



ACCELERATED CARBONATION OF RECYCLED CONCRETE AGGREGATES FOR THE PRODUCTION OF CO₂-NEGATIVE CONSTRUCTION MATERIALS

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Preamble

This thesis work has been carried out amidst the coronavirus pandemic, with strict measures regarding social distancing and work ethics in and outside VITO premises. All these measures have been taken in order to prevent contagion.

However, these measures did not affect the nature of the work done and the results achieved through it. In line with the original plan, the literature review and detailed discussions about the thesis topic were held with supervisors and researchers at VITO, as well as preparations were done to facilitate the experimental program conducted at a later stage. Moving out of Ghent to live close to my workplace in Mol helped in saving a lot of time and facilitated in smooth execution of the experimental program.

Communication with my promotors and tutors were maintained through online meetings and video calls. Meetings in person with my non-academic promotor also helped in discussing pressing matters and flow of future work.













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Abstract

Cement production accounts to about 8% of global CO_2 emissions which if gone unchecked will cause irreparable damage to the environment. Of all the construction materials used in the European Union, concrete accounts to about 42% and construction and demolition waste constitutes about 25-30% of the total waste generated.

The construction sector, however, seldom reuses the recycled concrete aggregates (RCAs) in high-grade construction projects such as building walls, floors, bridges etc. and the aggregates are mostly used in low-level processes such as a base material for road construction. However, due to the advent of newer policies regarding infrastructure systems, the capacity of aggregate absorption by roads is becoming increasingly limited and new upcycled applications are the need of the hour.

The quality of the RCAs is dependent on the composition of the initial concrete structure, which in turn can be selectively demolished and kept separate to ensure proper quality management and lessen the variability of composition. The major hindering factor to use RCAs is their water absorption capacity, which can be as high as 10% in this thesis work, while the natural aggregates can have a value of less than 1%. This increased water absorption is due to the adhered mortar on the aggregates and can have profound impact on the workability and strength development of recycled aggregate concrete.

Mineral carbonation process has been chosen to deal with the high water absorption capacity of the aggregates which can carbonate Ca and Mg containing cement hydration products into stable phases like calcite and dolomite. As a result, the porosity and the water absorption capacity decreases, thereby increasing their usability in recycled concrete.

Experiments reveal that carbonation at 40°C with 70% CO_2 for 24 hours result in a 25% reduction in water absorption whereas, similar results can be achieved in 6 hours if a temperature of 60°C is used. Carbonation of RCAs sequester around 35 grams of CO_2 per kilogram with a 3-3.5% increase in particle density. This led to a reduced porosity, enhanced interfacial transition zones between the original aggregate and adhered mortar and an 11-12% increase in solid volume.













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Nomenclature

IPCC - Intergovernmental Panel on Climate Change GHG – Green House Gases CDW - Construction and Demolition Waste NA – Natural Aggregates RA-Recycled Aggregates RCA - Recycled Concrete Aggregates RAC – Recycled Aggregate Concrete CCU - Carbon Capture and Utilization CCUS – Carbon Capture Utilization and Storage LCA – Life Cycle Analysis ITZ - Interfacial Transition Zone EU – European Union PC – Preconditioned RH - Relative Humidity XRD - X Ray Diffraction SEM – Scanning Electron Microscopy TC/TIC - Total Carbon/Total Inorganic Carbon













Chapter 1: Introduction

The scientific evidence on climate change and global warming has become compelling and substantial over the last few decades with scientists around the world being simultaneously unequivocal and concerned. The age of globalization has shaped the needs of mankind and accelerated the rate of consumption of natural resources. This has created resource criticality on one hand and major environmental concerns on the other. Since the mid 20th century, human activities have been the most dominant cause of global warming and according to the IPCC 2014 report, the climate changing trends are continuing at unprecedented rates. Another report has suggested to reduce CO₂ emissions by 45% of 2010 standards before 2030, in order to restrain global warming under 1.5° C (IPCC 2018). The atmospheric CO₂ concentration has reached an all-time high of 407.38 ± 0.1 ppm in 2018 (Dlugokencky et al., 2018), which is a substantial increase from the pre-industrial era levels of 277 ppm (Joos et al., 2008).

CO₂ emissions from fossil sources around the globe have increased from levels of 3.0 ± 0.2 Gt C yr⁻¹ in 1960s to an average of 9.5 ± 0.5 Gt C yr⁻¹ in the span of 2009-2018 (Friedlingstein et al., 2019). This comes as a result of a strong market expansion of industrial firms and a lack of sustainable business strategies. *Figure 1(a-d)* shows CO₂ trends over a period of 1960-2019.



Figure 1: Fossil CO₂ emissions. a) Global emissions with 5% uncertainty marked by the shaded area. b) Emissions by fuel type (coal-salmon), (oil-olive), (gas-turquoise), (cement-purple). c) Emissions of top-emitting countries and EU 28; (olive-USA), (salmon-China), (purple-India), (turquoise-EU28); solid lines-territorial emissions (Gilfillan et al., 2019), dashed lines-consumption-based emissions (Peters et al., 2011). Territorial emissions are those that take place within a country's boundaries which includes exports but excludes imports. Consumption based emissions are calculated based on domestic final consumption and includes imports. d) Per capita emission trends. Source: Friedlingstein et al., 2019.













Despite of emerging climate policies being formulated by various countries and global consortiums; CO_2 emissions have grown over the last decade. The growth in emissions slowed down to 0.9% after 2010 and went further down in 2014-2016 (Peters et al., 2020). The emission imbalance created by various large economies is the main reason of the continual growth, although this imbalance is often created by societal and geopolitical factors as well as insufficient access to low-carbon energy sources and technologies. Industrial production is necessary to meet societal needs and they require energy to operate. Therefore, the manufacturing industries and energy producing conglomerates have become one of the leading emitters of CO_2 with more than one-third of total emissions in 2006 (Allwood et al., 2010). Fossil fuel oxidation along with deforestation and carbonate decomposition are the three main

anthropogenic sources of CO_2 emissions (Andrew, 2019). Since ancient times, cement has been used as a binder material for aggregates in construction activities and is regarded as one of the biggest sources of emissions from carbonate decomposition. Cement production skyrocketed after the end of World War II and has been increasing since. The rise of developing economies such as China, India and others after 1990s have kept the upward trend of global cement usage. *Figure 2* provides an understanding of global cement and fossil fuel production trends.



Figure 2: Global fossil fuel and cement production trends. Source: Andrew 2019.

The increasing usage of cement brings into account the CO_2 emissions coming from the industry, which amounts to about 8% of global CO_2 emissions. To put this into perspective, it













is higher than global shipping, trucking and air travel combined. This has sparked the interest of using various Carbon Capture Utilization and Storage (CCUS) technologies which can sequester CO_2 and utilize or store them away for a long time. Mineral carbonation is one such technique and this thesis builds on the route of recycled concrete aggregates carbonation.

Chapter 2: Literature review

 CO_2 emissions from the cement industries constitute of two components; firstly, the production of clinker from limestone, where CO_2 is evolved. Calcium carbonate (CaCO₃) of limestone, when calcined in a kiln, produces carbon-di-oxide as a byproduct. The reaction is given below:

$CaCO_3 + Heat = CaO + CO_2$

The second component of emissions is the production of energy needed to produce the clinkers. Cumulatively, the emissions from cement industries constitute to about 8% of global CO_2 emissions (Andrew, 2019). However, around 50% of these emissions are generated from complex material reactions within the kiln, 40% from fuels and the rest is divided between electricity and transportation (Maddalena et al., 2018 and Summerbell et al., 2016). CO_2 evolution due to the decomposition of limestone by thermal processing is the major material derived GHG emission. Thus, it is evident that renewable energy usage alone will not solve the problem, it must be a cluster of different approaches including reducing the use of Portland cement.

The thermal energy requirement of producing Portland clinker is around 2.9 GJ/ton, whereas the total emission rate amounts to ~866 kg CO₂/ton, including the chemical emission and energy demand (Klee, 2009). In order to reduce the overall environmental impact of Portland cement, various material combinations have been under consideration. Supplementary Cementitious Materials (SCMs) are being widely used in Europe for substituting Portland clinker in cement, while attaining good strength characteristics after casting. Fly ash, a fine residue generated by coal-fired power plants and ground granulated blast furnace slag are the most commonly used SCMs. These SCMs substitute clinkers in different amounts in different grades of cement and the limits of SCMs used in them are provided in the table below:















| Cement | Composition (%) | | | | | | |
|--------------|-----------------|-------|---------|-----------|--------|--|--|
| Grade | Clinker | Slag | Fly Ash | Limestone | Others | | |
| CEM II / A-M | 80-94 | - | - | 6-20 | - | | |
| CEM II / B-M | 65-79 | - | - | 21-35 | - | | |
| CEM III /A | 35-64 | 36-65 | - | - | 0-5 | | |
| CEM III / B | 20-34 | 66-80 | - | - | 0-5 | | |
| CEM III / C | 5-19 | 81-95 | - | - | 0-5 | | |
| CEM V / A | 40-64 | 18-30 | 18-30 | - | 0-5 | | |

Table 1: Cement grades according to Standard NBN B12-001.

It has been reported that the use of SCMs in concrete mixtures can reduce the CO₂ emissions by 13-22%, though the actual reduction is based on local conditions of energy price, technological abilities and transportation distances (Flower et al., 2007). The utilization of byproducts of other processes in the production of concrete has the advantages of waste-toresource valorization. Geopolymers are also considered as alternative binders and are defined as inorganic materials rich in aluminum and silica reacting in a medium of alkaline activators (sodium hydroxide and sodium silicate being the most commonly used) (Davidovits, 1991). Some geopolymer-based concrete is cured in elevated temperatures (40-80°C) for at least 6 hours to achieve a comparable strength of Portland cement (Duxson et al., 2007 and Palomo et al., 1999) whereas others can be cured at ambient conditions depending on the composition of geopolymers. It has been found that ambient cured geopolymer concrete having 5% of Portland cement as admixture can accelerate the geopolymerization as well as setting time, thereby yielding compressive strengths of 40 MPa at 28 days (Nath et al., 2015). As a result of using geopolymers, a wide range of reduced CO₂ emission values have been found, depending on the calculation of energy used in curing, transportation of raw materials, manufacturing of alkaline activators etc. Values ranged from 26-45% reduction of emissions (Stengel et al., 2009 and Habert et al., 2011) to as high as 80% (van Deventer et al., 2010 and Duxson et al., 2007). Life cycle assessments of geopolymer concrete mixtures have reported a reduction of 44-64% of GHG emissions and costs of 7% lower to 39% higher than Portland cement (McLellan et al., 2011).













