used to obtain the C-A-S-H composition [Rossen, 2017], to analyze the composition of complex SCMs [Meulenzyer, 2013/ Durdzinski, 2015], to calculate the degree of reaction [Mason,2004/ Kocaba,2012], and to interpret the results of other methods such as nanoindentation [Krakowiak, 2015/ Wilson, 2018]. A particular use of SEM EDS is the acquisition of multispectral or hyperspectral mappings. In these mappings, each pixel contains a complete EDS spectrum, which can be quantified to obtain the chemical composition, and then combined with spatial information to provide mappings of all quantified elements. In combination with backscattered electron (BSE) micrographs, such mappings can be used to study hydration (Meulenzyer, 2013). Microstructure analysis was conducted using the Scanning Electron Microscopy (SEM) method to achieve following objectives: a) observation of morphology of carbon-reach precipitates and reacted fly ash particles, b) chemical analysis of precipitates using EDS.

• Sample preparation

To achieve the above stated objectives, we prepared reference and carbonated samples to be analyzed in SEM. Two types of samples for two different analyses: fracture surface for Secondary Electron Imaging and flat polished sample for EDS analysis (Figure 3.16 and 3.17). For both sample preparation types, miniature beams were cut from the sample discs, which included the entire length of the cross section. The cut section was fractured at the prescribed location, where the core and rim sections are as shown in Figure (3.16) to see the microstructure fractured image. In another attempt, the small beam is

leveled and polished starting with a course with P 1200 silicon carbide polishing pad and getting a fine polish with P 4000 silicon carbide polishing pad. Finally, the sample was covered with a 60 nm of gold coatings in a high vacuum evaporator (Denton Vacuum). JEOL JSM-6610A (JEOL<JAPAN) tungsten filament SEM was working on an accelerating voltage of 20kV. The objective aperture and the beam parameters were altered to get respective optimum Secondary Electron Imaging and qualitative compositional analysis.



Figure 3.15: Method for sample preparation for SEM (a) unpolished and polished samples (b) polishing beam on Buehler CarbiMet pad P1200 (c) Branson ultrasonic bath (d) Polishing pads of different coarse level (e) different kinds of surfaces for SEI and EDS analysis in SEM (f) Sample etching process (g)Gold plating of samples for SEM analysis (h) Gold coated samples for SEM analysis.



Figure 3.16: Sample mounting and process run for SEM (a) sample mounting (b) JEOL JSM-6610A (JEOL<JAPAN) tungsten filament SEM (c) Sample mounting on the SEM base plate (d) Operating on SEM software.

3.2.4.8 Uniaxial compression testing

Uniaxial compression test was performed using ASTM standards [113] to determine the compressive strength of the fly ash samples cured using various approaches. Same chemistry fly ash samples were cured using three approaches, namely, normal curing for 2 days, normal curing for 2 days and "hydrothermal curing" for 3 days, and normal curing for 2 days and carbon dioxide curing for 3 days. The cylindrical samples were cut to a ratio of 1 to 2 (d/h= 22/44). The top and bottom surfaces were also treated with sandpaper to ensure a flat surface of contact and to minimize the possibility of tilt. The Instron 5969 universal testing machine, Figure 3.17, was used in testing and according to ASTM C39 at the prescribed stress rate of 0.25 ± 0.05 MPa/sec. In this preliminary test, the single compression specimens were evaluated for the three types of samples (given the limited availability of the material). The compression test for just a single sample from each of three sample systems were compared as a qualitative test, because of the limited amount of material for testing. More in-depth study must be carried out on larger number of specimens for the statistically meaningful quantitative comparison.





(b)

(a)

Fig 3.17: Compression test setup: (a) Instron 5969 universal testing machine (b) Carbonated fly ash sample post compression test.

3.3 Mix design

After conducting a through literature review and performing few initial trials, it was realized that the bivalent metal oxide content, the moisture content, the temperature, and open porosity in the samples have significant influence in carbonation rates and extents. Therefore, a set of experimental designs were made to affirm our hypothesis. The main parameters selected were sample mix type (chemistry), moisture content, and solid volume fraction.



Figure 3.18. Diagram of experimental matrix for parametric study that includes three variants of mixes (Fly ash Class C, Fly Ash Class C+ Cement Type G, Newton Fly ash + Gypsum) being cured at Temperature of 75 C with corresponding pressure at phase diagram path with CO₂ concentration of 230 grams consisting of various Solid Volume Fraction (SVF) and Moisture Content (MC).

3.3.1 Sample mix:

Two sample mix types were adopted as shown in the tree diagram below. The first mix included 60% of Fly Ash Class C and 40% of cement type G. The second mix type included a 100 % of neat Fly Ash Class C.

The mix was designed for a prescribed solid volume fraction (SVF) to achieve desired porosity. The water to solid ratio was controlled in the mix to get the desired solid volume fraction. The theoretical mix bulk density was computed and compared to the experimentally obtained to check if the desired solid volume fraction was achieved. Furthermore, the achieved SVF was cross validated using a derived relationship based on experimental density, solid density, and water to solid ratio.

The Solid Volume Fraction (SVF), which is defined as the volume of the solid per total volume, was the key parametric constraint in the mix design for the various samples. The SVF is important because it allows the achievement of a degree of control in the sample porosity (η). The prescribed thought process to achieve the desirable SVF ratio is described as follows.

Let us consider the solid mass to be a known quantity. Then, the volume of the solid can be computed using following equation where,

$$V_{solid} = \frac{W_{solid}}{\rho_{solid}}.$$
 3.3.a

Given a SVF (already prescribed) and V_{solid} , the sample total volume can be computed as,

$$SVF = \frac{V_{solid}}{V_{total}},$$
 3.3.b

$$V_{total} = \frac{V_{solid}}{SVF}.$$
 3.3.c

At a Surface Saturated Condition, the sample total volume is given by,

$$V_{total} = V_{solid} + V_{water}, \qquad 3.3.d$$

And the water weight can be computed using,

$$V_{water} = V_{total} - V_{solid}, \qquad 3.3.e$$

$$W_{water} = V_{water} \times \rho_{water} . \qquad 3.3.f$$

Finally, the water to solid ratio (W/S) by weight is calculated to design the mix according to the desired SVF. To check the feasibility of the mix design, an experimental bulk density (ρ_{exp}) is computed as,

$$\rho_{exp} = \frac{W_{paste}}{V_{paste}}.$$
 3.3.g

The error associated with the bulk density was,

$$Error = \frac{\rho_{Exp} - \rho_{Th}}{\rho_{Th}} x \, 100\%, \qquad 3.3.h$$

and the experimentally value of the SVF (derivation attached at the end of this paragraph) can be calculated as,

$$SVF_{exp} = \frac{\rho_{exp}}{\rho_{solid} x \left[1 + \left(\frac{W}{S}\right)\right]} .$$
 3.3.i

Three Solid Volume Fraction (SVF), namely, 0.65, 0.55 and 0.45 were considered for Mix I while one SVF was considered for Mix II for parametric study (see Table 3.3). A SVF of 0.45 was considered for Mix II, which assumes that the highest porosity has a positive effect on increasing carbonation efficiency.



