DISSERTATION

ENGINEERING AND SCALING CEMENT-BASED CARBON STORAGE SYSTEMS

Submitted by

Dahl Winters

Department of Systems Engineering

In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Fall 2024

Doctoral Committee:

Advisor: Steven Simske

Thomas Bradley
Mazdak Arabi
Wade Troxell
Christopher Goemans

ABSTRACT

ENGINEERING AND SCALING CEMENT-BASED CARBON STORAGE SYSTEMS

This work is a contribution to the body of knowledge surrounding cement-based carbon storage systems, their engineering, and their scaling to meet the requirements of global sustainability in a relevant timeframe. Concrete is the most produced material by weight per year, surpassing water and all biomass we use per year, thus requiring by virtue of its total mass the largest share of total energy produced. Today, it is a source of net greenhouse gas emissions and environmental damage because of our appropriation of natural resources for its use in construction. However, it could serve as our largest land-based engineered sink for such emissions. Such potential is the focus of this work, addressed not only by experiments to improve the engineering of cement-based carbon storage systems, but also by suggested practices to achieve scale for such systems to have a beneficial impact on our economy and environment. The ubiquity of concrete means that cement-based carbon storage can also be ubiquitous, offering continued opportunities for carbon removal and sequestration within built materials. To engineer and scale the world's largest product into its largest engineered carbon sink, this research focuses on the use of biochar and calcium carbonate within structural and non-structural concrete uses, such as tetrapods: structures offering the benefits of reduced sand mining, protections against sea level rise, and enabling cement industry decarbonization. The results demonstrated that 4 wt% biochar with 1.5 wt% $CaCO_3$ can replace cement for carbon storage while maintaining sufficient compressive strength. Along with the use of 30 wt% biochar as aggregate, 100,000 10-tonne tetrapods could sequester 1 million tonnes of CO_2. Over a year of global emissions, 40 Gt CO_2, could be stored in such stacked tetrapods within a land area smaller than Kuwait, 17,400 km^2. Thus, this work contributes to the engineering of systems with industrial significance capable of countering the effects of global warming at meaningful scales.

ACKNOWLEDGEMENTS

I wish to acknowledge my partner in life and work, Loren Winters, for his never-ending support and companionship, and to my other co-founders at TerraNexum, Oscar Quezada and Thomas Bogdan, for their unwavering commitment to the pursuit of sustainability despite the great challenges of such a pursuit. To all three for learning alongside me while inspiring the best from me - a level of dedication to a breadth of ceaseless inquiry, yet also the focused application of knowledge on the challenges that matter. Most importantly to my advisor, Dr. Steve Simske, and my colleague Dr. Kwaku Boakye, who never stopped believing in my work or found fault in my placement of the needs of others before my own and before the timely completion of this research. To have Dr. Simske as my advisor, easily one of my life's joys. Also to the Open Source Hardware Association (OSHWA), for seeing value in my work as an Open Hardware Trailblazer Fellow, and to the CSU Systems Engineering Department for a world-class program serving the needs of those like myself whose professions require the engineering of complex systems that are themselves embedded within larger contexts of other complex systems. To Drs. Bradley, Arabi, Troxell, and Goemans for their support as my graduate committee, and most especially to you, the reader. Your interest in this work given your reading of this, and hopefully your application both now and in the future of what is learned here, is the reason this work was worth my effort.

DEDICATION

To my friends, coworkers, and family members in all senses of the word who have come and gone, as well as to those I have yet to meet and the countless others I will never meet. I am grateful for sharing this time and space with you. Some deserve more honor than I can ever bestow for exemplifying the best of humanity. I'd need several lifetimes to fully pay my gratitude. To all fellow travelers through life, it's an honor for our worldlines to be so close. To share this journey and to know it for what it is.

The events of our lives that have happened and will happen will never happen again. Thank you for helping me to make this time count. This is the only block of time we will ever have in which to change our future for the better. Some of us will work to live, others will live to work. Others like me will take a step back and ask what more there might be. With awareness comes curiosity, a drive to explore. But always to be a part of something shared.

I dedicate my work to everyone, and to the future. With the hope that it is a better future than the present or the past. If not from anything I do, then from the work I inspire you to do, and others we will both inspire. Who will carry on with things after we have given our best and our all. Those we leave today's world to deserve nothing less.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1: INTRODUCTION: CONCRETE SOLUTIONS TO CARBON STORAGE

1.1 Background

1.1.1 The Challenges and Opportunities of Decarbonization as a Response to Climate Change

The accumulation of greenhouse gas emissions, primarily CO_2, since the Industrial Revolution has disrupted Earth's natural carbon cycle (1). This disruption stems from the rapid combustion of fossil fuels, releasing carbon that was sequestered over millions of years within a geologically brief timeframe. The rate of anthropogenic emissions has overwhelmed the capacity of natural carbon sinks, leading to a rise in atmospheric CO_2 concentrations and associated climate change effects (2). Reaching sustainability goals necessitates the reduction of atmospheric CO_2 concentrations. Existing natural carbon sinks today are insufficient to absorb anthropogenic CO_2 emissions due to the net release of CO_2 from wildfires, melting permafrost, and other sources (2), creating a requirement for engineered carbon capture and storage (CCS) solutions (3) (4) alongside nature-based carbon dioxide removal (CDR) solutions (5). These solutions include those that involve biomass, for which the abbreviation BiCRS (Biomass Carbon Removal and Storage) is in common use (6). All such carbon-removing processes, whether biological or technological, share the aim of capturing CO_2 from emission sources or directly from the atmosphere, followed by permanent storage in geological formations (4), utilization in industrial processes (7), or incorporation into durable products.