2.1. Upcycling of C&D waste

Natural aggregates consisting of stone, gravel and sand are produced by crushing bedrock and are a major component of concrete and asphalt (Langer 2016). They remain the largest non-fuel mined resource both in terms of volume and value. According to the 2019-2020 review of the European Aggregates Association (UEPG), the EU28 and EFTA countries generate a demand of 3 billion tons per year with an annual turnover of \notin 15-20 billion. Though the impact of aggregate mining on resource depletion and global warming is lower than other industries (Bleischwitz et al., 2006), extraction and processing have some impact on the environment including loss of groundwater and surface water, landscape changes and dust problems.

A huge amount of Construction and Demolition waste (CDW) is generated on a daily basis due to economic development and industrial activities (Babu et al., 2015). The construction industry is estimated to generate around 13-30% of total global waste (Thongkamsuk et al., 2017); while C&D waste constitutes about 25-30% of EU's total waste generation. This waste stream has been defined as a priority area by the Circular Economy Action Plan (EC 2015) and the Waste Framework Directive (WFD 2008/98/EC, amended 2018/851) has set a mandatory target of 70% recoveries by 2020. The Flanders region in Belgium has an aggregates recovery rate of more than 95% and further focus has been made on high-grade applications of recycled aggregates (Deloitte 2015). Economic drivers such as expensive landfilling options compared to treatment plans encourage recovery of various fractions of CDW.

The revised Waste Framework Directive defines the waste hierarchy as depicted in Figure 3.



Figure 3: Waste hierarchy according to EU WFD 2008.













The framework suggests that the EU states should promote selective demolition to facilitate handling and sorting of CDW. Materials that can be salvaged for reuse and recycling should be sent to appropriate channels, whereas the remaining components can be incinerated to recover energy. Landfilling is considered as the last option, which is in line with the wider objective of setting recycling and preparing-to-reuse targets of wastes by 2024. *Figure 4* shows the amount of C&D waste generated per person in the EU countries.



Figure 4: C&D waste generation per person, EEA 2016. Source: Eurostat (2019a).

According to Eurostat, the average recovery of CDW in the EU was 89% in 2016, where recovery rates are defined as the CDW prepared for reuse, backfilling, recycling or material recovery divided by the amount of CDW treated.

The main application of using recycled CDW aggregates has been as a base material for road construction but according to the EU *zero land take objective 2050*, the market for road building materials will also decrease over time. On the contrary, the building sector seldom uses recycled aggregates; secondary materials constitute to about 3-4% of all the building materials used in Netherlands (Schut et al., 2016). For this reason, a large part of recycling of CDW can be termed as downcycling. Low-grade applications of CDW are generally done when there are no economically feasible ways to upcycle them.. To ensure enough recovery options for the stony fraction of CDW in the future, the development of increased high-value applications through innovation is necessary.













High-grade applications of CDW are defined by the incorporation in structural elements of buildings or high-durability infrastructure. The durability of these structures has impact on the CO₂ savings, generating less waste and less need of waste disposal. Concrete accounts for about 42% of used construction materials, thereby reiterating the importance of high-grade concrete recycling (Enkvist et al., 2018). The replacement of natural aggregates (NA) by recycled coarse aggregates is limited up to 50% for low-grade applications as set in EU standards such as EN 206 and EN 12620. Dutch standard NEN-5905 provide allowance of up to 50% by volume of natural aggregates replaced by recycled ones while the Flemish standard specifications for roadworks permit up to 20% replacement of coarse aggregates with high-grade concrete aggregates without further testing of the produced concrete.

The main barriers for using recycled aggregates (RAs) are it's variability of composition and higher water absorption when compared to NAs (Cardoso et al., 2016). However, existing green protocols such as Building Research Establishment Environmental Assessment Method (BREEAM), US Green Building Council's Leadership in Energy and Environmental Design (LEED) and future sustainability legislations may accelerate the usage of recycled aggregates in the construction of buildings.

One of the major impediments of using recycled aggregates is the issue of an increased water absorption, which can negatively impact the performance of the concrete mixture (Quattrone et al., 2016). The higher water absorption of RA will reduce the concrete workability and hence increase the water demand. The water/cement ratio (w/c ratio) of concrete is an important indicator of its strength and workability (Joseph et al., 2015). High water absorption is linked with the presence of old mortar attached to the recycled natural aggregates (De Juan et al., 2009). A further factor are the air voids and capillary pores at the interfacial transition zone (ITZ) (Basheer 2001 and Basheer et al., 2001) and the presence of impurities such as gypsum and ceramic materials (such as bricks) (Agrela et al., 2011). The amount of water absorption is also influenced by the crushing and grinding process, generating recycled aggregates with varying amount of mortar paste attached to it (Quattrone et al., 2016). Values of water absorption may be less than 1% for natural aggregates whereas for recycled aggregates, the values can be around 10% (Boehme et al., 2012). Experimental results show that the compressive strength decreases in a linear manner as a function of additional water added, with reductions around 10-25% of compressive strength (Kou et al., 2007 and Li et al., 2006). Joseph et al. (2015) reported a decrease of 5 GPa in elasticity modulus of a concrete mixture for every 1% additional water content.













The two common strategies used to negate the negative effects of water absorption on workability and mechanical properties are the usage of additives (Etxeberria et al., 2007 and Evangelista et al., 2007) and pre-soaking of the recycled aggregates (Sagoe-Crentsil et al., 2001) and Zaharieva et al., 2003). Reports have indicated that pre-soaking of aggregates can reduce water suction from the cement phase, however, proper saturation levels must be maintained to avoid bleeding. Proper knowledge of water absorption kinetics is key to achieve optimal mechanical properties.

Various recommendations have been reported for concrete mixes made from recycled crushed concrete to account for the extra water absorption by the RCAs (Rao et al., 2007 and Ferriz-Papi et al., 2017). Some of them are discussed below:

- A higher standard deviation for mean strength determination should be taken into i. account while working with RCAs of variable quality.
- ii. While using coarse RCA fractions with natural sand, it can be assumed that the free water/cement ratio of the RAC will be similar to conventional concrete. Moreover, the sand/aggregate ratio of RAC would be similar to conventional concrete using natural aggregates. However, the increased water absorption of the RCAs should be kept in mind and compensated while making RACs.
- iii. Trial mixes are recommended to optimize workability, suitable water/cement ratio and final strength of RACs.

Since conventional concrete is a mix of water, cement and aggregates, replacing the NAs with similar quantities of RCAs increase the total mortar content in the concrete. It has been observed that the decrease of the aggregate/cement ratio increases the compressive strength up to a certain point and then starts to decrease (Poon et al., 2008). An equivalent mortar volume method has been proposed, in which the volumetric ratio of the NAs in conventional concrete is equivalent to the original aggregates in the RCAs and the mortar volume ratio of conventional concrete is equivalent to the sum of adhered mortar and fresh mortar used in recycled aggregate concrete (Fathifazl et al., 2009). In this case, determination of adhered mortar content on the aggregates becomes important. Various processes have been suggested such as the freeze-thaw method, where RCAs were immersed in s sodium sulfate solution and then subjected to 5 freeze-thaw cycles (Abbas et al., 2007). Another method suggested heat treatment at 500°C after soaking the RCAs in water, causing cracks and stresses in mortar while separating it from the original aggregate.

Another used technique to separate the aggregate and cement phases is microwave fragmentation and dehydration. Since the thermal expansion of aggregates and cement differs













with 50-300%, the microwaves cause internal tension along the phase boundaries and promote the formation of cracks. Dehydration of cement also reduces its binding properties and thereby facilitates the separation of the aggregates and cement phases (Tam et al., 2021).

The problem of degradation of mechanical properties of RCAs has been addressed in various ways, (Zhang et al., 2015) like ultrasonic cleaning of attached mortar from aggregates (Katz, 2004), heating and rubbing of RCAs (Tateyashiki et al., 2001) or presoaking them in HCl, H₂SO₄ and H₃PO₄ (Tam et al., 2007). However, negative effects on the RCA properties or on the environment has been encountered in all the above cases (Zhang et al., 2015).

There have been other techniques proposed to upcycle recycled aggregates and these processes generally focus on optimal separation of sand, gravel and cement fractions. Smartcrusher BV has developed a new crushing technique called Slimbreker, which breaks through the calcium-silicate-hydrate (binder of the sand and gravel) while keeping the sand and gravel fractions intact. The breaking is done by transverse and frictional forces and uses only about 15% of energy needed per ton of concrete rubble when compared to traditional crushers. However, adding more steps before the RCAs can be actually used in new concrete and usage of new equipment can add to costs and environmental impacts and detailed LCA studies are needed to gauge the actual impacts from this process.

2.2. Carbonation Technologies

The Intergovernmental Panel on Climate Change released a special report on the impacts of global warming at 1.5° C. The report suggests different pathways to reach climate goals based on four Integrated Assessment Models. These models consider various factors, such as contribution of renewable energy, legislative procedures, maturity of different technologies and so on. According to these models, carbon capture and utilization/storage technologies will have a huge impact in sequestering CO₂ from the atmosphere and redirecting it to different applications. Carbon Capture and Utilization (CCU) technologies have caught the attention worldwide, due to their applications in turning CO₂ to a resource for products like fuels and chemicals (Balucan et al., 2013). Another way to utilize the captured CO₂ is to store it for a long period of time through mineral carbonation (Di Maria et al., 2020). Carbonation involves reaction between CO₂ and an alkaline source, which typically are secondary aggregates or industrial residues and the end product can be used for activities such as construction (Santos et al., 2013). A schematic of the mineral carbonation process is given by *Figure 5*.