Figure 3.19: Visualization of sample packing at various Solid Volume Fractions (SVF) (a) Sample visualization at SVF=0.65 (b) Sample visualization at SVF=0.55 (c) Sample visualization at SVF=0.45.

Table 3.3. Sample preparations mix design of two different material mixes along with their corresponding Solid Volume Fraction (SVF), Moisture Content, expected bulk density and weight percentage of respective solid materials.

Mix	SVF	Saturation Degree	МС	Fly Ash	Cement	W/S	Pbulk (Th.)	ρ _{bulk} (Exp)	Error	SVF
	(Th)	(%)	(%)	(wt. %)	(wt. %)		(gm/cm ³)	(gm/cm ³)	%	(Exp)
0.45 Mix I 0.55 0.65	0.45	66	7.75	60	40	0.42	1.86	1.89	1.6	0.46
	0.45	33	3.88	60	40	0.42	1.86	1.88	0.29	0.45
	0.55	66	12.58	60	40	0.28	2.05	2.11	3.6	0.56
		33	6.29	60	40	0.28	2.05	2.13	3.7	0.56
	0.65	66	19.78	60	40	0.19	2.22	2.22	0	0.65
		33	9.89	60	40	0.19	2.22	2.22	0	0.65
Mix II	0.45	66	27.05	100	-	0.45	1.78	1.78	0	0.45

Derivation of the experimentally achieved Solid Volume fraction is derived starting from,

$$\rho_{exp} = \frac{M_{paste}}{V_{paste}},$$
3.3.j

where,

$$M_{paste} = M_{solid} + M_{water}, \qquad 3.3.k$$

so,

$$\rho_{exp} = \frac{M_{Solid} + M_{water}}{V_{paste}},$$
3.3.1

$$W/S = \frac{M_{water}}{M_{solid}},$$
 3.3.m

$$M_{water} = Water - Solid \ ratio \ x \ M_{solid}$$
, 3.3.n

now substituting M_{water} to equation 2.1,

$$\rho_{exp} = \frac{M_{Solid} + (W/S) x M_{Solid}}{V_{paste}},$$
3.3.0

$$\rho_{exp} = \frac{\left[1 + \left(\frac{W}{S}\right)\right] x M_{solid}}{V_{paste}},$$
3.3.p

re-arranging equation,

$$\rho_{exp} \, x \, V_{paste} = \left[1 + \left(\frac{W}{S}\right)\right] x \, M_{solid}, \qquad 3.3.q$$

dividing equation by solid density,

$$\frac{\rho_{exp} \, x \, V_{paste}}{\rho_{solid}} = \frac{M_{solid}}{\rho_{solid}} \, x \, \left[1 + \left(\frac{W}{S}\right) \right], \qquad 3.3.r$$

$$\frac{\rho_{exp} \, x \, V_{paste}}{\rho_{solid}} = V_{solid} \, x \, \left[1 + \left(\frac{W}{S} \right) \right], \qquad 3.3.s$$

$$V_{solid} = \frac{\rho_{exp} \, x \, V_{paste}}{\rho_{solid} x [1 + \left(\frac{W}{S}\right)]} , \qquad 3.3.t$$

now, SVF is given by:

$$SVF = \frac{V_{solid}}{V_{paste}},$$
 3.3.u

substituting V_{solid} from equation 2.20 to equation 2.21

$$SVF = \frac{\rho_{exp} \, x \, V_{paste}}{\rho_{solid} x [1 + \left(\frac{W}{S}\right)]} \, x \frac{1}{V_{paste}},$$
3.3.v

$$SVF = \frac{\rho_{exp}}{\rho_{solid} x \left[1 + \left(\frac{W}{S}\right)\right]} .$$
 3.3.w

3.3.2 Sample preparation for batch curing experiments

The sample preparation encompassed the mold preparation, mixing, placing, and demolding. The sample mold was made from polycarbonate tubes of 22 mm in diameter and 76 mm in height. These molds were coated with a lubricant (WD-40) and sealed at the bottom using a duct tape. The constituents were weighed in the Ohaus NAVIGATOR

weighing balance. The mixture was mixed in the Kitchen Aid mixing pan. Master Glenium 7920 was added as a super plasticizer for the samples with a Solid Volume Fraction (SVF) of 0.55 and 0.65. The mold is sealed at the top after completing the placement of the sample paste. The samples were demolded using the Klutch probing tool.



Figure 3.20: Preparation process diagram for sample carbonation.



Figure 3.21: Sample preparation for sample carbonation (a) Weighing mix constituents (b) Mixing the mix (c) Weighing the empty mold (d) Mix II sample being weighed (e) Klutch probing machine to demold the sample (f) Demolded samples.
All samples required pre-conditioning before being placed for carbon curing into the chamber. For fly ash and cement mixes all samples were prehydrated in the saturated condition for the period of 7 days, while the neat fly ash mixes were prehydrated for 2 days under sealed conditions. Next the cylindrical samples were demolded and cut to the regular size 5-inch length before proceeding into the next step of preconditioning (achieving the desired saturation), Figure 3.22.



Figure 3.22: Sample sizing for carbonation of mix II samples (a) sample marked for 5cm height with reference to the ruler (b) Mix II samples with 5cm height ready for carbon curing.

Samples were dried in the oven at 105 degrees Celsius to achieve the desired saturation. The prescribed saturation is defined as the percentage of wet moisture content of samples normalized to 100%. The time of drying was derived from the normalized saturation graph obtained from drying of reference samples. Three samples of the respective mixes were measured in terms of dimension and weight in a Surface Saturated Dry (W_{SSD}) condition. Then, these samples were dried in the oven and weight ($W_{time=t}$) was noted for prescribed time intervals. The final dry weight was noted (W_{dry}), and the maximum moisture content and wet moisture content was calculated as,

$$[MC]max = \frac{W_{time=0} - W_{dry}}{W_{dry}} \times 100\%, \qquad \text{Eqn. 2.9.a}$$

$$MC = \frac{W_{time=t} - W_{dry}}{W_{dry}} \times 100\%, \qquad \text{Eqn. 2.9.b}$$

Degree of Saturation =
$$\frac{MC}{[MC]max} \times 100\%$$
, Eqn. 2.9.c

Where,

- [MCwet]max = Maximum Normalized Moisture Content with respect to sample SSD weight
- MC_{wet} =Normalized Moisture Content with respect to weight of SSD sample
- W_{SSD} = Weight of the samples in Surface Saturated Dry condition
- W_{dry} = Weight of the samples in dry condition.



Time to reach 66% Sat. Time to reach 33% Sat.

Figure 3.23: Saturation (%) versus time duration (hours) for FA_CG_60_40_65 SVF reference samples.

3.4 Summary

In this chapter, the development and adaptation of the experimental setup of carbonation techniques were presented. At first, the sample mix materials were introduced including their theoretical carbon sequestration abilities. Then, the mix designs were introduced for each sample condition. The sample preparation process was also described including sample casting, demolding, and preconditioning. Moreover, the chapter described the supercritical curing cycle along with the technical specification of the pressure cell system and the heating protocols. Finally, four different tests were presented to assess the carbonation efficiency. The next chapter presents the experimental results and discusses the reasoning behind the results obtained.