Of all the materials we produce, concrete by far is our most massive, with more tonnes made per year than all biomass we use per year; all human-made mass of which concrete is about a third is now greater than all biomass that exists on Earth (8). Concrete serves as the material of choice for the literal building blocks of modern civilization given it is what buildings, highways, runways, and other critical infrastructure are made from, in which the activities of business, governance, and our daily lives take place. Moving mass requires energy. To move the quantities of earth needed to provide enough cement, sand, aggregate, and water to make concrete, each segment of each of these four supply chains requires its own supply of energy, in each step of production, transportation, refinement, and further transportation of each resource to a location where blending can occur, controlled for quality, and ultimately be used at a site for either structural or non-structural construction. This movement of mass, where energy is supplied by combustion, leads to the production of greenhouse gas emissions, primarily of CO_2. If the excess CO_2 we release through the manufacture of concrete and through the combustion of fuels needed to perform that manufacture and to transport it to a construction site can be captured and held within the concrete itself, then CO_2 is no longer a pollutant but an ingredient of value. This process of valorizing CO_2 would enable market forces to contribute to driving down CO_2 emissions, since CO_2 would no longer be a net cost to society to remove, but a benefit due to its uses and the prevention of further worsening of climate change impacts.

Continued progress in not only the capture but also the storage of atmospheric CO_2 means finding more future locations for both. While the demand in developed countries such as Europe for cement and concrete is predicted to decline after many years of stability, the demand for cement and concrete in developing countries is projected to increase (9). New capture locations should be built with storage in mind, as the energy, emissions, and financial costs for transportation can be significant, potentially requiring infrastructure with long timelines for planning and approvals. The source of carbon is important to consider. Sequestering carbon from sources that will decompose, later releasing CO_2, into durable storage forms is one way to ensure atmospheric carbon that has been taken up by biomass does not re-enter the atmosphere to cause further warming. Carbon from combusting fossil fuels, which represent essentially concentrated biomass, can be captured at its source more efficiently than direct air capture from the atmosphere due to the higher concentration of CO_2 in flue gases (about 10% vs. 0.04% for direct air). Industrial point sources of greenhouse gas emissions offer easier planning for carbon capture; there are over 10,000 such sources registered with the EPA that must report their emissions annually with the EPA if they exceed a reporting threshold. However, there are also many distributed emissions sources such as transportation and residential/commercial heating using fossil sources; their removal will require distributed emissions sinks. Direct air capture has a large energy and construction materials requirement whereas trees are able to grow on their own in many places left to rewild, decreasing the need for construction or reforestation labor.

Living biomass in robust ecosystems may be a temporary storage form, but it can be a consistent storage form where not overwhelmed. The amount of biomass in robust ecosystems tends to be significant, partitioned into trophic levels of primary producers that make energy available to an ecosystem, followed by primary, secondary, and higher consumers to include detritivores responsible for the release of CO_2 back into the atmosphere. Given the hands-free growth of biomass, carbon storage in robust ecosystems as well as the prevention of biomass decomposition through methods like biochar for agricultural and food waste offer methods of low to no cost for sequestering carbon. However, the rate and amount of land area needed for sequestration are often insufficient in many areas. That studies have been published indicating insufficient global land area for planting trees to counteract climate change, combined with their slower rate of growth compared to our faster rate of emissions, helped spur growth of the idea that a significant effort for technological carbon capture and storage (CCUS) was needed. It is also the case that at present, all of Earth's land sinks are only taking up a net 0.44 Gt/yr of CO_2 (2), given the increased deforestation and loss of biodiversity (particularly in the Amazonian rainforest), extensive wildfires in both Russia and Canada, the release of methane from permafrost throughout the Arctic region, and the release of N_2O from fertilized agricultural areas.

These last two greenhouse gases are significant to mention given their production in an industry currently able to use CCUS profitably, that of ethanol production. This demand helps to further CCUS adoption by lowering the cost of the technology. The energy intensiveness of ethanol production has also been estimated as 20-40% less carbon intensive than gasoline, but a recent study has also suggested that ethanol is likely at least 24% more carbon intensive than gasoline. The reason is due to the need to grow extensive quantities of corn, requiring nitrogen-based fertilizers that require large CO_2 emissions to produce and that also leads to the release of significant quantities of N_2O, a greenhouse gas more than 300 times the warming ability as CO_2. Research at NOAA indicates that from 1980 to 2020, the concentration of N_2O has grown by 40 percent (10). The growth rates of N_2O were higher from 2020 to 2022 than any previous years since 1980, with China, South Asia, Southeast Asia, Central America, Northern Africa, and Brazil being the highest contributors over this timeframe. European emissions have declined while those in the US and other countries have remained mostly unchanged. The authors suggest that meeting climate goals will be challenging if these emissions continue at their current pace.