Figure 5: The concept of mineral carbonation. Source: Di Maria et al., 2020.

Construction materials based on mineral carbonation routes have the potential to consume 3-6 Gtons of CO_2 emissions by 2030 and generating annual revenues of \$1 trillion (McCord et al., 2018). Mineral carbonation technologies have been viewed as a bridge between Carbon Storage and Carbon Utilization technologies as they store CO_2 for a long time along with generating economic value out of it (Geerlings et al., 2013).

The source of alkaline materials varies from mining to metallurgical wastes and C&D wastes as well. One of the patented processes of Orbix in Belgium uses metallurgical slags from the mineral processing industry and carbonates them through accelerated carbonation. Accelerated carbonation is nothing but a faster natural carbonation process in artificial conditions, where the reaction parameters can be modified to enhance the carbonation rate and other associated properties. Usually, accelerated carbonation is done in a reactor where CO_2 concentration and pressure, temperature, relative humidity can be controlled to generate optimal results. One of the major advantages of using industrial byproducts such as slags and fly ash is the availability within the proximity of large CO_2 point sources.

2.2.1. Carbonation of concrete

There is an innate necessity of durability when it comes to concrete structures, lack of which can be detrimental and pose risks to safety. The main parameter considered to be directly linked to durability is the permeability of concrete and is generally governed by the constituents such as hydrated cement paste, aggregates, their geometric alignment and the interface transition zone (ITZ) (Mehta, 1980). Other methods include addition of pozzolanic materials such as













granulated blast furnace slag or fly ash to improve the matrix structure of the concrete. The basic idea of all the procedures has been to increase durability of concrete to offset the mechanical limitations posed by the usage of RAs. Carbonation of RAs can also enhance the mechanical properties of Recycled Aggregate Concrete (RAC) (Xuan et al., 2016). Alkaline materials, through reaction with CO₂ can form carbonates and other residues thereby storing CO₂ for a long time. CDW contain calcium and magnesium that can react to form respective carbonates which are relatively stable and can effectively stabilize and valorize alkaline waste (Ho et al., 2020). The concrete carbonation strategies can be divided into direct and indirect methods.

2.2.1.1. Direct Carbonation

In the case of direct carbonation, concrete wastes are reacted directly with CO_2 without the use of additional treatment methods which can be performed in a gas-solid or an aqueous system (Ho et al., 2020). Also known as dry carbonation, these processes are used in many industrial processes and a general reaction of a gas-solid system is given below:

 $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$

There has been usage of liquids within direct carbonation systems as well such as placement of additional water to boost the relative humidity of a carbonation chamber, however a relative humidity range of 40-70% has been found beneficial to produce better quality aggregates (Gholizadeh-Vayghan et al., 2020). The direct carbonation of concrete waste involves three consecutive steps as calcium extraction, CO_2 dissolution and $CaCO_3$ precipitation.

- i. Calcium extraction involves the release of Ca²⁺ and OH⁻ ions into aqueous phase, thereby producing an alkaline environment.
- ii. CO_2 gets dissolved at pH>10 to form HCO³⁻, CO_3^{2-} and releases H⁺ ions in the aqueous phase.
- iii. Ca^{2+} from the concrete waste and CO_3^{2-} from the dissolved CO_2 reacts to produce $CaCO_3$ within the pore solution.

The carbonation reaction is partially diffusion-controlled and partially moisture-controlled and the main product CaCO₃ can be deposited in three crystalline polymorphs viz. calcite, aragonite and vaterite. The dominant precipitate variety depends on conditions such as temperature, pH and supersaturation (Dubina et al., 2013) or can be modified by the presence of additives such as sulphate groups (Fernández-Díaz et al., 2013) and impurities. Hydration products present in













concrete and prone to carbonation are the portlandite, AFm, ettringite and C-S-H phases (Gholizadeh-Vayghan et al., 2020). Formation of CaCO₃ results in the release of some water previously bound to hydrates such as portlandite and thereby changing the total solid volume (von Greve-Dierfeld et al., 2020). Changes in volume have tremendous effects on the porosity and the transport properties of the carbonated concrete. Carbonation of portlandite results in increase of solid volume by 11-12% (Xuan et al., 2016), which can be interpreted as an increase in mechanical strength and decrease in porosity (Zhan et al., 2014). C-S-H is the most abundant calcium bearing phase within the hydrated cement paste and displays the most complex carbonation mechanism, with the process depending on the CO₂ concentration, Ca/Si ratio and the presence of portlandite (Visser, 2014). It has been found that at CO₂ concentrations above 3%, C-S-H undergoes complete decomposition resulting in the formation of calcium modified silica gels, on the other hand, partially decalcified C-S-H was found with lower concentrations (Steiner et al., 2020). Studies have shown that carbonation of C-S-H can increase solid volume up to 23% with reduced water absorption (Shi et al., 2016), but the exact extent of volume increment is still under debate. The carbonation of ettringite however results up to 50% shrinkage in volume due to complete carbonation reaction (Gholizadeh-Vayghan et al., 2020) and therefore, carbonation conditions must be chosen carefully to achieve experimental aims. A typical reaction of carbonation of ettringite is given below:

 $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3 CO_2 \rightarrow 3CaSO_4 \cdot 2H_2O + 3 CaCO_3 + 2 Al(OH)_3 + 23 H_2O$

Several authors have put forward their interpretations of the influence of carbonation of RAs with relation to the water absorption, porosity, gas and chloride permeability and mechanical properties. It has been reported that the RACs prepared with carbonated RCAs have lower porosity than the RACs prepared with non-carbonated RCAs as measured by Mercury Intrusion Porosimeter (Xuan et al., 2017). *Figure 6a* shows total porosities of concrete made from carbonated and non-carbonated RCAs and *6b* shows a good linear relationship of water absorption to porosity.















Figure 6: (a) Total porosities of concrete made from various amounts of carbonated and non-carbonated RCAs. (b) Relationship between water absorption and porosity. NRCA = Newly crushed RCA Source: Xuan et al., 2017.

While most of the literature focuses on ambient pressure carbonation processes, a number of accelerated carbonation processes have been studied as well. These studies report a considerable decrease in the porosity of the RAC due to carbonation, which can range between 23-28% decrement when carbonating RCAs at 20°C, 60% RH and 20% CO₂ concentration (Zhang et al., 2015). Clearly, carbonation conditions (RH, temperature, moisture condition, CO_2 pressure, duration of carbonation) have a profound effect on the properties of the end product. CO_2 pressures above 5 bars have been termed as unnecessary for accelerated carbonation as the property enhancement achieved through portlandite carbonation can be counteracted by the degradation of other hydrates present in the cement such as C-S-H (Shi et al. 2016).

Carbonation temperatures up to 60° C have been reported to be useful as carbonation reaction itself is exothermic in nature. However, the increase in temperature promotes the formation of metastable forms of CaCO₃ (Bertos et al., 2004). The most favorable RH range for carbonation has been found to be 40-70% (Morandeau et al., 2014).

The increment of durability of RAC with carbonated RCAs has been reported by many authors. With a usage level of 100% of carbonated RCAs, chloride ion permeability, bulk electrical conductivity and gas permeability decreased by 36.4%, 15.1% and 42.4% respectively when compared to non-carbonated RCAs (Xuan et al., 2017). The porosity decreased considerably with the disappearance of pores larger than 200 nm and reduction of pores of sizes between 50 nm and 200 nm.

















(a) Non-carbonated NRCAs(b) Carbonated NRCAsFigure 7: Morphology of NRCAs before and after carbonation. Source: Xuan et al., 2017.

Figure 7 demonstrates the conversion of common cement hydration products into polymorphs of CaCO₃ such as calcite and aragonite.

2.2.1.2. Indirect Carbonation

Indirect or multi-stage carbonation mainly refers to a two-step process: In the first stage, calcium from waste rock materials are lixiviated by acids or bases as Ca²⁺ (Mazzotti et al., 2005). In the second stage, the Ca^{2+} is brought in contact with a CO_2 or CO_3^{2-} source and thermodynamically stable CaCO₃ is precipitated. Calcium availability is critical to the carbonation reaction and therefore, the rate of dissolution of alkaline rocks is the controlling factor for the reaction (Abe et al., 2013). Various lixiviants have been reported by various authors when it comes to dissolving concrete waste, distilled water (Iizuka et al., 2004), nitric acid (Shuto et al., 2014), acetic acid (Mun et al., 2017), ammonium chloride (Mun et al., 2017) and ammonium hydroxide (Lee et al., 2016) being some of them. While using HCl or CH₃COOH, pH was adjusted with NaOH for effective carbonation. However, using NH₄Cl has proven to be effective as carbonation occurs without surplus alkali addition and the solution can be regenerated, making NH₄Cl an optimum leaching agent for indirect carbonation (Ho et al., 2020). In case of alkaline earth metals, high silicate dissolution rates are often achieved at lower pH, making it difficult for carbonate precipitation (Pan et al., 2012). In order to tackle this problem, serpentinite carbonation techniques are used, which utilize weak acids and chelating agents to bring minerals into the solution. pH is then increased stepwise with the precipitation of iron oxide and nesquehonite (MgCo₃(H₂O)₃) (Park et al., 2004). In an indirect













basic carbonation using concrete waste, NH₄OH and desulfurization gypsum, following reactions were encountered.

 $NH_4OH + CO_2 \longrightarrow NH_4HCO_3$ $2NH_4HCO_3 + CaSO_4 \longrightarrow CaCO_3 + (NH_4)_2SO_4 + CO_2 + H_2O$ $(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2NH_3 + H_2O$

Desulfurization gypsum was provided by the $CaSO_4$ and calcium hydroxide was supplied by the concrete waste. Calcium carbonate and calcium sulfate were recovered, and ammonium hydroxide solution could be used in a repetitive manner.

One of the major problems regarding indirect carbonation processes is their cost (Iizuka et al., 2013). Concerns regarding power consumption, waste water treatment, utilities and waste disposal hinder its use in a feasible scale. Bipolar membrane electrodialysis systems are proposed to be used in treatment of the waste solution (Ho et al., 2020).