CHAPTER 4 Experimental Results

Chapter 4 discusses the detailed experimental results of the carbonation experiments. Three samples were evaluated for each material to assess the reliability of the proposed method and the measurement repeatability. Post carbonation assessment included carbonation efficiency derived from the weight change, qualitative measure of carbonation efficiency from the coupled indicator test and image analysis which subsequently serves as a guide for extracting samples for Thermogravimetric Analysis. Finally, the SEM imaging was used to perform a microstructural analysis of the samples along with the qualitative elemental analysis used to confirm the ongoing carbonation process in the samples.

4.1 Weight change measure

Table 4.1 reports the respective moisture contents, pre and post curing dry bulk densities, weight gain from CO₂ and achieved carbonation efficiency for different sample systems. The first mix ID (FA+C_65_66%) is a Fly Ash and Cement mix at prescribed 65% SVF and 66% of degree of saturation (SAT). The weight change is 0.18 grams per unit volume which corresponds to an average value of 8.7% of the CO2 intake with a standard deviation of 0.29%. For this sample system (mixture of fly ash and cement at wt% 60:40) the theoretical CO2 efficiency is 38% which corresponds to the complete conversion of the CaO and MgO oxides into their respective carbonates. The normalized CO2 efficiency was measured to be 22.89% which is the least among the 10 batches of

experimental run conducted. $FA+C_65_33\%$ reports 28.08% of carbonation efficiency which is slightly higher than $FA+C_65_66\%$.

 $FA+C_55_66\%$ has CO2 efficiency of 53.79% which is the highest efficiency reported among the fly ash and the cement samples if the "abnormal" value in the 45 SVF category is excluded. $FA+C_55_33\%$ achieves an efficiency of 44.37% which is in line with the value of 43.34% for second run of same sample system; $FA+C_55_33\%$ _II. This also shows reproducibility of the CO2 curing process, as well as pre and post curing sample conditioning and characterization protocol.

 $FA+C_45_66\%$ II is the second batch for the fly Ash and cement sample at 45 SVF and 66% of SAT which has the highest normalized CO2 efficiency of 68.89 among the fly ash and cement samples. The observed data collected from four batches of FA+C_45 tends to suggest that this result can an outlier; it is located at around 1.5σ from the mean value obtained from 4 batches. The exact reason for this discrepancy could not been identified in the current work. The other three batches from the same sample system refer to an aligned values of 47.68%, 52.39% and 48.26%, respectively. The FA+C_45_33% has a CO2 efficiency of 48.26%. Neat Fly ash system (FA_45_66%) achieves the highest CO2 efficiency with respect to its potential with a value of 73.81%.

Based on the collected data several important observation can be made: a) the CO₂ uptake during the supercritical conditions mineralization process increases for samples consolidated at the lower packing efficiency, b) the systematic trend of the initial saturation of samples at the pre-carbonation stage on the CO₂ immobilization could not been observed, which suggests that more refined experimental design and process control must be assured to resolve it, c) for fly ash and cement mixes at low SVF (55% and beyond) the

 CO_2 mineralization is able to reach \approx 50% its theoretical carbonation potential. Finally, the dry bulk density of the mineralized solid increases as a consequence of weight gain given the negligible macroscopic shrinkage recorded (1% error on dry bulk density estimates due to complete drying at 105°C from the SSD state of pre and post-carbonated samples).

			Pre			Post			Experimental	Theorectical		
Mix ID	Sample #	MC	Density _{bulk}	Density_{bulk}	MC	Density _{bulk}	Density _{bulk}	Δ bulk density	CO ₂ weight gain	CO2 Potential	CO2 eff. (Normalized)	Remarks
		(%)	(gm/cm ³)	(gm/cm ³)	(%)	(gm/cm ³)	(gm/cm ³)	(gm/cm ³)	(%)	(%)	(%)	
EALC 65 660/	#1	100 T 001	2.05	CO 03-EO C		2.21	CU 011C C	0 10 10 01	00 0+2 0	00	00 66	
FATC_02_00/0	#3	1.07±0.04	2.01	70.0±00.7	76.0±66.4	2.21	70.0±12.2	10.0±01.0	0./±0.29	00	60.77	
	#1		2.05			2.3						
FA+C_65_33%	#2	3.64±0.55	2.03	2.03±0.02	5.39±2.65	2.18	2.25 ± 0.02	0.22 ± 0.06	10.67 ± 3.01	38	28.08	
	#3		2.01			2.26						
E∆+C 55 66%	#1	12 10+0 37	1.75	1 74+0 01	5 81+2 73	2.14	2 1/1+0 01	0.4+0.07	20 11+1 95	38	53 70	
	#3	10.0-01.71	1.73	10.0-1.1	C7.C-LO.C	2.07	10.0-11.7	0.0-1-0	C/17+LL.07	0	1.00	
	#1		1.75			2.04						
FA+C_55_33%	#2	$6.32 \pm 0.0.01$	1.74	1.74 ± 0.01	6.06±0.0.27	2.03	2.03 ± 0.01	0.29 ± 0.01	16.86 ± 0.33	38	44.37	
	#3		1.73			2.03						
	#1		1.75		- 1	2.06						Re-run as the sample
FA+C_55_33%	#2	6.37±0.19	1.74	1.74 ± 0.01	9.41±2.47	1.98	2.03 ± 0.04	0.29 ± 0.04	16.86 ± 2.39	38	43.34	has a unique pattern
	#3		1.73			2.04						in the indicator test
	#1		1.48			1.76						Only one sample
FA+C_45_66%_I	#2	21.73±1	1.48	1.49±0.02	12.275		1.76	0.27	18.34	38	47.68	was measurable due
	#1		1.51			18						to sample snattering
FA+C 45 66% II	¢#	19 64+0 13	1 48	1 49+0 02	11 19+6 85	<i>c</i>	1 88+0 11	0 39+0 11	26 18+7 1	38	68 89	
	#3		1.51			1.84)		
	#1		1.48			1.79						
FA+C_45_66%_III	#2	19.8 ± 0.01	1.48	1.49 ± 0.02	5.97±1.18	1.79	1.79 ± 0.01	0.3 ± 0.01	19.91 ± 0.39	38	52.39	
	#3		1.51			1.78						
	#1	,	1.48			1.79						
FA+C_45_66%_IV	#2	19.83±0.15	1.48	1.49 ± 0.02	17.45±2.42	1.76	1.76 ± 0.02	0.27 ± 0.03	18.34 ± 1.69	38	48.26	
	#3		1.51			1.74						
	#1		1.48			1.76						
FA+C_45_33%	#2	9.11±0.34	1.48	1.49 ± 0.02	9.07±0.03	1.77	1.76 ± 0.02	0.27 ± 0.01	18.34 ± 0.39	38	48.26	
	#3		1.51			1.76						
	#1		1.29			1.55						
FA_45_66%	#2	27.15±0.03	1.27	1.28 ± 0.01	10.61±0.38	1.54	1.54 ± 0.01	0.26 ± 0.01	20.57±0.45	27.87	73.81	
	#3		1.28			1.54						

Table 4.1: CO₂ uptake efficiency and corresponding dry weight prior to carbonation, post carbonation, moisture content, theoretical CO₂ potential.