However, the carbonation of cement-based materials for carbon-neutral concrete offers a significant solution to climate change according to (11) - current carbonation technologies can reduce emissions by up to 25% at production and 50% over their lifetime, with the potential to reduce net future emissions by over 100%. Without significant changes to demand for resources that require large energy expenditures, fossil sources of energy will need transitioning to renewable sources. However, the sourcing of minerals through mining equipment which is still largely fossil fuel-driven, along with the manufacture and transportation of equipment for these renewable energy technologies to their locations of end use will also require energy. Over time, the renewable energy percentage will grow, but a key limiting factor will be the cost of scaling such energy sources. That carbon capture also requires significant energy today as well as significant expenditures and tax credits such as the 45Q to make construction feasible does not make it less necessary to build, only less likely to see a fast buildout to keep up with the expected rate of emissions increases. An all-of-the-above approach appears to be necessary to mitigate climate change as long as projections of market demand and the unavailability of less expensive renewable and carbon-free sources of energy are expected to hold. This research focuses solely on the carbon storage aspect; we cannot capture what there is no room to store.

More than one carbon storage form can occupy the same area of land. For example, biochar is an organic material derived from agricultural and forestry waste that can be used in cement as well as in concrete as aggregate. It can also be used as carbon storage directly within the carbon removal markets or as an agricultural amendment to hold onto moisture and nutrients for time-releasing these back into the soil. Calcium carbonate is an inorganic storage form of carbon that is more abundant in nature, as the minerals calcite and aragonite. lithium carbonate, and others, and can also be used within agricultural settings as lime. It is a primary constituent of limestone and thus finds readily available uses in the cement industry due to calcium oxide being a primary ingredient of cement. The process of calcination refers to the treatment of calcium carbonate at high temperatures to form calcium oxide. It is an example of the class of materials called carbonates which includes other storage forms of carbon: magnesium carbonate, lithium carbonate, and more commonly, sodium carbonate (washing soda) and sodium bicarbonate (baking soda). Calcium carbonate finds its highest value as precipitated calcium carbonate; a wide array of specialized chemical applications is enabled by the ability to control the precipitation process to yield finer, more uniform particle sizes. Calcium carbonate today can be made with CO_2 removed from power plants through scrubbers, where the resulting high purity CO_2 streams can be compressed and transported to locations for geologic carbon storage (GCS).

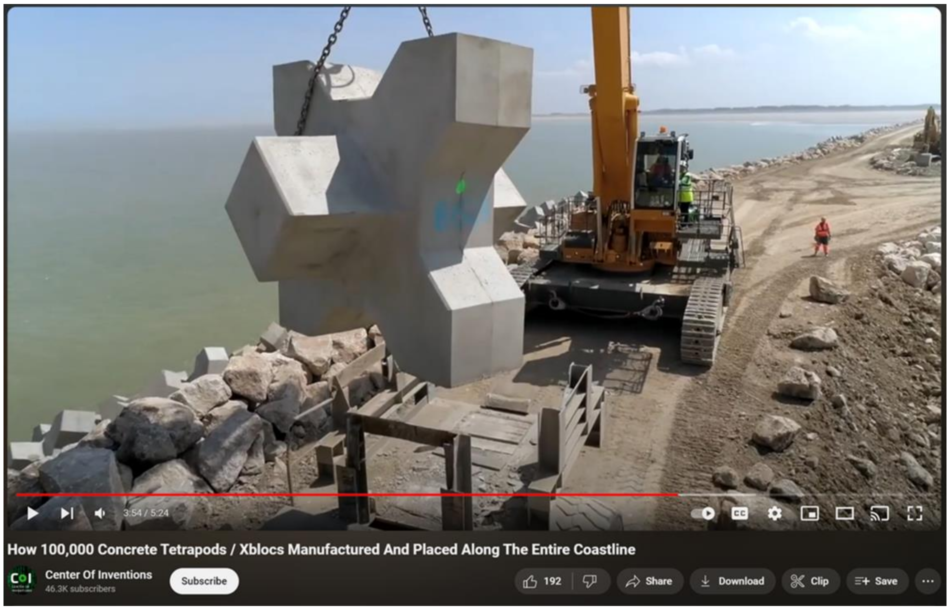
GCS entails injection of this CO_2 under pressure, with CO_2 occupying the pore space to a degree given by the porosity and permeability of the rock. Mineralization can occur, but so might the migration of CO_2 plumes deep beneath the surface over time. Mineralization can also be a primary means of carbon storage; commercial operations exist where the equivalent of sparkling water containing dissolved CO_2 is injected into basaltic rocks such as those at depths of 400-800 m in Iceland (12) where durable sequestration occurs as carbonates for most of the injected CO_2 in under 2 years. GCS offers the benefit of carbon being stored out of sight below ground, while having a different set of challenges compared to above-ground carbon storage. The most efficient and economical transport from industrial point sources to injection well sites today, in terms of energy density, is hydrocarbon-based fuels. This presents a difficulty, given the likelihood of CO_2 emissions being produced during the compression process, if this power was not generated in a renewable, carbon-free manner, combined with the greater likelihood of tonnes of compressed CO_2 stored in metal cylinders and tanks requiring CO_2-emitting forms of transport. The loading and transportation of pressurized metal cylinders and tanks can be avoided, but through the use of pressurized metal pipelines that enable CO_2 to be transported instead. The construction of these pipelines can be lengthy and expensive, during which landowner and public approvals as well as permits must be secured to proceed. Even after proceeding, changes in market conditions and public sentiment can still lead to project failure.