The use of indirect carbonation methods has become an important part in different Carbon Capture Utilization and Storage (CCUS) projects where highly pure calcite crystals can be generated without the interference of iron or silica at an economical scale (Boone, 2015). Further studies of cost evaluations are needed to get a better idea of this route in valorizing concrete waste.

Chapter 3: Scope of this study

The scope of the present study is to take into account the work that has been done till now on direct carbonation of secondary aggregates and build on those parameters to generate better properties. Initially, cement mixes with varying compositions will be made and aged till 90 days. The coarse fraction of the RCAs of sizes 8-20 mm prepared from this concrete will be the focus of this study. Carbonation tests will be focused on the effect of parameters such as temperature, CO₂ concentration and duration of carbonation experiments. The evolution of the physical properties such as water absorption, density and porosity will be discussed. The minerology of the aggregates will be investigated in detail ranging from the natural, non-carbonated and the carbonated aggregates and characterization such as XRD and TC/TIC will be used. Microstructural investigations with the help of SEM will be carried out and the effect













of experimental parameters will be discussed. Lastly, a conclusion will be drawn on the results achieved with an outlook into the future research prospects.

Chapter 4: Research Methodology

The experimental program was carried out in the laboratory in different stages. In order to have better control over the composition and quality of the RCA, four different concrete mixes were prepared, casted and cured for 90 days, although the present study will involve the first two mixes designated as Mix 1 and Mix 2. The casted concrete was then crushed in steps using a hydraulic press and jaw crusher and sieved into different size fractions. Only the 8-20mm aggregates were used for the subsequent experiments involving carbonation, while the other size fractions were stored away in air-tight conditions. The 8-20mm RCAs were then tested for their water absorption, apparent particle density and saturated surface-dried particle density to provide a starting point for comparing the subsequently produced carbonated RCAs. The RCAs were subjected to varying carbonation conditions concerning the CO₂ concentration, temperature and duration of carbonation and the optimal conditions were determined on the basis of water absorption results and the characterization techniques applied. The carbonated RCAs were subjected to X-ray Diffraction (XRD) to study the evolution of mineralogy of the RCAs with different carbonation conditions. Total Carbon (TC) tests were performed in order to determine the carbon-sequestering capacity of the RCAs. Lastly, the evolution of morphological characteristics of the RCAs at different carbonation conditions were investigated with the help of Scanning Electron Microscopy (SEM) and compared to the noncarbonated RCAs.

4.1. Materials Used

Coarse and fine natural aggregates for the base concrete mixes were sourced from Hobbyland. The coarse aggregates used were Cobo Garden Parelgrind 4/16 gravel, while the fine aggregates were Cobo Garden Rivierzand 0/4 (river sand), where the numerical designations specify the minimum/maximum nominal aggregate sizes based on EN 12620:2013. Both aggregates were siliceous in nature and their phase composition were determined with XRD. The results from the rietveld analysis are presented below:















Figure 8: XRD results of natural fine aggregates.



Figure 9: XRD results of natural coarse aggregates.

From *Figure 9* it can be seen that there is a considerable amount of calcite and dolomite in the coarse natural aggregates. The coarse and fine aggregates were received in batches and water













absorption test was performed on them in accordance to EN 1097-6:2013. The water absorption of coarse and fine aggregates was in the range of 2.7-3.5% and 0.30-0.37% respectively. Portland Cement (CEM I, 52.5N and CEM III/A, 42.5N) was sourced from Holcim Belgium and used as the cementitious material for making the base concrete mixes. Two different water/binder ratios were used for the four mixes, however for Mix 1 and 2, the value is around 0.5.

4.2. Methods

4.2.1. Production of base concrete

A total of four concrete mixes were made in the laboratory using the two types of cement discussed above. The proportions of mixing are shown in *Table 2*. In the beginning, the natural aggregates were dried in an oven to remove any residual moisture. Water is added to the aggregates in a tumbling mixer to reach the saturated surface-dried (SSD) state. The amount of water added was calculated from the total weight of dry aggregates and their water absorption capacity. The SSD aggregates were kept in covered buckets for at least 48 hours before they were used to make concrete.

At the day of the mixing, the weighed SSD aggregates were added to a Silla BB350S tilting drum mixer along with 1/3 of the water required to make the concrete mix. The mixer is started, and the cement is added gradually, followed by the rest of the water. The mixer is let to run for an additional 3-4 minutes and then stopped. A slump test is done according to EN 12350-2 to determine if slump has reached Class 4 (160-210mm) workability. Since there was no need to add Glenium superplasticizer, the concrete mix was then poured from the mixer. 16 cylinders (110 x 220 mm) and 4 cubes (150 x 150 x 150 mm) were filled with the concrete mix, tampered after every 1/3 filling with a steel rod. The rest of the mix is poured into plastic buckets, closed with lids and stored.















| Mix No. | Cement | Cement | Water | Coarse | Fine aggregates | W/C Ratio |
|---------|-----------|---------|---------|------------|-----------------|-----------|
| | type | (kg/m³) | (kg/m³) | aggregates | (kg/m³) | |
| | | | | (kg/m³) | | |
| 1 | CEM III/A | 340 | 170.7 | 1022.2 | 715.4 | 0.50 |
| 2 | CEM I | 340 | 169 | 1022.2 | 792.0 | 0.49 |
| 3 | CEM I | 426.7 | 179.3 | 954 | 571.5 | 0.42 |
| 4 | CEM III/A | 445 | 187 | 1030 | 597.7 | 0.42 |

Table 2: Concrete mix design and mixture proportions.

4.2.2. Production of RCA

The concrete samples were stored for 90 days in ambient laboratory conditions. Compressive strength tests (according to EN 12390-3) were carried out on the cylindrical samples, results of which are shown in *Table 3*. The concrete samples casted in the buckets were selected for the preparation of the RCAs. One bucket each for Mix 1 and Mix 2 were randomly chosen and the chunks were broken down first with a hand-driven point press hydraulic jack to about 30-35mm aggregates. The broken concrete chunks were then subjected to further size reduction with a jaw crusher. Care was taken in order to get a sizeable 8-20 mm fraction by sieving the broken aggregates after each passing through the crusher. Sieve sizes of 20 mm, 12.5 mm, 8 mm, 4 mm and 2 mm were used to separate the recycled aggregates into different fractions. Jaw crushers tend to produce high amounts of flaky or needle shaped aggregates (Gholizadeh et al.,2020) and therefore while operating the jaw crusher, the opening was reduced gradually from 35mm to 15mm. All the aggregate size fractions were stored in buckets with pouches of silica gel inside. The buckets were then closed and taped to make them air-tight to prevent carbonation.













| | | Dime | nsions | Compres | Specimen | |
|--------------------------|---|-------------|------------------|-----------|----------------|-------------------------------|
| Day 90 | | Height (mm) | Diameter (mm) | Load (kN) | Strength (MPa) | age at test date (days) |
| //c | 1 | 214.86 | 112.65 | 369.55 | 37.07 | 93 |
| × 1 /A W 50 | 2 | 213.51 | 113.65 | 404 | 39.82 | 93 |
| M II O | 3 | 209.14 | 113.08 | 380.63 | 37.9 | 93 |
| CE | 4 | 214.98 | 112.78 | 334.78 | 33.51 | 93 |
| .50 | 1 | 212.92 | 112.7 | 398.27 | 39.92 | 93 |
| x 2 //C 0 | 2 | 213.15 | 112.76 | 380.96 | 38.14 | 93 |
| Z _ Z | 3 | 213.66 | 112.53 | 311.19 | 31.28 | 93 |
| CEN | 4 | 212.94 | 112.57 | 354.43 | 35.61 | 93 |

Table 3: Compressive strength of cylindrical samples after 90 days.

4.2.3. Design of experimental variables

For this study, a number of variables have been defined and investigated. Temperature and duration of carbonation, CO_2 concentration and mix type of RCAs are the variables. Some constant parameters such as moisture condition and reactor pressure were kept within the labelling technique to keep it in line with previously generated technique by Gholizadeh et al., 2020. A detailed description of the carbonation variables/constants are shown in *Table 4*.

| Variables/Constants | Levels | Abbreviation | Description |
|-------------------------------|-----------------|--------------|---|
| Concrete mix type | Mix | Mix1/Mix2 | Denotes the type and number of concrete mix |
| Moisture condition of | Preconditioned | PC | The samples are stored in a climate chamber |
| the RCA | | | with 80% RH for at least 48 hours. The samples |
| | | | are taken out, weighed and directly put inside |
| | | | the reactor for carbonation. |
| Pressure | | *b | The pressure is kept ambient, so 1b |
| Temperature | 40°C/60°C/80°C | *°C | The temperature used for the particular |
| | | | carbonation experiment |
| Duration | 1h, 2h, 4h, 6h, | h | The time through which the carbonation |
| | 24h, 30h | | experiment has been carried on. |
| CO ₂ concentration | 50%/70%/100% | - | Denotes the concentration of CO ₂ used for |
| | | | carbonation. |













4.2.4. Experimental Design

The design of experiments was performed after careful consideration of the previous research findings at VITO with the aim of further modifying the experimental parameters to reach optimal carbonation conditions. The set of conducted experiments are shown in Table 5. Several series of experiments were conducted under variable carbonating parameters. The results derived from the first series influenced the setting of parameters for the second one and so on. The first two series of experiments were conducted at 40°C and 60°C keeping CO₂ concentration at 70% and RH at 50-60%. The duration of the experiments ranged from 1 to 30 hours. It is to be noted that the experiments done for 1 hour had lower relative humidity, the reason of which will be discussed in the consecutive section. Selected experiments from the first two series that provided satisfactory results were then repeated to see if the characterization values were repeatable. The next series of experiments were mainly repetitions based on the results generated from the first two series mainly looking into the water absorption and total carbon content of the carbonated RCAs. In order to gauge the effect of concentration of CO₂ used for carbonation, 100% CO₂ was used for the next series at 40°C, however this was found not very beneficial for the RCA properties. After converging in to the best experimental parameters at 40°C and 60°C, the CO₂ concentration was decreased to 50% to see if the other parameters hold and provide satisfactory results.