Figure 4.1: Chart reporting bulk density of dry sample prior and post carbonation

4.2 Change in the moisture content and degree of saturation

Table 2 reports the Moisture Content (MC) and the corresponding degree of saturation (SAT) of the samples in two different phases of the carbonation experiment (preand post-carbonation) with their mean values and respective standard deviations. The prescribed parameters being reported in second, third and fourth column corresponds to the prescribed moisture content and its corresponding saturation which is targeted. Overall, the achieved moisture content and saturation degrees are close to target values. However, for some samples the max discrepancy of up to 10% relative is observed. The post carbonation moisture content in SSD state, which is measured in the water re-saturation test and estimated degree of saturation are reported in the last columns.

Comparative analysis id data in Table 4.2 reveals the important observations indirectly related to the overall changes in the open voids network and its degree of saturation caused by the deposition of the carbon dioxide bearing phases. For example, FA+C_65_66% has a similar SAT, 60.4% and 61.45% values, prior and post carbonation, however, its pore space takes less relative volume compared to the pre-carbonated original material. This fact is reflected by the decline in MC value at SSD state, which is a common and strong trend observed across all samples. This recorded trend also explains the observed free water accumulating in the bottom section of the curing chamber, which must had been expelled from the sample during the mineralization process. As for the moisture and saturation degree of post-carbonated materials, the MC ranges from 5% to 11%, while SAT degree ranges from 34% to 64% with no apparent trends.

			Pre-Carl	bonation			Pos	t-Carbonation	
Mix ID	Sat (prescribed)	*MC _{SSD} (expected)	*MC (prescribed)	MC (achiev ed)	Error	Sat (achieved)	MC _{SSD}	MC (observed)	Sat (observed)
	%	%	%	%	%	%	%	%	%
	66	11.75±0.12	7.75±0.08	7.09±0.04	9.31	60.4	8.12±0.77	4.99±0.92	61.45
FATC_03	33	11.75±0.12	3.88±0.04	3.64±0.55	6.59	30.97	9.99±2.3	5.39±2.65	49.45
	66	19.07±0.11	12.58±0.08	12.19±0.37	3.2	63.9	8.94±0.47	5.84±3.23	65.32
ratc_oo	33	19.07±0.11	6.29±0.03	6.32±0.01	0.47	33.13	9.41±0.35	6.06±0.27	64.4
	66	29.98±0.18	19.78±0.12	19.8±0.01	0.1	66	17.59±0.41	5.97±1.18	33.94
FA+C_45	33	29.98±0.18	9.89±0.06	9.11±0.34	8.56	30.4	18±0.48	9.07±0.03	50.39
WAP_45	66	40.99±0.45	27.05±0.29	27.15±0.03	0.37	66.27	24.92±1.11	10.61±0.38	42.58
*MC _{SSD} is the moistu	re content of t	the sample at s	surface saturate	ed dry or fully s saturation	aturated con	Idition, *MC is t	he moisture cor	tent of the sar	nple at X%

Table 4.2 : Degree of saturation and moisture content of the samples prior and post carbonation along with the error associated with the moisture content.

4.3 **Porosity changes due to supercritical CO2**

The result presented in the Table 4.2 are corroborated with the observed trends in the open porosity. In all cases supercritical mineralization of consolidated fly ash and cement mixtures, or neat fly ash, leads to reduced open porosity. However, the extent of porosity reduction varies with the initial SVF of the sample as well as the targeted degree of saturation.

Table 4.3: Porosity prior and post carbonation on the fly ash cement system and the neat fly ash system with their respective mix ID, sample extraction position, reference porosity, discrepancy, its mean and standard deviation.

		Gammala	Pre-Carbonation			Post Carl	oonation	
Mi	x ID.	extraction Position	Porosity _{reference}		Porosity	Porosity	Δ	$\Delta_{\mathbf{Porosity}}$
		1051001	%		%	%	%	%
		Т			17.8		6.15	
	65 66%	В	23 95+0 04	22.05	15.5	17 75+1 62	8.45	6 2+1 62
	05_0070	Int_1	25.95±0.04	23.95	19.3	17.75±1.02	4.65	0.2±1.02
		Int_2			18.4		5.55	
		Т			9.4		14.55	
	65 220/	В	22.05+0.04	22.05	9.1	11 1+2 10	14.85	12 85+2 10
	03_33%	Int_1	23.95±0.04	23.95	13.5	11.1±2.19	10.45	12.03±2.19
		Int_2			12.4		11.55	
		Т			17		17.09	
	55 660/	В	24.00+1.74	24.00	18.1	10 50 1 20	15.99	15 52 1 20
	33_00%	Int_1	54.09±1./4	34.09	20.3	18.38±1.39	13.79	15.52±1.39
FA+C		Int_2	1		18.9		15.19	
		Т			18.4		15.69	
	55 220/	В	34.09±1.74	24.00	20.2	19.4±0.81	13.89	14.69±0.81
	33_33%	Int_1	54.09±1.74	34.09	19.9	19.4±0.81	14.19	14.09±0.81
		Int 2	1		19.1	1	14.99	
		Т	43.26±2.01	43.26	31.1	30.7±0.58	12.16	
	45 ((0)	В			30.2		13.06	12561059
	45_66%	Int 1			30.2		13.06	12.30±0.38
		Int_2			31.3		11.96	
		T			32		11.26	
	45 220/	В	12 26 2 21	12.04	29.7	20.50.1.04	13.56	10 (0) 1 04
	45_33%	Int 1	43.26±2.01	43.26	29.9	30.58±1.04	13.36	12.69±1.04
		Int 2			30.7	1	12.56	
		T			37.3		15.47	
	15 6 60 1	В	50.77.0.7	50.77	39.6	27.611.04	13.17	15171104
FA	45_66%	Int 1	52.77±0.7	52.77	35.6	3/.6±1.04	17.17	15.17±1.04
		Int_2			37.9		14.87	

4.4 Indicator (Phenolphthalein) test

The table 4.4 reports result of the indicator tests for all sample types and across the three different sections extracted from positions along the sample height. According to the tests specifications, the pink region signifies the area where the pH value is higher than 9 while the gray region has a neutral pH level (7-8). The FA+C 65 66% sample discs has very less of gray region and most of the area has high pH which signifies partial or no carbonation that is further confirmed from TGA and SEM analysis. The trend decreases as we move to FA+C 65 33% with grayer region as compared to the first sample ID. FA+C 55 66% has large surface portion of gray area while there is a small yet intense burgundy color that corresponds to pH levels higher than 11. We observe an unusual pattern for FA+C 55 33% with a halo pattern of pink pigment in the rim area while a gray core which is beyond our understanding and could not be resolved in the current experimental campaign. FA+C 45 66% has a completely gray is and looks completely carbonated at least apparently which is further confirmed by TG analysis and SEM analysis. The results of the indicator test performed on the FA+C-45 33% are inconclusive as the presence of a clear cut between the carbonated and noncarbonated portions of the section cannot be observed. In contrary quite homogeneous mixture of pH-indicator marked areas with grey areas is observed. Finally, although the neat fly sample (FA 45 66%) does not react to the pH indicator test, the presence of carbonated front can be hypothesized based on the "yellowish" color contrasting from the core of the sample.