CCUS today is difficult to make profitable due to the high cost on the carbon capture side. For power plants, the use of carbon scrubbers enables high purity CO_2 streams, but their regeneration requires energy which comes at the cost of part of the revenue stream from coal, oil, or natural gas. The CO_2 streams from flue gas have a concentration on the order of 10% compared to just over 0.04% that is the concentration of CO_2 in the atmosphere. That atmospheric CO_2 concentrations are much lower than those in flue gas means that direct air capture is much less efficient in terms of the quantity of CO_2 removed per unit of energy consumption. To obtain a sufficient stream of CO_2 for as much adsorption as the scrubbers in a power plant can adsorb per second, it requires significant additional airflow. If this airflow is provided by large fans, their need for energy adds cost and will add emissions if not powered by carbon-free energy. CCUS today is of minimal profitability due to the large energy costs associated with capture: it is more cost-effective to continue emitting than to sequester our emissions. Projects are able to proceed based on the availability of carbon tax credits such as 45Q as well as initiatives taken by ethanol producers to adopt CCUS at their plants, to remove emissions from corn-based fuel production.

Through the ability of concrete to store carbon, it can also be a major storage form for CO_2 emissions that simultaneously offers value. Durable goods in the US today contribute less to our gross domestic product than nondurable goods (7), suggesting that at present, manufacturing what is temporary and fleeting today provides for more wealth creation than manufacturing durable materials for durable structures. If rebuilding is inexpensive and landfills are inexpensive, no lessons will be learned about why building for useful permanence is better than the permanence of non-useful waste. This is likely to change in the future, given that debris is considerable after every storm that destroys homes while construction waste is considerable after every project to build and rebuild homes. Concrete construction waste could be repurposed as recycled concrete aggregate (RCA) which could be added as needed to form thick, sturdy walls with 30 wt% biochar for carbon storage, offering a lighter weight concrete for the same compressive strength. Fiber-reinforced polymers such as carbon fiber could be added for tensile strength, but basalt fiber could also be used, possibly that on which CO_2 mineralization has already occurred, given the use of basaltic rocks for carbon mineralization (12). Biochar offers excellent fire resistance and insulation ability. Much larger blocks could be made and shipped. If not used for buildings, then non-structural uses are also plentiful. The next section will cover one of these uses.

1.1.2 Tetrapods of Low-Carbon Cement and Concrete for Carbon Storage: Significance and Innovation

Low-carbon cement can be produced to reduce CO_2 emissions through decreased clinker production. Clinker is the major contributor of CO_2 due to limestone calcination involved in cement production. Increasing the volume of cement produced while reducing the clinker required will reduce the emissions directly related to clinker manufacturing. Our group's work has pointed to several other methods that would aid in cement industry decarbonization. The chemistry of materials being fed into cement kilns can be optimized (13) with digitization and data analytics (14), both of which can enable more efficient ways of continuously assessing both the environmental and economic characteristics of cement production (15). The use of optimized cement in carbon-neutral concrete is another (16). Cement volume can be increased by blending cement with other materials to produce a composite low-carbon cement product. However, the amount of such a product remains a small percentage of the total volume of concrete, most of which is composed of sand and aggregate. If either of these is replaced with a material containing a high degree of sequestered carbon, the finished concrete can store much more carbon. Depending on its compressive strength, a wider array of carbon storage options becomes possible beyond load-bearing structural uses of concrete such as 3D printed and sprayed concrete structures, as backfill in underground mining, as panels for insulation, and as tetrapods.



How 100,000 Concrete Tetrapods / Xblocs Manufactured And Placed Along The Entire Coastline

Figure 1. One of many tetrapods manufactured by Xbloc for the prevention of beach erosion along a coastline. The video is of a project featuring the manufacture and placement of 100,000 tetrapods (17).

Tetrapods are non-structural forms for preventing beach erosion that can serve a dual purpose as carbon storage forms. Such a use evolved from an approach (Simske, personal communication) to use concrete tetrapods for general environmental remediation (e.g. mercury and other sea toxins). Each tetrapod is a multi-ton unit of concrete that interlocks with other tetrapods to dissipate waves that cause beach erosion. A 10-ton tetrapod that is 30 wt% carbon would provide 3 tons of carbon storage. A beachfront of 100,000 tetrapods (previous figure) would thus contain 300,000 tons of carbon, which equates to just under 1 million tonnes (Mt) of CO_2. Just 23 of these tetrapods would occupy 100 m^2 (18), meaning that 1 Mt CO_2 can be stored within 0.435 km^2 of land area. The potential of such storage in small land footprints becomes clear: the entire global annual emissions of approximately 40 Gt CO_2 could be sequestered in 4 billion tetrapods, occupying a total volume with a land footprint of 17,400 km^2. This is a footprint smaller than the land area of Kuwait at 17,818 km^2 (17).

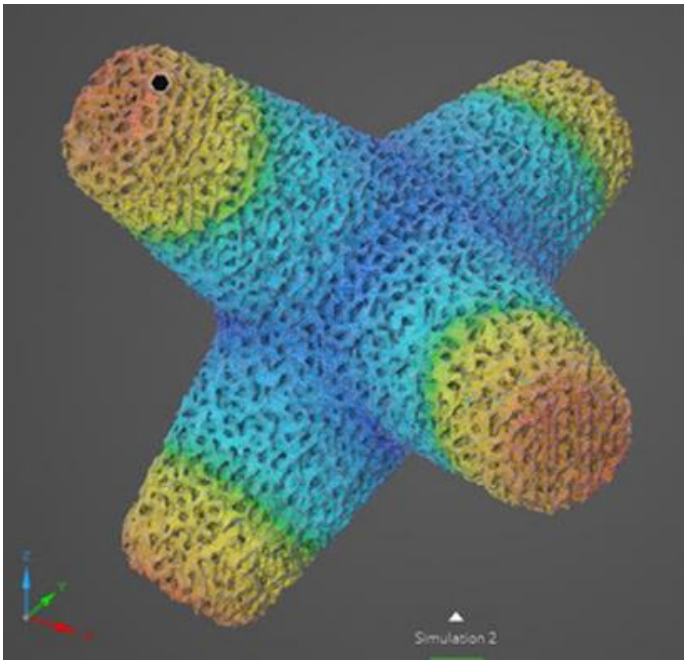


Figure 2. A CO_2-storing tetrapod was modeled in ANSYS software to explore likely stress distributions.