| Exp. | Moisture | Relative | Temperature | Pressure | Duration (hrs) | CO2 | Sample Label |
|------|-----------|----------|-------------|----------|------------------|-------|---------------------------|
| set | condition | humidity | | (bars) | | conc. | |
| 1 | PC | 50-60% | 40°C | 1b | 1/2/4/6/18/24/30 | 70% | M1/S9/PC/40C/70%/1b/2h |
| 2 | PC | 50-60% | 60°C | 1b | 1/2/4/6/18/24/30 | 70% | M1/S5/PC/60C/70%/1b/1h |
| 3 | PC | 50-60% | 40°C/60°C | 1b | 6/18/24 | 70% | Repetitions |
| 4 | PC | 50-60% | 40°C | 1b | 1/2/4/6/18/24 | 100% | M2/S11/PC/40C/100%/1b/24h |
| 5 | PC | 50-60% | 40°C | 1b | 24/30 | 50% | M1/S29/PC/40C/50%/1b/24h |
| 6 | PC | 50-60% | 60°C | 1b | 4/6 | 50% | M2/S35/PC/60C/50%/1b/4h |













4.2.5. Carbonation procedure

All the samples undergoing carbonation were preconditioned in a climate chamber at 80% RH for at least 48 hours. After preconditioning, one sample each (500-550 g) from Mix 1 and Mix 2 were spread into a mono-layer in nylon trays and put into a 245 liters Finec BVBA reactor. The reactor is equipped with a temperature and RH indicator which helped in visualization and control. Another nylon tray was loaded with about 700 g of NaBr salt and a thin water layer was made on top. Care was taken that the solution always remained super-saturated as to absorb the excess water vapor generated during carbonation reaction and general evaporation from the pre-conditioned RCAs. The salt tray is placed next to the trays containing the aggregates within the reactor and the reactor is closed and sealed with bolts.

The reactor is then flushed with a $CO_2(70\%)/N_2(30\%)$ mixture for 1 hour to set the reactor atmosphere at 70% CO₂ needed according to the experimental design. The reactor atmosphere was changed to 100% CO2 or 50% CO2/50% N2 in the subsequent experiment sets as described in Table 6. An over-pressure of 0,05 bars was set using the reactor controls, thereby generating a flow of gas from the capsule into the reactor. Due to the initial unavailability of a CO₂ meter within the reactor, the flushing flowrate of 9.5-10 liters/min for a duration 1 hour was chosen to ensure similar reaction atmosphere and was kept constant for all the experiments conducted. The flowrate was measured by a flowmeter placed in the gas inlet line to the reactor. The reactor atmosphere was later tested with the help of a CO_2 meter to see if the above-described flushing procedure was adequate to generate favorable reaction conditions. Similar flushing procedure was followed while working with CO₂ concentrations of 100% or 50%.

After the flushing procedure is completed, the outlet valve of the reactor is closed, and the over-pressure is reduced to zero thereby keeping atmospheric pressure conditions within the reactor. The gas inlet to the reactor is changed to the 100% CO₂ cylinder to replenish the CO₂ utilized within the reactor due to carbonation. The reactor settings allowed the replenishment of CO₂ once the reactor pressure dropped to 0.95 bars. In this way, the reactor atmosphere is always kept at the desired CO₂ concentration and carbonation is allowed to proceed for the desired time duration. After carbonation, the aggregates are taken out from the reactor and dried in a ventilated oven at 80°C for 24 hours for complete water removal.

It should be noted that the 1 hour duration experiments signify only the first hour after the flushing procedure is started, or in other words the samples are also taken out of the reactor after the flushing procedure was completed. This means the CO₂ concentration within the













reactor rises from normal atmospheric levels to 70% in exactly 60 mins, which was later quantified with a CO_2 meter present inside the reactor. However, while using 100% CO_2 , the reactor atmosphere became 100% at around 20 minutes. The reactor temperature almost reaches the desired value even with flushing, however RH decreases considerably (20-35%) due to the water vapor escaping through the reactor outlet and the gas in the reactor constantly being replaced with a dry gas mixture. The RH stabilizes again after about 30 mins after the flushing is completed (1.5 hours in the experiment).

4.2.6. Test procedures

Various characterization tests are made on the carbonated RCAs in order to understand the evolution of microstructure, mineralogy and change in physical characteristics based on the carbonation parameters. For this, a representative sample (around 115-125 g) was taken from the carbonated RCA fraction by quartering and milled in a two-step process to generate a fine powder (d90<170 μ m), which was used for Total Carbon (TC) and XRD tests. The rest of the sample was used for the water absorption and density measurement test. At a later stage of the research program, when there was a better understanding of the optimal carbonation parameters, 3-4 carbonated aggregates were randomly selected from certain batches for SEM characterization. All dried carbonated samples were stored under air-tight conditions – buckets with pouches of silica gel inside, closed and taped around the lid for better isolation.

4.2.6.1. Water absorption, Particle Density and Porosity

Determination of water absorption capacity and particle densities were carried based on the standard EN 1097-6:2013. The carbonated RCA specimens were put in pycnometers and soaked in water for 24 hours. The next day, the pycnometers were gently tilted and rolled to let all the entrapped air to escape and water is filled up to the mark. Subsequently, the weights of aggregates in water with pycnometer (M2), water-filled pycnometer alone (M3) and saturated surface dried (SSD) aggregates (M1) are determined. The aggregates were dried at 110°C for 24 hours and weighed again (M4). Using the weights M1-M4, apparent particle density, oven-dried particle density, SSD particle density and water absorption at 24 hours are determined.













It was deemed imperative to determine the porosity of the aggregates as it has a significant role in water absorption, freeze-thaw resistance and drying shrinkage of concrete (Gholizadeh et al., 2020). As there are no unanimous agreement on the definition of cement porosity, a similar approach as Gholizadeh et al., 2020 was taken where:

Porosity (p) = $\frac{p_a}{p_{od}}$ - 1, where p_a and p_{od} are the apparent particle density and oven-dried density of the aggregates respectively.

4.2.6.2. Mineralogical analysis

The representative sample from the carbonated RCA fraction was quartered into four parts with each part weighing approximately 30 g. These fractions were then milled in two consecutive steps to obtain finely milled powder for TC and XRD characterizations. First, the aggregates were milled with a Retsch DM 200 disk mill to generate a particle size of <1 mm. Then the aggregates were fine milled in a Retsch Planetary PM 200 ball mill to reach a particle size of $d50 < 100 \mu$ m. The samples are then labelled, put into zip lock bags and vacuum sealed before sending them for testing.

Total Carbon Analysis was done with Analytik Jena Multi EA4000 fully automated analyzer as per EN 15936:2012. The samples were burned at 1300°C in an oxygen-rich environment where an infra-red (IR) detector detects the CO₂ formed and then converted to the percentage of carbon (TC). In a later stage of the research, a few samples were tested for total inorganic carbon (TIC) where the sample is hydrolyzed by H_3PO_4 and the mixture is heated and stirred, forming CO₂ gas. This CO₂ is then detected by the IR detector and is subsequently converted into a percentage of carbon.

XRD was done with a 3rd generation Malvern Panalytical Empyrean multi-purpose diffractometer with a Cobalt tube, operating with a 0.013° step size and a scanning speed of 0.067335°/s. From the generated diffractograms, the common naturally occurring three crystal forms of calcium carbonate i.e., calcite, vaterite and aragonite are detected and quantified alongside dolomite and portlandite with the help of Rietveld Analysis. These phases were studied in detail to better understand the evolution of minerology of the carbonated RCAs and the effect of different parameters on the phase quantities.













4.2.6.3. Microstructural investigation

The randomly selected aggregates from the RCA fractions having outstanding characterization results were stored in a N₂ atmosphere, after which they were dry-cut using a fine saw. The cut samples were then placed down-faced inside impregnation cups and filled with a resin-hardener mixture. The impregnated samples are cured for 24 hours and the polished with the help of a LARGO disk polisher down to 1 μ m diamond powder grit size. The SEM was carried out by a FEI NOVA NANOSEM 450 with EDX analyzer BRUKER QANTAX 200 with SDD detector. From the results generated, a holistic view about the changes in surface porosity and the effect of carbonation on the un-hydrated cement grains was derived. The evolution of microstructure based on the improvement of the ITZ between the natural aggregate and the adhered mortar is studied along with quantifiable changes in the surface porosity.

Chapter 5: Results and Discussion

5.1. Water absorption and porosity results

5.1.1. Effect of temperature and carbonation duration on water absorption and porosity of RCAs

Experiment set 1:

Water absorption results carried out with the process described earlier was able to quantify considerable changes in porosity and absorption values (percentages) of the carbonated RCAs when compared to non-carbonated control samples. *Figure 10* showcases clear trends of the evolution of water absorption by Mix 1 and Mix 2 RCAs with time at 40°C and 70% CO₂ concentration. Water absorption of both mixes decrease considerably from 7.41% and 6.31% for control samples to 5.33 and 4.8% after 30 hours respectively. However, the lowest absorption values were found after 24 hours at 5.26% and 4.64% respectively. This slight increase of water absorption at 30 hours can be due to different amounts of cement paste on the RCAs as every sub-sample subjected to carbonation are slightly different from one another.













The 24 hour experiments result in 28.04% and 27.61% decrease in water absorption for Mix 1 and Mix 2 respectively. The decrease of water absorption for both mixes are due to the formation of $CaCO_3$ on the surface of the aggregates, thereby aiding the transformation to a less porous microstructure. The porosity values along with apparent particle densities and oven-dried densities and water absorption of Experiment set 1 can be found in *Table 6*.