Mix ID.	Sample	Sample	Sample
FA+C_65_66 %			
	1	2	3
FA+C_65_33 %			
	1	2	3
FA+C_55_66 %			
	1	2	3

 Table 4.4: Images of sample discs after indicator test along with their corresponding mix IDs





4.5 Image Analysis

Qualitative results of the pH-indicator test were used in the further "semiquantitative" analysis of the fly ash and cement sample systems. For this purpose the image analysis protocol was developed (ImageJ) through which the surface fraction areas of carbonated, noncarbonated portions of the section were estimated. Additionally, the depth of the carbonation front was quantified. In that process, $FA+C_55_33\%$ had an anomalous pattern of indication pigments which resulted in the exclusion of that mix ID from analyzing through ImageJ. $FA+C_45_66\%$ had a visual appearance of a fully carbonated surface for which the image analysis is skipped as it did not leverage a significant aid with the assessment. Similarly, $FA+C_45_33\%$ had a sporadic arrangement of indicator pigments which did not signify any definite pattern and hence was excluded from this analysis. The value for carbonation front and the area fractions is reported in the Table 4.5, and Figures 4.2 and 4.3.

The highest carbonation front was achieved for FA+C_45_66% as 11mm which is the radius of the typical sample that we are testing. FA+C_55_66% followed with 7.7 mm of carbonation front achieving the second highest carbonation front among the analyzed sample systems. The trend followed with FA+C_65_33% reporting the carbonation front of 3.32 mm and FA+C_65_66% reporting 1.11mm of carbonation front. This trend confirms the important role of the initial SVF, and thus the available pore space, on the CO₂ mineralization extent; lower SVF leads to the higher carbonation efficiency. Naturally, the surface fraction metric follows the similar trend; FA+C_65_66% has 83.66% of partially carbonated surface while 16.34% of fully carbonated surface. Fa+C_65_33% has 50.5% of partially carbonated surface while 49.5% of fully carbonated surface. FA+CC_55_66% has 7.67% of partially carbonated surface while 92.33% of fully carbonated surface. FA+C_45_66% has whole the area carbonated to the full extent.

						Area		Surface A	rea Ratio
Mix ID	Radius	Radius	Carbona	tion Front	Total	Partially Carbonated	Partially Carbonated	Partially Carbonated	Completely Carbonated
	mm	mm	ШШ	mm	mm ²	mm2	mm ²	%	%
	10.97		1.2			318.98			
FA+C_65_66%	11.13	11.01 ± 0.11	1.11	1.11±0.09	383.47±10.42	324.81	320.81±3.47	83.66	16.34
	10.92		1.03			318.65			
	11.06		3.76			190.85			
FA+C_65_33%	11.17	11.13±0.12	3.47	3.32±0.54	397.61±0.74	199.69	200.79±10.53	50.5	49.5
	11.17		2.72			211.83			
	10.97		7.76			20.62			
FA+C_55_66%	9.2	10.49±2.26	7.75	7.7±0.02	398.1±0.77	32.04	30.53±9.25	7.67	92.33
	11.31		7.79			38.93			
	11.3		5.44						
FA+C_55_33%	11.42	11.3±0.24	5.26	*5.46±0.21	410.11±9.41	N/A	N/A	N/A	N/A
	11.19		5.67						
FA+C_45_66%					N/A		*		
FA+C_45_33%					N/A				
	10.86		2.2						
FA_45_66%	10.68	10.8±0.21	2.35	2.18±0.19	N/A	N/A	N/A	N/A	N/A
	10.86		1.98						
* the "carbon	ation front"	is the distan	ce of the pink	pigment rangin core in th	ig from the rim e radial directic	of the sample d	lisc to the end o	f the pink region	n towrads the

Table 4.5: Carbonation front and surface area ration (%) for samples that were successfully analyzed using image analysis software.



Figure 4.2: Carbonation front of different carbonated fly ash and cement sample system after analysis on ImageJ.



Mix ID (FA+C System)

Figure 4.3: Surface fraction for different carbonated fly ash and cement after analysis on ImageJ.

4.6 Results from TGA

The test results from the carbonated samples were compared with the reference samples. The reference samples are shown in figure 4.4. The figure 4.4(a) represents fly ash and cement sample system. The primary Y-axis in all of the following graphs form TG analysis represents the weight loss percentage while the secondary Y-axis represents derivative of weight loss percentage. The X-axis represents the increase in temperature starting from 100 degrees Celsius to 1100 degrees Celsius. The weight percentage is represented by a solid line while the derivative of weight percentage (DTG) is represented by a dotted line. The image in the graph is the visual representation of the sample and the marking in the image represents the section form where the sample is extracted.

In figure 4.4(a), the primary Y-axis ranges from 100% to 80% while the primary Y-axis ranges from 100% to 90%. The alteration in range is done to get a contrasting weight percentage drop graph for respective samples. In fly ash – cement reference systems the gradual weight decline is observed up to around 400°C. The weight loss associated with this temperature range is mainly attributed to the dehydroxylation of the cement hydration products. However, two important events can be noticed above 400°C: a) portlandite decomposition at around 430°C, and b) carbonated decomposition at around 600°C. Finally, the significant weight loss is recorded at around 800°C, which is also present in the TGA curve obtained on the neat fly ash, Figure 4.4b.



Figure 4.4: Graphic results from Thermo-gravimetric analysis (a) Weight% and derivative of weight % for reference sample of fly ash and cement system (b) Weight% and derivative of weight % for reference sample of Fly ash system.



Figure 4.5: Graphic results from Thermo-gravimetric analysis (a) Weight% and derivative of weight % for FA+C_65_66% system (b) Weight% and derivative of weight % for FA+C_55_66% system (c) Weight% and derivative of weight % for FA+C_45_66% system.

The figure 4.5(a) represents the results from TG analysis for Fly and Cement sample system with 65 Solid Volume Fraction (SVF) and prescribed at 66% degree of saturation. The graph has three runs of the sample taken from a single disc at three locations: the core, the intermediate zone, and the rim which is clearly shown with the combined aid of the legend, the image, and the marking with red, yellow and blue dots for the rim, the intermediate zone and the core zone respectively. There is a faint dotted curve in every graph following the FA+C 65 66% graph which represents the derivative of weight percentage curve for corresponding reference sample. The details of the results obtained from the graph is reported in the Table 4.6. In all cases the significant decomposition event takes place in the temperature range from around 400°C to 720°C followed by the small peak at around 850°C. Both events are attributed to the decomposition of CO₂ bearing phases in carbonated samples. It is demonstrated that the regions extracted from different depths along the radius of the sample show changing CO₂ mineralization extent which is reflect by decreasing weight drop as the sampling point approaches the center of the sample. Similar trends are observed in the Figure 4.6, however, an often appearance of the portlandite decomposition peak is noticed in the multiple regions of the samples cured at targeted 33% of saturation degree.