Figure 2 shows the general shape and possibility for a porous tetrapod design to reduce weight while dissipating wave energy. A strong shell might also be formed around a softer but more carbon-dense interior. The general shape and purpose of tetrapods offers design flexibility when it comes to their use. Many grades of concrete carbon storage and compressive strength may find use in such structures. Other than on beaches, they could underlie earth berms with terraced slopes instead of retaining walls, back retention ponds for restoring wetlands, and be used as backfill wherever significant but sturdy grading of terrain is required.

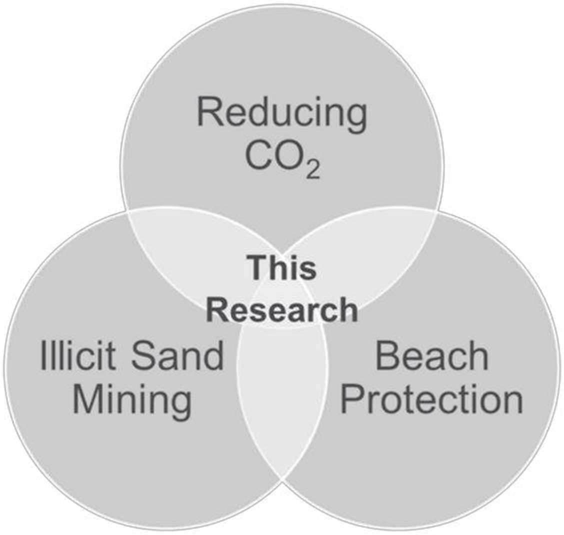


Figure 3. The social and environmental co-benefits of tetrapods used for carbon storage.

The tetrapod concept offers three key benefits (Figure 3). Not only can they provide a land-based carbon sink serving the purpose of beach protection from erosion caused by increased storms and sea level rise, but the use of carbon-storing materials in place of sand in tetrapods would reduce the amount of sand that would be needed in these. This would lessen the impact overall of illicit sand mining to provide sand for other construction uses. To provide such carbon storage, two materials offer a wide range of possibilities for different engineering applications. Biochar (BC) is known as a relatively inexpensive filler that can improve polymer mechanical properties (19), having been studied for use as a carbon sequestering additive in cement mortars (20) and in cement-based composites (21). Calcium carbonate is another carbon-sequestering additive that can be made from waste calcium alkalinity sources such as fly ash, and it can be found in Portland cement at concentrations up to 5% (22). Both BC and $CaCO_3$ will not burn at high temperatures and are durable forms of carbon storage. The combination of both BC+$CaCO_3$ to assess mechanical properties relative to carbon storage has not been studied well with cement. Such a study could prove fruitful since the combination of both has been shown to modify typical biochar properties, such as an enhancement of cation absorption (23), in ways that could improve the resulting strength of a carbon-storing cement composite.

1.2 Problem Description and Solution Need

The cement industry is a major emissions source today; both Nehdi et al. (24) as well as our group (25) have already performed extensive reviews of decarbonization technologies for the cement and concrete industry. However, concrete can also store carbon, either through mineralization or through the incorporation of biochar and calcium carbonate either in cement or as aggregate. There is a need if we are to sequester CO_2 and reduce the impacts of climate change to ensure that CO_2 can be stored somewhere, and that less new CO_2 is released through the decomposition of waste biomass. The USDA reports that between 30 and 40% of all food in the United States is left to become waste (26). This will eventually decompose to form CO_2 and methane in landfills, not counting the emissions from significant quantities of plant material from agriculture left to decompose before and after food is harvested and processed, means that biochar can be a significant solution to valorizing both forms of biomass waste while benefiting the climate. Its inclusion in carbon-neutral concrete production is technically feasible at larger quantities by weight in concrete than in cement. Such concrete has the potential for wide implementation in both structural and non-structural applications. The valorization of CO_2 as an essential component in a circular economy is necessary if CO_2 is to become a new term in the economic equation seeking to match the supply of sustainable materials with demand. Thus, the problem this research seeks to address is whether such a valorization of CO_2 is possible through cement-based carbon storage systems able to make use of biochar and calcium carbonate in concrete. Specifically, what are the engineering possibilities for such systems and the options for scaling these into a useful land sink?

1.3 Goals of This Research

The main research objective: to examine the engineering of a cement-based carbon storage system with the potential to achieve scale as a significant land-based carbon sink, how its properties and potential uses might vary in different settings and applications, and what would be necessary for it to scale to reach its potential usefulness.