Figure 10: Water absorption of RCAs at 40°C with 70% CO2 concentration (Exp. Set 1).

| Sample | Apparent Oven-dried particle density density (kg/m ³) | | Water absorption | Porosity (%) |
|--------------------------|--|------|------------------|--------------|
| | 2646 | 2227 | 6.67 | 47.46 |
| M1/S4/PC/40C/70%/1b/1h | 2616 | 2227 | 6.67 | 17.46 |
| M2/S5/PC/40C/70%/1b/1h | 2595 | 2248 | 5.94 | 15.41 |
| M1/S9/PC/40C/70%/1b/2h | 2590 | 2200 | 6.84 | 17.74 |
| M2/S14/PC/40C/70%/1b/2h | 2854 | 2444 | 5.87 | 16.75 |
| M1/S3/PC/40C/70%/1b/4h | 2586 | 2222 | 6.31 | 16.33 |
| M2/S13/PC/40C/70%/1b/4h | 2560 | 2238 | 5.61 | 14.37 |
| M1/S12/PC/40C/70%/1b/6h | 2598 | 2230 | 6.35 | 16.51 |
| M2/S9/PC/40C/70%/1b/6h | 2591 | 2271 | 5.43 | 14.09 |
| M1/S19/PC/40C/70%/1b/18h | 2606 | 2255 | 5.98 | 15.59 |

Table 6: Water absorption, Porosity values of RCA along with related densities.(Exp. set 1).













| M2/S17/PC/40C/70%/1b/18h | 2609 | 2282 | 5.48 | 14.30 |
|--------------------------|------|------|------|-------|
| M1/S1/PC/40C/70%/1b/24h | 2588 | 2278 | 5.26 | 13.61 |
| M2/S2/PC/40C/70%/1b/24h | 2587 | 2310 | 4.64 | 12.02 |
| M1/S6/PC/40C/70%/1b/30h | 2560 | 2252 | 5.33 | 13.65 |
| M2/S6/PC/40C/70%/1b/30h | 2596 | 2304 | 4.88 | 12.67 |

Initial porosity values for Mix 1 and 2 RCAs were found to be 19.09% and 16.59% respectively. Porosity can be seen decreasing along with water absorption due to the formation of calcium carbonate as a result of conversion of portlandite and deposition of the same within the microstructure of the aggregates. At 24 hours carbonation, the porosity of RCAs decreased by 28.7% and 27.54% for Mix 1 and 2 respectively. The decrement stabilizes after 24 hours and further duration of experiments do not yield marked improvements. For particle density, carbonation after 24 hours yielded an increment of 3.18% and 3.58% for Mix 1 and Mix 2 respectively.

Experiment set 2:

Accelerated carbonation at 60°C yields lower water absorption values at lower experimental durations but the effect weans out at longer times. Figure 11 shows the evolution of water absorption for both mixes. Both Mix 1 and 2 have a marked drop of water absorption after the first hour of carbonation. It might be recalled that one hour experiments were essentially flushing with CO₂, starting from atmospheric concentration to 70% (in experiment set 2). The relative humidity is also generally lower (30-40%) at 60°C during most of the first hour experiments, when compared to experiment set 1. The exact time when the reactor reaches 70% CO₂ concentration will be determined in the future when a CO₂ meter will be attached to analyze the reactor atmosphere. Nonetheless, the higher temperature results faster dissolution of portlandite and conversion into calcium carbonate. In addition, the water produced as a reaction product has faster evaporation rates from the pore system due to higher temperatures and lower relative humidity within the reactor. This results in water absorption of 5.44% and 5.34% or a decrease of 25.58% and 16.69% for Mix 1 and 2 respectively for a 1 hour experiment. This fast decrement of water absorption remains true until the 6 hour experiments, and by the 24 and 30 hour experiments, the values of water absorption and porosities are similar to the experiments carried out at 40°C. This may be attributed to the initial faster deposition rates of calcium carbonate and formation of a layer on the periphery of the aggregates, thereby reducing the diffusion of CO_2 into the deeper layers. Porosity after 6 hours of carbonation













decreased by 23.10% and 22.66% for Mix 1 and 2 respectively. The water absorption, density and porosity values can be found in Table 7.



Figure 11: Water absorption of RCAs at 60°C with 70% CO2 concentration (Exp. Set 2).

| Sample | Apparent | Oven-dried | Water absorption | Porosity (%) |
|--------------------------|------------------|-----------------|------------------|--------------|
| | particle density | density (kg/m³) | | |
| | (kg/m³) | | | |
| M1/S5/PC/60C/70%/1b/1h | 2602 | 2279 | 5.44 | 14.15 |
| M2/S7/PC/60C/70%/1b/1h | 2587 | 2272 | 5.34 | 13.83 |
| M1/S10/PC/60C/70%/1b/2h | 2611 | 2266 | 5.83 | 15.22 |
| M2/S3/PC/60C/70%/1b/2h | 2598 | 2284 | 5.28 | 13.73 |
| M1/S11/PC/60C/70%/1b/4h | 2605 | 2258 | 5.88 | 15.34 |
| M2/S10/PC/60C/70%/1b/4h | 2597 | 2309 | 4.80 | 12.48 |
| M1/S7/PC/60C/70%/1b/6h | 2600 | 2267 | 5.64 | 14.68 |
| M2/S4/PC/60C/70%/1b/6h | 2608 | 2312 | 4.91 | 12.83 |
| M1/S18/PC/60C/70%/1b/18h | 2623 | 2284 | 5.65 | 14.82 |
| M2/S20/PC/60C/70%/1b/18h | 2621 | 2324 | 4.86 | 12.74 |
| M1/S26/PC/60C/70%/1b/24h | 2604 | 2262 | 5.79 | 15.09 |
| M2/S18/PC/60C/70%/1b/24h | 2597 | 2305 | 4.88 | 12.67 |
| M1/S17/PC/60C/70%/1b/30h | 2604 | 2281 | 5.43 | 14.14 |
| M2/S25/PC/60C/70%/1b/30h | 2606 | 2317 | 4.79 | 12.50 |
| | | | | |

Table 7: Water absorption, Porosity values of RCA along with related densities.(Exp. set 2).







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Experiment set 3:

Looking into the water absorption results of the previous two series of experiments, it can be inferred that carbonation at 40°C yields the best results at 24 hours while at 60°C, the results are best at 6 hours with little change afterwards. Thus it can be said that carbonation at higher temperatures can bring relatively similar improvements in the durability properties of RCA but at a lower time. Of course, higher temperatures would mean higher operating costs during upscaling, so the optimal carbonation parameters would be a combination of temperature and duration and detailed Life Cycle Assessment studies are needed for determining them.

In the light of the best time durations perceived in experiment sets 1 and 2, some experiments were repeated in order to get an idea about the reproducibility of the same. For experiments at 40°C; 6, 18 and 24 hour experiments were repeated while for 60°C experiments; 6 and 18 hour experiments were looked into. The results have been depicted by *Figures 12, 13, 14 and 15* where R1 refers to 'Repetition 1'.



Figure 12 Water absorption of Mix1 RCAs at 40°C with 70% CO2 concentration (Exp. Set 3















Figure 13: Water absorption of Mix2 RCAs at 40°C with 70% CO2 concentration (Exp. Set 3).

Before diving into the repeatability of the data, it should be understood that although care has been taken to work with representative subsamples by properly quartering it, the samples themselves vary in the quantity of cement paste adhered to the aggregates. Therefore, while we can visualize proximities of data points, perfect reproducibility cannot be gauged due to the unavailability of exact replication of samples.

Figures 12 and 13 shows the initial and repeated experimental data points in terms of water absorption at 40°C for Mix 1 and 2 respectively. For Mix 1, values at 6, 18 and 24 hours vary by -4.7%, 5.01% and -11.6% while for Mix 2, the variations are -6.26%, 2.18% and -21.55% respectively.

Figure 14 and 15 shows the data for Mix 1 and 2 at 60°C with experiments repeated at 6 and 18 hours. For Mix 1, values at 6 and 18 hours vary by -2.8% and -1.23%; while for Mix 2, the variations are -12.62% and 1.44% respectively. These values show good conformity despite the variation of sample composition. Further repetitions of these experiments would be needed to generate better confidence over the accelerated carbonation temperature and durations.

Porosity measurements along with densities and water absorption values of the repeated experiments are given by *Table 8*.













| Sample | Apparent particle density | Oven-dried density (kg/m³) | Water absorption | Porosity (%) |
|--------------------------|------------------------------|-------------------------------|------------------|--------------|
| | (kg/m³) | | | |
| M1/S30/PC/40C/70%/1b/6h | 2607 | 2222 | 6.64 | 17.31 |
| M2/S30/PC/40C/70%/1b/6h | 2613 | 2271 | 5.77 | 15.08 |
| M1/S32/PC/40C/70%/1b/18h | 2604 | 2268 | 5.68 | 14.80 |
| M2/S36/PC/40C/70%/1b/18h | 2585 | 2269 | 5.36 | 13.88 |
| M1/S31/PC/40C/70%/1b/24h | 2596 | 2253 | 5.87 | 15.24 |
| M2/S34/PC/40C/70%/1b/24h | 2608 | 2297 | 5.19 | 13.55 |
| M1/S28/PC/60C/70%/1b/6h | 2603 | 2261 | 5.80 | 15.10 |
| M2/S29/PC/60C/70%/1b/6h | 2614 | 2283 | 5.53 | 14.47 |
| M1/S27/PC/60C/70%/1b/18h | 2599 | 2262 | 5.72 | 14.89 |
| M2/S37/PC/60C/70%/1b/18h | 2604 | 2315 | 4.79 | 12.48 |

Table 8: Water absorption, Porosity values of RCA along with related densities.(Exp. set 3).



Figure 14: Water absorption of Mix1 RCAs at 60°C with 70% CO2 concentration (Exp. Set 3).















Figure 15: Water absorption of Mix2 RCAs at 60°C with 70% CO2 concentration (Exp. Set 3).

5.1.2. Effect of CO₂ concentration on water absorption and porosity

Experiment sets 4,5 and 6:

In order to gauge the dependence of water absorption and porosity on CO_2 concentration in the reactor atmosphere, gas mixtures of 100% and 50% CO_2 were used in the subsequent experiments. Experiment set 4 used 100% CO_2 at 40°C to compare the changes in water absorption and porosity with 70% while experiment set 5 used 50% CO_2 at 40°C. *Figures 16 and 17* depicts the evolution of water absorption values. It can be inferred that 100% CO_2 produces slightly better water absorption values along the curve when compare to 70% CO_2 . This slight betterment of water absorption might not be a good reason to upscale with 100% CO_2 as this will entail higher costs of refining CO_2 coming from point sources of emission.