Figure 4.6: Graphic results from Thermo-gravimetric analysis (a) Weight% and derivative of weight % for FA+C_65_33% system (b) Weight% and derivative of weight % for FA+C_55_33% system (c) Weight% and derivative of weight % for FA+C_45_33% system.



Figure 4.7: Graphic results from Thermo-gravimetric analysis: Weight% and derivative of weight % for FA_45_66% system.

The Table 4.6 represents the weight percent drop from the TG analysis at the respective temperature which is determined using the combined aid from literature knowledge for possible CO₂ bearing phases decomposition and the peaks for calcite obtained from DTG. The first column reports the cement chemistry, the second reports the solid volume fraction followed by the degree of saturation, the third column reports the position of the samples extraction from the sample discs, the fourth, fifth and the sixth column reports the weight percentage at 400 degrees Celsius (C) 750 degrees C and 950 degrees C. The seventh and eight column reports the change in weight while the sample is burnt from 400 C to 750 C and 750 C to 950 C respectively. The ninth column sums the weight percentage change from seventh and eight column and the last column averages the weight percentage change from core and intermediate zone as we have just the partially carbonated zone area from image analysis to couple together to find out the CO₂ weight gain percentage.

Figure 4.7 represents the graphical representation for TG analysis of neat fly ash sample where the peaks from 400 C to 950 C represent the weight loss due to the decomposition of calcite while the earlier peak at the temperature ranging from 300 C to 450 C represent the weight loss due to decomposition of hydrates about which we do not have information yet. This peak ranging from 300C to 450 C is considered in the calculation of CO₂ uptake so as too cross check the CO₂ uptake from weight change metric because this peak corresponds to a significantly large amount of weight drop beyond the calcite decomposition and physically, is a relevant addition to the CO₂ uptake to get a comparable weight gain with respect to the weight gain obtained from taking weight of the samples dried at 105C prior and post carbonation.

				Wt%		$\Delta_{\mathbf{W}}$	Vt%		Core Int
System	Mix ID	Section	Α	В	С	A-B	B-C	ΣΔ _{Wt%}	$\Delta v \sigma \sum \Delta m \omega$
			400C	750C	950C	400C-750C	750C-950C		Avs. ∠⊐Wt%
		Core	94.41	89.85	88.23	4.56	1.62	6.18	7 845
	65_66%	Int	95.41	87.59	85.9	7.82	1.69	9.51	7.045
		Rim	95.91	83.8	82.36	12.11	1.44	13.55	13.55
		Core	94.94	88.03	86.51	6.91	1.52	8.43	0.79
	65_33%	Int	95.22	85.79	84.09	9.43	1.7	11.13	9.78
		Rim	95.65	81.43	79.82	14.22	1.61	15.83	15.83
		Core	95.31	88.6	87.64	6.71	0.96	7.67	7.67
	55_66%	Int				N/A			/.6/
TALC		Rim	92.77	77.41	76.69	15.36	0.72	16.08	16.08
FA+C		Core	95.68	78.25	77.5	17.43	0.75	18.18	10.10
	55_33%_I	Int		•		N/A			18.18
		Rim	95.68	78.07	77.33	17.61	0.74	18.35	18.35
		Core	95.02	75.11	74.9	19.91	0.21	20.12	20.27
	45_66%_III	Int	95.32	75.11	74.9	20.21	0.72 0.75 0.74 0.21 0.21 0.21 0.49	20.42	20.27
		Rim	95.32	75.11	74.62	20.21	0.49	20.7	20.7
		Core	95.65	77.95	77.25	17.7	0.7	18.4	19.70
	45_33%	Int	95.65	77.14	76.53	18.51	0.61	19.12	18.70
		Rim	96.17	76.92	76.2	19.25	0.72	19.97	19.97
		Core	95.39	83.54	82	11.85	1.54	13.39	12 705
FA	45_66%	Int	94.19	81.91	79.99	12.28	1.92	14.2	15./95
		Rim	92.99	83.8	81.46	9.19	2.34	11.53	11.53

Table 4.6: Weight % drop calculation from Thermogravimetric analysis for fly and cement mix and the neat fly ash system along with their respective location for sample extraction and mix ID.

4.7 CO₂ efficiency from coupled ImageJ-TGA analysis

The weight loss percentage reported in the Table 4.6 are used in the coupled analysis with the pH-indicator tests (Table 4.5). Here the carbonation efficiency is calculated as the weighted average of the TG-measured carbonation efficiency weighted by the respective surface area fractions of the rim (pH indicator shown no change in the color) and the area composed of "core and intermediate zone" (pH indicator shows change in color and the TG tests shows carbonates decomposition peak). Such obtained semi quantitative results are compared against the weight gain measurements reported previously. Both metrics used to quantify the CO₂ uptake show reasonable agreement. However, it must be noted that they cannot be compared at 1-to-1 basis since direct weight increase measurements is quantified w.r.t 105°C dry state, while the coupled TG-ImageJ analysis considers the temperature range above threshold value of 400°C. A proper correction considering the dehydroxylation should be designed.

Table 4.7: Calculation of weight gain percentage coupling TG results with sutface area from image analysis along with the weight gain percentage from weight control assessment and the error associated with the method.

		Surface Ar	ea Fraction]	GA (Wt.	%)	Wt. %	Emor
М	ix ID	РС	FC	PCavg	FC	Combined	(Wt. Control)	EII0I
		%	%	%	%	%	%	%
	65_66%	83.66	16.34	7.84	12.16	8.55	8.70	1.72
	65_33%	50.50	49.50	9.78	13.97	11.85	10.67	11.10
TALC	55_66%	7.67	92.33	7.67	17.85	17.07	20.44	16.49
FA+C	55_33%	100).00	18	.27	18.27	16.86	8.36
	45_66%_III	100.00		20.49		20.49	20.13	1.79
	45_33%	100	0.00	19.37		15.76	18.34	14.07
FA	45_66%	75.00	25.00	13.80	11.53	13.23	20.57	35.69
*FA	45_66%	75.00	25.00	21.30	19.03	20.73	20.57	0.79
* The weight	percentage loss	from 300C to 4	450C is added t	o calculatio	on on the l	last row as it	the decomposit	tion of

hydrates and has a significantly large value eventhough it may not be associated with the calcite decomposition

4.8 Scanning Electron Microscopy

Scanning Electron microscopy images are used in combination with results from EDS analysis to confirm the carbonates formation in the sample which can be clearly observed in the figure 4.7. The figure 4.7 is a SEM image of a section of a fractured surface of the fly ash and cement system containing large pores of approximately 50 µm. The zoom into these large voids reveals the presence of the large deposits of crystalline matter as

suggested by the clear geometrical forms of angular plate-like texture, Figure 4.7 and 4.8. The chemical identity of this deposit was confirmed with the help of EDX spectrometry, Figure 4.9. The EDX spectra contains three major peaks corresponding to the characteristic energy levels of C, O and Ca, all of which are the elements of calcite mineral. The peaks of other elements e.g. Mg, Si, were significantly less intense suggesting the trace concentrations of the other elements in this deposit. The full quantitative EDX analysis confirms this, Table X. Finally, the spherical objects are fly ash particles, with the chemical composition dominated by Si, Figure 4.10.