1.3.1 Research Questions

To accomplish the above goal, this research seeks to answer the question posed at the end of the problem description through acquiring the following experimental results:

1) The development of curves describing the variation of biochar wt% vs. cement mortar compressive strength as well as $CaCO_3$ wt % vs. compressive strength, from which the relationship between compressive strength and carbon storage can be determined;
2) Analytical support of whether the combination of BC+$CaCO_3$ can improve the compressive strength of its cement mortar composite more than BC alone, and under what ranges of BC and $CaCO_3$ wt% this might be so;
3) A mix ratio of cement+BC+$CaCO_3$ in terms of wt% that yields both a favorable compressive strength and high quantity of carbon storage.

The hypothesis is that there will be a much lower wt% of biochar possible in cement than concrete, but that the addition of $CaCO_3$ due to its fine particle size and void-filling capability will favorably contribute to increasing compressive strength compared to the same wt% of biochar alone up to an optimal value. This is because C_3S (alite, tricalcium silicate), the most reactive phase and major constituent of cement that is the main source of calcium silicate hydrate (C-S-H) responsible for concrete's mechanical properties, is known to interact with $CaCO_3$ (27), accelerating the hydration of C_3S and causing capillary porosity changes due to several physical effects that will generally decrease the amount of water needed for workability (28). It is known that the lower the amount of water added to either cement or concrete, the higher the compressive strength that results. Thus, for a given water-to-composite ratio, there should be composites with biochar and CaCO3 together with a larger compressive strength than composites with a given wt% of biochar alone. Beyond that, as the biochar wt% increases further, compressive strength is expected to decline due to too much cement replacement. The expectation from this research is that an understanding of compressive strength vs. carbon storage for a biochar-cement-calcium carbonate composite will be found that provides guidance on its use as a carbon storage system with many potential applications.

1.3.2 Contributions

This research will advance the knowledge within systems engineering through its focus on the engineering and scaling of a single system that happens to have a wide range of variation in terms of structural properties, composition, as well as function - the latter in terms of its multiple economic uses in construction as well as environmental uses in the mitigation of sea level rise and climate change. Many systems within systems engineering, such as those of aircraft design/operation and artificial intelligence systems, demonstrate greater complexity in their composition and structure than in the functions the system was designed to provide. An airplane requires extensive systems design; also, requirements validation and verification of function are necessary throughout the engineering process to ensure ample tolerances within safety limits. A cement-based carbon storage system has the functions of storing carbon, but compressive strength is a variable that determines a variety of potential uses for this system. It is also possible for the composition of such systems to grow in complexity with the many potential ingredients that exist throughout the world for concrete, but such complexity can be reduced through recognition that only a few functional categories for input materials in concrete based on particle sizes and chemistries. This research aims to highlight the factors essential to engineering and scaling such systems to meet the needs of carbon storage, enabling systems engineers as well as civil and environmental engineers to operate with flexibility in recommending and implementing such systems across a wide range of geographies and use cases. Such highlighting will be done through the experimental and modeling results to be provided.

1.3.3 Assumptions and Limitations

This research involves testing samples of a composite mixture of biochar, $CaCO_3$, and cement for compressive strength and carbon storage capacity. The experiments carried out were to determine how both vary and how both might be maximized. The conclusions drawn from these results are assumed to not vary significantly by any other variables such as those pertaining to particle sizes and porosities where applicable of the biochar, calcium carbonate, water, and Portland cement used. While several tests involving composition, physical properties, and compressive strength were performed of my prepared mixtures under my colleague and co-author Kwaku Boakye's direction at a Lehigh-Hanson laboratory, the experimental plan I derived from use of the Taguchi method, available from within the Minitab software, did not make use of measured properties such as particle sizes or porosities of biochar. Only compressive strength as a function of the wt% of BC, $CaCO_3$, and the water-to-cement ratio WC were used as variables given that Portland cement is already highly standardized in terms of its composition, and the Taguchi method's use of wt% of various inputs vs. the measured result of compressive strength offers a straightforward means of analyzing many different parameters with a very low amount of experimentation, to make results faster and cheaper to obtain. This method has previously been applied in the design of cement mortars using waste materials (29), borrowing 3 of the 4 factors from that study: aggregate type, aggregate content, and cement content. The usefulness of the Taguchi method with only these factors without other variables such as particle size and porosity necessary to understand the variation in compressive strength provided confidence that the same would be done in this research. This research has modified those 3 factors to BC content, $CaCO_3$ content, and water-to-composite ratio to produce a cement mortar that is specifically a BC-$CaCO_3$-Cement (BCC) product. Two of these three ingredients store carbon and the third can be made with a lower-carbon footprint through clinker reduction and other methods. Thus, the assumption is that insights can be gained about the variation of compressive strength and carbon storage even with a relatively small number of tests through the use of the Taguchi method.

CHAPTER 2: LITERATURE REVIEW AND EXISTING METHODS

2.1 Carbon-Neutral Concrete and Biochar–Cement–Calcium Carbonate Composites

Many solutions are being explored to reduce the greenhouse effect, especially solutions regarding carbon capture and storage. This is because reducing greenhouse gas emissions alone is no longer sufficient to meet 1.5 or even 2 °C warming targets, and it will take a significant cumulative CO_2 uptake of 200–400 gigatonnes CO_2 over the course of the century to limit global temperature increases to 2 °C or less (30). In view of this, there is a need to develop higher-density, highly permanent forms of carbon storage, to reduce the volume required on land or sea to store the captured CO_2. Carbon-neutral concrete is one such solution.