It is interesting to see that even using 50% CO_2 concentration, comparable values of water absorption can be reached within the same duration of experiments. For Mix 1, the water absorption after 30 hour experiments at 40°C were 5.35% and 5.33% for 50 and 70% CO_2 concentrations respectively. For Mix 2, the values were 4.87% and 4.88%.













This trend continues at 4 hour experiment at 60° C (Experiment set 6) as well, as seen from *Figure 18*. Here only 50% and 70% CO₂ have been compared. The water absorption of Mix 1 and Mix 2 were 6.04% and 4.78% at 50% CO₂ and 5.88% and 4.80% at 70% CO₂ respectively. The values at 6 hours were 5.64% and 4.91% at 70% CO₂ and 5.86% and 5.70% at 50% CO₂ for Mix 1 and 2 respectively. The variation between the water absorption values of Mix 2 were considerably high in this case, so these values can be an outlier in the graph. Repetitions should be made in the future to ascertain the water absorption at this temperature.

The values of water absorption at 50% CO_2 particularly impressive as this approaches the typical concentration of CO_2 being emitted in flue gases from cement industries (20% CO_2). However, more experiments and repetitions are required at 50% CO_2 before decreasing the concentration further.

Only one experiment was carried out at 60°C and 100% CO₂ concentration. It was decided not to carry out more of the series as it was deemed unnecessary, given the little benefits and potential increment of costs due to higher temperatures. The water absorption results were 5.95% and 5.11% for Mix 1 and 2 respectively, both of which are slightly higher than the 70% CO₂ concentration series. The porosity of the aggregates decreased in accordance with the changes in density and these data has been summarized in *Table 9*.



Figure 16: Water absorption of Mix 1 RCAs at 40°C with 50, 70 and 100% CO2 concentration (Exp. Set 4&5).













| Sample | Apparent | Oven-dried | Water absorption | Porosity (%) |
|---------------------------|------------------|-----------------|------------------|--------------|
| | particle density | density (kg/m³) | | |
| | (kg/m³) | | | |
| M1/S24/PC/40C/100%/1b/1h | 2573 | 2207 | 6.43 | 16.57 |
| M2/S19/PC/40C/100%/1b/1h | 2577 | 2236 | 5.91 | 15.25 |
| M1/S25/PC/40C/100%/1b/2h | 2597 | 2240 | 6.12 | 15.91 |
| M2/S21/PC/40C/100%/1b/2h | 2596 | 2252 | 5.87 | 15.25 |
| M1/S22/PC/40C/100%/1b/4h | 2584 | 2232 | 6.10 | 15.77 |
| M2/S22/PC/40C/100%/1b/4h | 2575 | 2242 | 5.75 | 14.82 |
| M1/S23/PC/40C/100%/1b/6h | 2593 | 2231 | 6.24 | 16.18 |
| M2/S23/PC/40C/100%/1b/6h | 2602 | 2272 | 5.59 | 14.56 |
| M1/S14/PC/40C/100%/1b/24h | 2578 | 2289 | 4.90 | 12.64 |
| M2/S11/PC/40C/100%/1b/24h | 2590 | 2304 | 4.78 | 12.39 |
| M1/S29/PC/40C/50%/1b/24h | 2611 | 2273 | 5.68 | 14.84 |
| M2/S26/PC/40C/50%/1b/24h | 2594 | 2282 | 5.26 | 13.66 |
| M1/S36/PC/40C/50%/1b/30h | 2584 | 2269 | 5.35 | 13.84 |
| M2/S28/PC/40C/50%/1b/30h | 2580 | 2292 | 4.87 | 12.56 |
| M1/S38/PC/60C/50%/1b/4h | 2578 | 2230 | 6.04 | 15.58 |
| M2/S35/PC/60C/50%/1b/4h | 2586 | 2301 | 4.78 | 12.37 |
| M1/S21/PC/60C/50%/1b/6h | 2597 | 2253 | 5.86 | 15.23 |
| M2/S32/PC/60C/50%/1b/6h | 2609 | 2271 | 5.70 | 14.88 |
| M1/S20/PC/60C/100%/1b/6h | 2597 | 2250 | 5.95 | 15.46 |
| M2/S16/PC/60C/100%/1b/6h | 2588 | 2285 | 5.11 | 13.24 |

Table 9: Water absorption, Porosity values of RCA along with related densities. (Exp. set 4,5,6).











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Figure 17: Water absorption of Mix 2 RCAs at 40°C with 50, 70 and 100% CO2 concentration (Exp. Set 4&5).



Figure 18: Water absorption of Mix 1&2 RCAs at 60°C with 50 and 70% CO2 concentration (Exp. Set 6).













5.2. Mineralogical investigation

5.2.1. Total Carbon Content

Total carbon content was determined in order to see the evolution carbon uptake during the process of accelerated carbonation. The general idea was to see if there is a gradual increasing trend in total carbon content with longer experiment times and the effect of temperature and CO_2 concentration on it. Total carbon content will also give an idea about the carbon sequestering capability by the RCAs under the carbonation conditions carried out in this work. *Figure 19 and 20* shows the evolution of total carbon content for Mix 1 and 2 as a function of temperatures 40°C and 60°C respectively.



Figure 19: Evolution of carbon content of Mix 1 and Mix 2 at 40°C.













Figure 20: Evolution of carbon content of Mix 1 and Mix 2 at 60°C.

Total carbon content of Mix 1 and 2 are seen to have an increasing trend at both 40°C and 60°C. The initial carbon content for Mix 1 and Mix 2 RCAs were 1.2% and 1.5% respectively. At 40°C, the carbon content dips a bit in the first hour and then progressively rises for longer durations. The initial dip can be associated to the heterogeneity of the samples with different amounts of adhered mortar and therefore, different amounts of carbonatable materials. The overall trend shows an increase of carbon content, which is logical for the experiments carried out and at 30 hours, the carbon content becomes 2.16% and 2.15% for Mix 1 and 2 respectively. At 60°C, the carbon content also showcases similar increasing trends with values reaching 2.07% and 2.6% for Mix 1 and 2 respectively at a duration of 18 hours. Judging from the values, it can be inferred that carbonation at higher temperatures tend to produce similar to marginally better values at similar carbonation durations. It can be interesting to determine the adhered mortar content of the RCAs in the future and then subjecting them to carbonation, in order to determine the effect of temperature on carbon content in a better way.













Figure 21: Evolution of carbon content of Mix 1 at different CO₂ concentrations.

It was imperative to determine the effect of CO_2 concentration on the carbon content trends to get an idea about the feasibility to use point source of CO_2 emissions directly into the accelerated carbonation. Carbon content of samples were tested for different experimental durations performed at 50%, 70% and 100% CO2 concentrations. *Figures 21 and 22* showcases the trends of Mix 1 and Mix 2 respectively.













Figure 22: Evolution of carbon content of Mix 2 at different CO₂ concentrations.

From *Figure 21* it can be seen that using 100% and 50% CO2 concentrations provide similar results to the initial experiments carried out with 70%. At 24 hours, the carbon contents for Mix 1 are 1.76%, 2.18% and 2.12% for 70%, 100% and 50% respectively. In this case, 100% and 50% CO2 provide very similar values and higher than that of 70%. At 30 hours duration, although 70% CO2 provides a better value than 50%, it can be attributed to the heterogeneity of the samples subjected to carbonation.

Similar trends were encountered in case of Mix 2, where the usage of 100% CO2 and 50% CO2 had no marked effect on the final carbon content of the samples. Carbonation at 30 hours resulted in total carbon content of 1.99% and 2.15% for 50 and 100% CO2 respectively. This shows that even with lower concentrations of CO2, similar levels of carbon sequestration can be achieved through accelerated carbonation. This is a good start towards achieving good results with concentrations similar to point CO2 sources in the industries and will make way for simpler upscaling processes.













5.2.2. XRD Analysis

When it comes to understanding the underlying minerology of the samples, XRD is a powerful tool which can provide accurate analysis. XRD measurements were done on uncarbonated and carbonated RCAs to gauge the evolution of the crystalline phases with respect to various carbonation conditions. The carbonatable phases of hardened cement paste are the calcium and magnesium bearing hydration products such as portlandite, C-S-H, Ettringite and AFm phases. The XRD curves generated from the non-carbonated samples are presented below.



Figure 23: Mix 1 non-carbonated sample composition.













Figure 24: Mix 2 non-carbonated sample composition.

From the above figures it can be seen that Mix 2 has higher levels of portlandite than Mix 1, which is logical as pure portlandite clinker cement CEM I was used in that mix. The curves generated from XRD were similar in nature as both mixes had the highest composition of quartz, which in turn was generated from the siliceous natural aggregates. From this point, carbonated samples from all experimental sets were prepared and analyzed. The XRD curves from the experiment labels M1/S1/PC/40C/1b/24h and M2/S9/PC/40C/1b/6h are presented below.

















Figure 25: Mix 1 carbonated sample composition.



Figure 26: Mix 2 carbonated sample composition.

While comparing the composition of the non-carbonated and the carbonated samples, we can see a decrease in the portlandite concentration in both Mix 1 and Mix 2. This is in line with the theory of carbonation, where portlandite is generally the first phase to be carbonated. The concentration of calcite is seen to increase in case of Mix 1 whereas in case of Mix 2, the trend













is seen to be decreasing. This can be due to an increased mortar content in the carbonated Mix 2 sample when compared to the control sample. It is plausible that the sample had more concentration of calcite to begin with. It can also be seen that the curves of the non-carbonated and the carbonated samples are similar in nature, only after rigorous analysis and refinements were the relevant peaks found and taken into account.

To find a trend that explains the effect of carbonation on the minerology of the samples, it became plausible to look into the concentrations of the carbonatable and the carbonated phases. In order to simplify our understanding, portlandite was chosen to be the carbonatable material and the calcite, aragonite and vaterite were chosen as the carbonated phases. The dolomite phase was excluded from the calculations as there was a considerable amount of dolomite in the non-carbonated RCAs and it was highly unlikely that dolomite was produced as a result of accelerated carbonation. The carbonatable phases/carbonate phases ratio was then plotted against time where the other parameters such as temperature and CO₂ concentration were varied. *Figure 27 and 28* depicts the trends of Mix 1 and 2 at 40°C/60°C and 70% CO₂ concentration.