Figure 4.8: Secondary Electron Imaging of a carbonated fly and cement sample system.



Figure 4.9: Image from Secondary Electron Imaging (SEI) of a fractured surface of the carbonated fly ash and cement mix sample (a) Microstructure near pores at 50 μm (b) microstructure zoomed at 5 μm for EDS analysis the prescribed point to confirm the calcite formation.



Figure 4.10: Qualitative analysis using EDS for the selected point in figure 4.8 (a).

From the quantitative analysis, the atomic ratio of the compound (Ca:O:C) was observed to be 1:2.57:0.97 in comparison to the theoretical atomic ratio of 1:3:1.



Figure 4.11: SEM approach to confirm the presence of the fly ash in the sample system (a) Fly ash sphere being marked for EDS analysis (b) qualitative analysis of fly ash sample using EDS technique.

4.9 Compressive strength of fly ash samples

A preliminary assessment of the effect of supCO₂ curing on the evolution of the compressive strength was performed in a very limited scope (only one sample for considered batches were tested due to material limitation). This includes the compressive testing of neat fly ash cement system at subject to three different curing regimes, Table 4.8: normal curing under ambient condition representing sample state prior to carbonation treatment, "hydrothermal" curing for 3 days at 75C (so separate possible effect of curing at elevated temperature in the absence of supCO₂, and carbonation for 3 days in 230 grams of CO₂ and 75 degrees Celsius of temperature. The fly ash system under normal curing achieved a compressive strength of \approx 1 Mpa, which seems to be at comparable level to the system under "hydrothermal". However, sample which undergone CO₂-curing has displayed almost fourfold increase if the compressive strength, thus indicating the beneficial role of mineralization on the strength of carbonated solids.

Mix ID	Curing Process	Curing Time Ambient Condition	Curing Time Special Condition	Force	Area	Compressive Strength
		Days	Days	Ν	mm ²	MPa
FA_45_66%	Normal curing	2	0	440	380	1.2
FA_45_66%	Hydro-thermal curing	2	3	575.83	380	1.5
FA_45_66%	Carbonation	2	3	1602.37	380	4.2

Table 4.8: Compressive strength test for fly ash samples with same porosity and moisture content undergoing different curing methods.

4.10 Summary

In this chapter, the qualitative and quantitative results on the carbonation efficiency and microstructure development were presented and briefly discussed. This included the direct measurements of weight gain, determination of the changes in the bulk density, porosity, moisture content as well as degree of saturation in the pre and post-carbonated samples. Moreover, the visualization of the carbonation extent was carried out with the help of pH –indicator test which show ongoing mineralization in all considered samples. However, for few samples this test was not conclusive as the obtained pattern diverged from the common trend, or the sample did not react to the indicator due to its inherent pH level (neat fly ash). Obtained results were supported with TGA analysis which allowed for quantification of the CO₂ uptake along the radial direction of the cured specimens. All tests confirmed the important role of the initial packing of the inorganic industrial waste on the carbonation efficiency with both metrics being negatively correlated (higher SVF leads to lower CO₂ uptake for fixed system chemistry and the saturation degree). Finally, the direct observation of the carbonates was confirmed in the SEM investigation supported by the EDX analysis.

Chapter 5

Summary, Contribution, and Future Works

This chapter summarizes the efforts made to perform carbonation on two different cement chemistry with super critical form of carbon dioxide and characterizing the product using various qualitative and quantitative methods. This further describes the future works that can be performed to optimize the research efforts on this field.

5.1 Summary and contributions

The work presented in this thesis represents the feasibility study of CO₂ mineralization using solid inorganic alkaline waste and supercritical state technology. For this purpose, the experimental trials were run on high calcium fly ash stabilized with Portland cement and the neat high calcium fly ash. For this purpose, the experimental matrix was designed to reveal the role of Solid Volume Fraction (free volume available for interaction with supercritical carbon dioxide), system chemistry, as well as the degree of pore space saturation with water on the CO₂ immobilization efficiency and microstructural changes occurring during the mineralization process. The experimental work is supported by the literature review presenting up-to-date technological approaches to CO₂ sequestration in the inorganic alkaline waste, as well as statistics on the potential availability of industrial waste for rapid carbon dioxide mineralization.

The experimental work presented in this thesis encompasses the design of protocols, data collection, and analysis, as well as critical evaluation of the experimental

design and gathered results. CO₂ mineralization trials were performed in the high-pressure high-temperature reactor, in which the supercritical state of CO₂ was achieved by prescribing carbon dioxide dosage (230g) as well as temperature (75°C) such that the pressure above the critical point was achieved. All curing tests were run in batches of three representative samples preconditioned to the required maturation and saturation degree and cured for 3 days. To infer the CO₂ immobilization efficiency, as well as the type and extent of microstructural changes in the consolidated materials subject to supercritical curing, the set of materials characterization techniques, was applied. This includes weight gain measurements, density and moisture content determination, pH-indicator tests to reveal the carbonation front advancement and the surface fractions of carbonated material, thermogravimetric analysis, as well as porosity measurements.

The main achievements of the author can be summarized as follows:

- Design and evaluation of experimental setup and protocol for supercritical CO₂ curing of consolidated inorganic industrial waste. This also includes the mix design routine and mi verification to achieve targeted solid packing as well as saturation degree. The experimental setup and method were designed based on an extensive literature review coupled with the preliminary test runs. The experimental setup successfully encapsulated a comparable amount of CO₂ in the cement and fly ash samples and the neat fly ash sample systems within 3 days of curing time.
- The parametric study design aiming at the inference of the effect of packing density, degree of saturation, and cement chemistry on the CO₂ mineralization efficiency. The results of this parametric study showed a clear correlation between the initial volume of free space of consolidated material and the CO₂ uptake; higher initial porosity

enhances the mineralization rate. However, the investigation of the effect of degree of saturation on the mineralization process was inconclusive, and the obtained data strongly suggested modification to the original experiment design such that more reliable and statistically significant measurements can be taken and relevant trends can be inferred.

- Design of method for assessment of CO₂ mineralization efficiency. A qualitative and semi-quantitative routine was proposed which combines Image analysis techniques of contrast images from the pH-indicator test with TGA measurements taken along the radial direction of the carbonated cross-section. This method allowed for quantitative analysis of the carbonation front and its dependence on the initial solid packing. Second, it provided the author with the semi-quantitative estimate of the mineralization efficiency, which was compared to the dry weight gain (a standard technique reported in the literature). This study showed that for the given set of technological parameters controlling the mineralization process, CO₂ immobilization of up to around 50% of the theoretical potential of the fly-ash cement mixture (at the mix ration 60:40), and up to around 70% for the neat class C fly ash could be achieved. These efficiency metrics were assessed via the weight gain approach. However, the obtained data from the coupled pH-image-TGA approach tends to suggest that the expected efficiency is slightly lower.
- CO₂ mineralization results in the densified microstructure. This effect is supported by the results of dry bulk density, and porosity assessments. In all cases, the dry bulk density of post-carbonated materials was significantly higher than the measured density at the pre-carbonated state, and the value of the open porosity was reduced.