Two forms of high-density carbon storage within concrete are biochar and calcium carbonate. Biochar, which is pyrolyzed biomass, is typically 50–93% carbon by mass (31). The International Biochar Initiative classifies biochar as class 1 if it has a C(organic) mass fraction $\geq 60\%$ (32). The energy needed to make it varies by feedstock; for example, biochar from pine requires 1.6 +/− 0.3 MJ/kg (32). Biochar is commonly used as a soil amendment, with agronomic biochar research alone being the subject of 15,000 publications thus far (33). However, only so much biochar can go into agricultural soils; application rates do not seem to exceed 20 tonnes/ha (34). Furthermore, biochar can remain in soil longer (>1000 years) if its oxygen-to-carbon (O/C) molar ratio is less than 0.2. If this ratio is greater than 0.6, its half-life is <100 years (32). Due to the dependence of biochar's durability on its chemistry when used in soil, the use of biochar in construction materials where it is more permanently bonded can provide a much-needed alternative to its use in soils.

Similarly, calcium carbonate, known as agricultural lime, is also used as a soil amendment. Although calcium carbonate offers a lower carbon percentage by weight than biochar, it is also known to be a highly permanent form of carbon storage, barring acid attack or exposure to extremely high calcination temperatures (35). However, as with biochar, only so much calcium carbonate can stay absorbed in agricultural soils.

Ideally, both high-density forms of carbon storage might find use in the construction industry, such as in a mixture that partially replaced the cement, sand, and aggregates used to make concrete. A target volume of such a size is needed to ensure adequate storage for the gigatonnes of CO_2 that need to be taken up to meet climate targets (30). Concrete is already the most abundant manufactured product by mass; it outweighs all living biomass on Earth, is mostly made of aggregates, and aggregate production alone was described as increasing from 24 gigatonnes/year in 2011 to 55 gigatonnes/year in 2060 (36). If a significant percentage of concrete could be replaced by high-density carbon storage, this would enable concrete to be carbon-neutral, offering great environmental benefits. A carbon-negative concrete has even been demonstrated, but it reveals a definite tradeoff between carbon storage content and compressive strength (37).

The application of both biochar and calcium carbonate in cement has been explored. For the application of biochar in cement, two conclusions can be drawn from the many research findings available [(38), (39), (40), (41), (42), (43), (44), (45), (46), (47), (48), (49), (50), (21), (51), (52)]. First, biochar can be effectively used as an additive and as a replacement for cement in cement mortars. There, it adds a small amount of carbon storage while raising the compressive strength. Second, biochar can also be used as a sand and/or aggregate replacement in concrete where it is possible to use it in larger percentages, thus resulting in significant carbon storage and an increase in compressive strength, up to a limit. Calcium carbonate is already a permitted additive in Portland cement at up to 5% weight (22).

The interaction between both biochar and calcium carbonate with cement has not been well explored. Thus, this paper will provide an overview of the literature on biochar and calcium carbonate regarding carbon storage and compressive strength, examine the potential benefits of combining both materials with cement in a carbon storage system, and help elucidate new areas of research needed to identify the optimal amounts of both biochar and calcium carbonate with cement. Even if this high-density carbon storage system achieves only lower compressive strength values, there are still many uses in other areas rather than structural building materials. However, as we will see later in this paper, it may be possible to have high compressive strength as well as high carbon storage using optimal amounts of both biochar and calcium carbonate with cement.

This paper is structured as follows. It will begin by examining methods for producing carbon-neutral concrete, which will outline the case for substituting cement with biochar and calcium carbonate. The next section will present the performance expectations for carbon-neutral concrete, namely, carbon storage and compressive strength, but also including other strength and material properties. Obstacles to scaling the use of carbon-neutral concrete will then be presented, which include the revision of architectural codes and standards, uncertainties and delays, material availability, and cost. The last section will cover six broad categories of research directions, to help guide future improvements and scaling efforts for carbon-neutral concrete.

2.2 Methods for Producing Carbon-Neutral Concrete

2.2.1 Greener Supply Chain and Production Through Recycled Materials

Recycled concrete aggregates (RCA) offer a means of recycling construction and demolition debris and are envisioned to play an important role in sustainable development (53). However, there are problems with using RCA as outlined by Lippiatt et al. (11) involving reduced concrete performance and inconsistent reductions in global warming potential (GWP). As an example, the use of RCA has in one implementation increased the GWP of concrete by 6.3%. This amount was dependent on the replacement fraction and the specific aggregate recycling technique used. RCA emission reduction was also found to be very sensitive to transport distances (11). However, carbonated RCAs were found to have increased strength compared to uncarbonated RCA, and a CO_2 sequestration potential of approximately 7 kg of CO_2/tonne of RCA was deemed to be generally achievable. Additional problems were described by D'Alessandro et al. (54): the recycled aggregates cannot be entirely separated from the mortar component and can contain impurities such as glass, metal, gypsum, or wood coming from demolition. Both these problems lead to decreased mechanical strength in the final recycled concrete. There are pretreatments that can reduce this decrease, such as RCA coating, impurity removal, oven curing, and RCA calcination. However, these are all additional steps that are likely to involve additional fossil energy input, thus decreasing the effective carbon storage of the final concrete.

2.2.2 Accelerated Carbonation Curing of Concrete

Accelerated carbonation curing, forced carbonation, or rapid carbonation of concrete are all terms for the artificial enhancement of the natural concrete carbonation process that occurs over time. When concrete naturally carbonates, CO_2 reacts with calcium di- and tri-silicate as well as hydration products such as calcium hydroxide and calcium silicate hydrates (C-S-H) to form stable carbonates. The process of carbonation involves the formation of carbonic acid from the available CO_2. Moisture is required for the carbonation of calcium hydroxide.