Figure 27: Portlandite / Carbonates evolution for Mix 1 and 2 at 40°C and 70% CO₂.













Figure 28: Portlandite / Carbonates evolution for Mix 1 and 2 at 60°C and 70% CO₂.

The evolution of the portlandite/carbonates ratio follow a downward trend for both Mix 1 and 2 and at both temperatures of 40 and 60°C. This is encouraging as this proves that the portlandite concentration is decreasing with increase of carbonation time and stable carbonates are deposited on the surface of the aggregates, thereby reducing their porosity and water absorption capacity. This is also in line with the evolution of the water absorption and porosity values exhibited by the carbonated aggregates. The deposition of the carbonates also helps in increasing the particle density of the aggregates.

Analysis was carried out to determine whether the concentration of the CO_2 poses a significant impact on the evolution of minerology within the carbonated aggregates. The influence of CO_2 concentration on the portlandite/carbonates evolution are depicted by *Figures 29 and 30* respectively. For both mixes, it can be seen that the concentration of CO_2 is not a determining factor in mineralogical evolution and similar trends with close values can be achieved even with lower concentrations. This is in line with the water absorption trends which strengthens the argument of using lesser CO_2 concentrations in the future, which will bring the system closer to direct industrial utilization.











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Figure 29: Portlandite / Carbonates evolution for Mix 1 at 40°C, at 50, 70 and 100% CO2.



Figure 30: Portlandite / Carbonates evolution for Mix 2 at 40°C, at 50, 70 and 100% CO₂.













5.3. CO₂ sequestering potential of RCAs

While analyzing the evolution of the total carbon content of the carbonated RCAs, it is interesting to investigate the carbon sequestering potential through the deployed carbonation procedure. For a demonstrative calculation, one experimental label from each of the two mixes were taken at 40°C and 24 hours experimental duration. The respective total carbon content of these two labels were:

- i. M1/S14/PC/40C/100%/1b/24h 2.18 (m/m % C ds)
- ii. M2/S11/PC/40C/100%/1b/24h 2.27 (m/m % C ds)

For the non-carbonated samples, the total carbon values for Mix 1 and 2 were 1.21 and 1.50 respectively. To determine the percentage of CO2 sequestered, the atomic mass ratio of carbon and carbon di-oxide was multiplied to the difference of the total carbon content of the carbonated and non-carbonated RCAs.

The atomic mass ratio CO_2/C gives a value of 44/12 = 3.66

The results are tabulated below:

| Label | Total | Difference | CO ₂ /C ratio | Percentage of | Amount of |
|---------------------------|--------|--------------|--------------------------|----------------|-------------|
| | carbon | with control | | CO₂ | CO2 |
| | | samples | | sequestered | sequestered |
| | | | | | (grams/kg) |
| M1/S14/PC/40C/100%/1b/24h | 2.18 | 2.18- | 44/12=3.66 | 3.66*0.97=3.55 | 35.50 |
| | | 1.21=0.97 | | | |
| M2/S11/PC/40C/100%/1b/24h | 2.27 | 2.27- | 44/12=3.66 | 3.66*0.77=2.81 | 28.10 |
| | | 1.50=0.77 | | | |

Table 10: CO₂ sequestration potential of carbonated RCAs.

5.4. Microstructural investigations

Scanning Electron Microscopy was used to investigate the evolution of microstructure of the carbonated RCAs when compared to the microstructure of the non-carbonated aggregates. The image of a non-carbonated aggregate sample is depicted in *Figure 31*.















From the figure the portlandite phase at the interfacial transition zone (ITZ) between the aggregate and the adhered mortar can be identified. Since Mix 1 was prepared with CEM III, slag particles can be identified in the image as well. The matrix texture shows no signs of carbonation.

These attributes are then compared to a carbonated aggregate sample which is depicted by *Figure 32*.



Figure 32: Carbonated (40°C/24h) aggregate sample of Mix 1.

Carbonation of recycled aggregates changes the texture of the matrix through the production of carbonation products. It is evident from *Figure 32* that the portlandite at the ITZ is depleted due to carbonation and deposited as calcium carbonates. The (cloudy texture) in the image are the carbonated locations.

There have been instances of the presence of dark rims around partially hydrated cement grains as visible in *Figure 32*. This is due to the decalcification process of C-S-H during carbonation,













which in turn can transform into silica gel upon complete carbonation (Gholizadeh-Vayghan et al., 2020). The carbonation reaction generates water which can facilitate the hydration of slow-hydrating cement components such as C_2S . Literature suggests that C_2S can undergo fast carbonation, sequester considerable amounts of CO_2 in the process while undergoing large volumetric expansion (Liu et al., 2019).

There have been indications of outward transportation of Ca from the inner carbonating parts of the RCAs and densification of the surface, thereby reducing the surface porosity (Gholizadeh-Vayghan et al., 2020). It can be logically assumed that this mechanism can be more relevant during high-pressure accelerating carbonation, nevertheless this process was also encountered to a lesser extent in ambient pressure carbonation reactions. Considering the water absorption and porosity values of the carbonated RCAs, it can be assumed that this may have happened in these set of experiments as well. Unfortunately, this could not be determined through backscattered images due to the unavailability of RCA edges during sample preparation.

Another important aspect is the role of reactor relative humidity on the transport of Ca-rich pore solution on to the surface of RCAs. There have been instances of liquid run-off from the RCA surfaces and accumulation at the bottom of the reactor which appeared to be milky white. Although the reactor RH was maintained in the range of 40-70%, it can be possible that the salt solution inside the reactor was saturated at times, which led to this result. In the case of inefficient evaporation of reaction water and liquid run-off, the calcium cannot deposit on the surface of the RCAs and can lead to the increase of porosity. Thus, optimal maintenance of reactor RH is absolutely important to achieve best possible results in the evolution of RCA microstructure.

Chapter 6: Conclusions and Recommendations

6.1. Main conclusions

The main aim of this study was to investigate the direct accelerated carbonation parameters deployed by researchers and improve on them. Various factors such as reaction temperature, experiment duration and CO_2 concentration were looked into and optimal conditions were derived. It also aimed at approaching real-world upscaling conditions where it would be













plausible to use RCAs in high-grade applications on a larger scale. In the light of these aims, the following general conclusions can be derived:

- a. Carbonation of RCAs in ambient pressure conditions is possible with optimal control of operation parameters and can generate good values of decreased water absorption. Carbonation at 40°C and 70% CO₂ for 24 hours resulted into 25% reduction in water absorption capacity with the best results yielding absorption values of less than 5%.
- b. Carbonation of RCAs lead to decrease of porosity by 26-28% and an increase in particle density by 3-3.5%.
- c. Carbonation reaction at 60°C can generate similar values of water absorption and porosity at much shorter time durations. There was a good correlation between the values at 40°C for 24 hours and the values at 60°C for 6 hours.
- d. Carbonation at 100% CO₂ produced similar to slightly better results than 70% CO₂ and was not deemed absolutely necessary, considering the added purification costs while upscaling the process. On the other hand, preliminary results from the 50% CO₂ experiments produced very similar results to 70% CO₂ and this can be seen as a major way forward to approach similar concentrations as industrial point sources.
- e. A steady increase on the total carbon content was found while characterizing the RCAs. This shows that CO₂ has been sequestered within the RCA as a result of the carbonation reaction. Through calculations it was found out that around 35 grams of CO₂ was sequestered per kilogram of recycled aggregates.
- f. XRD results showed that there was a considerable portlandite consumption as a result of carbonation and a corresponding increase of the calcite, vaterite and aragonite phases. The evolution of XRD results was determined through the ratio between the carbonatable and carbonate phases, which decreased over time showing the gradual depletion of carbonatable phases and increment of carbonate phases.
- g. Microstructural investigations through SEM were able to qualitatively detect changes in the microstructure of the RCAs as a result of carbonation. The depletion of portlandite from the ITZ was clearly seen as well as the decalcification of C-S-H around the semi-hydrated cement grains. Although images of the RCA edges were not available, it can be assumed that there was outward aqueous transportation of Ca and deposition of Ca-carbonates on the RCA surface, which led to a decrease in the porosity and increase in mechanical strength.













6.2. Recommendations

The results and the conclusions reached at the end of this thesis work can serve as an important basis for future recommendations for researchers to further improve and refine the conditions for accelerated carbonation. Starting from the optimal data points generating the best results, more iterations should be done to gauge the repeatability in a proper manner and will also provide a standard deviation of the results. The mortar content on the RCAs should be determined and steps should be taken to approach uniformity in mortar composition among different samples.

From the view of upscaling the process, future work should be around generating more data points at 50% CO₂ concentration. If the results support the conclusion of being at par with 70% CO₂, further reducing the concentration should be done in gradual steps. Experiments should be carried out at 30% CO₂, which will replicate actual industrial point sources of CO₂ and other parameters such as temperature and duration have to be optimized.

Another important recommendation would be the production of RAC with the help of the carbonated RCAs. This will help us gauge the actual performance of the RCAs when applied to high-grade applications. Factors such as workability, setting times and curing conditions will be crucial factors to investigate. After curing, the samples can be subjected to non-destructive and destructive testing to compare their mechanical properties with virgin concrete.

Lifecycle Analysis (LCA) can also be carried out to gauge the practicality and lucrativeness of the carbonation process to prepare RCAs suitable for high-grade applications. The location of the industries who will be the frontrunners of application of the accelerated carbonation process and the entire supply chain starting from the demolition sites to the final application of RAC should be considered while preparing an in-depth analysis. The operating parameters of the equipment and their respective efficiencies will also influence the overall impact of RCAs. Testing of operational carbonation parameters should also be done on RCAs produced from Mix 3 and 4 that were prepared at the beginning of the thesis work. Additionally, selectively demolished concrete samples can be sourced from demolition sites or recycling industries to test the performance of RCAs subjected to similar laboratory conditions. This will give a real-













world assessment of the optimal parameters developed and help in preparing RACs and upscaling of accelerated carbonation process.

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