The porosity reduction and density increase are the consequence of precipitation of the CO_2 – bearing phases within the pore space. The presence of such precipitation was confirmed in the independent SEM study, as well as EDX analysis which confirmed the crystallization of calcium carbonate. However, the precipitation of other carbonous microstructural phases cannot be excluded and requires a more detailed study using the x-ray diffraction technique.

• Preliminary qualitative ASTM compression testing on neat fly ash with high calcium with different methods of curing. Three samples of neat fly ash class C with the same packing density and degree of saturation and 66% were cured separately of three different forms of curing: normal hydro-curing for 2 days, normal hydro curing for 2 days coupled with hydrothermal curing for 3 days at 75 C and normal hydrothermal curing followed with 3 days of sup CO₂ curing at 75 C and 230 grams of CO₂. The presented initial data show the positive impact of CO₂ mineralization on the mechanical strength of cured materials: approximately 4 times more compressive strength for sup. CO₂ sample in comparison to the samples cured in a normal setting and "hydrothermal" curing while there was no contrasting difference for compressive test results in between samples undergone normal curing and "hydrothermal" curing.

5.2 Future works

The future work is divided into three subsections depending on the nature of the work and is stated as the following:

5.2.1 Refinement to the experimental design

This principle of using supercritical CO₂ to carbonate alkaline waste works and is producing better results than most of its preceding methods which use gaseous or liquid state of CO₂ for carbonation and even when compared to earlier methods that have used supercritical CO₂ in pure form or mixed with flue gas. But the process can be made more efficient by switching from dry ice to liquid CO₂ as a source of carbon dioxide. This solution will also allow for a significant reduction of experimental uncertainty, bypassing the drawback associate with the use of dry ice, and better control of the curing process. As a result, a more refined analysis and parametric study could be performed allowing for the statistically significant inference of the subtle trends between various technological processes controlling the mineralization process,

Currently, dry ice is being used as the source of CO_2 may contain some small amounts of water. However, the main drawback associated with the solid CO_2 is the rapid switch from -78.5°C (sublimation point) to room temperature, which could induce cracking in the samples, thus affecting the mineralization progress across the sample. Finally, since we must prescribe the concentration of CO_2 while using the dry ice, we have to precalculate the concentration of CO_2 compensating for the pressure drop due to carbon dioxide intake during carbonation, this can affect the regulation of constant CO_2 concentration in the system at the beginning and during the carbonation subsequently bring alteration in the extent, kinetics and morphology of the developed calcite network. Similarly, due to the pressure drop, the pressure cannot remain constant as we cannot control the influx of CO_2 into the chamber this can also affect the comparability in between the samples. The use of liquid CO₂ regulated using a pressure tank and volumetric valve could mitigate all the above obstacles, and provide more strict control of the experiment.

5.2.2 Extensive future works

5.2.2.1 Extension of scope of parametric study

The proposed hypothesis of this study was tested; the alteration of packing density also known as Solid Volume Fraction (SVF), moisture content or degree of saturation (SAT) and, change in material chemistry results in the variation in the achieved carbonation efficiency. However, one of the lines of future studies could be focused on a more refined parametric study aiming at the inference of the optimum conditions for maximized CO_2 immobilization rate. Such study would require further expansion of the domain of the studied parameters e.g. inducing the effect of sample size.

5.2.2.2 Extension of sample to a larger size and different geometry

A cylindrical sample of approximately 2.2cm diameter and 4.4 cm height is used in the experimental runs. The experiment can be upscaled to samples of larger sizes and of different geometries such as rectangular blocks and aggregates that could be made and reused for structural and nonstructural applications.

5.2.3 Improvement in the carbonation efficiency assessment methods

The post carbonation assessment can be performed more accurately at various stages and more reliable and quantitative metrics of carbonation efficiency could be obtained together with associated uncertainties.

5.2.4 Use of analytical methods to calculate the water generated during the carbonation

Different researchers proposed numerous analytical methods to calculate the excess of water in the sample system which is generated in carbonation portlandite. If the water vapor relative pressure can be controlled along the curing process then the excess moisture due to the mineralization could be estimated using analytical methods.

5.2.5 Use of MIP to obtain a more accurate description of the pore space

The porosity of the sample post carbonation was assessed using the fluid displacement method which has its limitations and requires re-saturation of the sample. This test does provide a quantitative estimate of the open porosity only. On the other hand, Mercury Intrusion Porosimetry (MIP) can be used as a more accurate method of measuring pore size and pore volume which can deliver more details about pore domain evolution and can facilitate the understanding of the ongoing mineralization process.

5.2.6 Use of XRD for identification of CO₂ mineral precipitates.

The TG graphs do help to infer the quantity of the compounds formed based on their temperature e.g. portlandite and magnesium carbonate decompose at 300- 450C and well-crystallized calcite at 750C – 950C. However, this method does not allow for a clear definite refinement of the type of mineral phase. Such identification requires the use of the x-ray powder diffraction technique, which would provide more insight into the microstructural evolutions due to supercritical curing.

5.3.3 Use of deconvolution techniques to separate compounds having same decomposition temperature

When we look at the TGA graphs, there is a formation of peaks of portlandite combined with the peaks of other compounds at the gray region of temperature ranging from 250 C to 450 C, and the explanation of which has been beyond our knowledge for the time being. Supported by the proposed x-ray diffraction study, we can use deconvolution techniques to separate those peaks and obtain a clearer picture of the compounds formed.

5.2.7 Use of more rigorous algorithms for analyzing samples with image analysis tools.

In this work, the image analysis has been used to analyze the data which later serves as a basis for finding out weight gain percentage due to CO₂ encapsulation into the system. Although works, the algorithm has its limitations: the bias may be introduced due to the operator judgment in terms of recognition of carbonation front and categorization of the carbonated surface areas revealed in the pH-indicator test. This can result in the accumulation of errors and can also lead to bias in the estimated values of CO₂ uptake. The image J is a powerful software that can be operated using MATLAB functions which can rigorously calculate the surface area using the pixel counts which relate to physical reality and makes the measurement metric objective which is far more accurate than the measurement through eye judgment that differs from user to user.

5.2.8 Use of SEM to understand the microstructure of the sample system

The scanning electron microscopy has been used to detect the calcite and fly ash in the thesis work and to view the microstructure of the sample post carbonation. The systems prior and post carbonation could not be compared due to time limitations. But SEM and EDS can be extensively performed on fractured and polished beam samples respectively to get the images of the microstructure and elemental composition which is crucial when it comes to understanding the microstructure of the sample system and tracking changes to learn the behavior of the material prior and post carbonation.
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