Several additional factors influence the rapid carbonation of concrete. One important factor is CaO content. Shi et al. (55) describe how, regardless of cement type, the theoretical maximum CO_2 concentration increases with CaO content—1.0 tonnes of cement could consume 0.5 tonnes of CO_2. The authors also highlighted the specific raw materials used, water-to-cement ratio, sand-to-cement ratio, compaction pressure, preconditioning before accelerated carbonation, effects of both concentration and pressure of CO_2, and further curing after accelerated carbonation as other important factors. However, the most important factors affecting the diffusion of CO_2 in concrete and the kinetics of carbonation reactions were the concentration and pressure of CO_2. A pressure above 0.6 MPa for CO_2 did not significantly affect the CO_2 curing degree and compressive strength. The optimal pressure appears to be 0.2 MPa, since in some cases 0.2–0.6 MPa also yielded no additional effect.

However, several problems exist with ACC. It can only be applied to prefab units and unreinforced cementitious materials because the lower pH during carbonation can trigger corrosion of the steel (41). It also requires exposure to a high level of CO_2 (up to 20%) and only at an early age so that the CO_2 can diffuse throughout the pores in the cementitious matrix (41). Otherwise, only the top layer receives CO_2, causing high shrinkage and restrained cracking. Furthermore, if ACC is to be conducted in a timely manner, special conditions are required that are at odds with energy conservation. Kaliyavaradhan and Ling (56) describe how the rapid carbonation of concrete construction waste within a timespan of hours requires high CO_2 concentrations (20–100%) along with elevated pressures and fine particle sizes.

Accelerated carbonation curing can be combined with the use of RCAs with the intention of greater sustainability, although there are shortcomings as well as uncertainties in what the expected results might be. Pu et al. (57) conducted an extensive review of RCA performance when treated with accelerated carbonation. RCAs with smaller particle sizes are more readily carbonated compared with larger ones. Many sources in Table 1 describe the advantages/disadvantages of different methods used to enhance the quality of RCAs. Shortcomings include high energy consumption, intensive cost, and negative impacts on RCAs such as micro-cracks, ion contamination, and the production of waste solutions and fine aggregates. Additionally, considerable variability exists in the literature concerning the best conditions for treating recycled aggregate with forced carbonation. Gomes et al. (58) present data from multiple sources in their Table 1 for CO_2 curing of crushed concrete aggregates. These data reveal carbonation conditions which include CO_2 concentrations of 5–100%, temperatures of 20–31 °C, RH of 35–75%, pressures of 0.1–4 bar, and durations of 30 min–3 weeks. Thus, despite a wide range of tested conditions, there is still an absence of consensus on what conditions are most favorable for treating RCA to maximize CO_2 storage from accelerated carbonation. The benefit of additional work on this from a CO_2 storage perspective is also unclear since 270 kg CO_2 can be sequestered if 1 tonne of waste cement is completely carbonated, but only about 11 kg CO_2 can be taken up by 1 tonne of crushed concrete aggregate (56).

An interesting method of accelerated carbonation of concrete is to add additional CO_2 into the concrete from the water rather than diffusion through air. The results differ markedly depending on whether the water is retained for curing or only added during mixing. Suescum-Morales et al. (59) found that wet curing concrete with either normal or carbonated water was not recommended for improving the CO_2 capture capacity or the mechanical properties of cement-based materials. This could be due to the fact that the samples cured in normal water were in closed containers, preventing further CO_2 addition, as well as a change in dissolution/leaching of calcium ions produced by curing in water. However, using carbonated water as the mixing solvent (not curing solvent) when forming concrete did increase the CO_2 sequestration.

Furthermore, commercial carbonated water as the mixing solvent along with the use of recycled masonry aggregate (RMA) increased CO_2 sequestration by 181% after 7 days of curing. The use of RMA in all studied samples increased CO_2 sequestration over not using it; this was considered to be due to the presence of portlandite (calcium hydroxide) in RMA. This non-carbonated ingredient, once it is carbonated to form CaCO3, is what offers a higher CO_2 sequestration capacity. Using carbonated water during mixing thus avoids the need to use an accelerated carbonation chamber to improve CO_2 sequestration.

2.2.3 Cement Substitution with Lower-Carbon Materials

A third method for producing carbon-neutral concrete is to substitute the most carbon-intensive component of concrete, Portland cement, with lower-carbon materials. Care must be taken, however, to preserve the natural carbonation ability of the concrete when substituting cement with other materials as per Lippiatt, Ling, and Pan (11), who argue that CO_2 emission reduction below 20% is counterproductive if it prevents natural carbonation. The range of possible cement substitutes is large. Al-Mansour et al. (60) describe, in their Table 2, the main microscopic features of just a few of these different cement replacement candidates including fly ash, rice husk ash, silica fume, ground granular blast-furnace slag, waste glass, and plastic. Plastic will not be covered in this section given there are several drawbacks to its use in concrete, first and foremost the loss of compressive strength in any concrete mixture as the plastic ratio increases, but also a decline in abrasion resistance and thermal resistance (60).

2.2.3.1 Biochar-Containing Concrete

Of the three ways of achieving carbon neutrality on a global scale—the use of renewable energy, enhancing carbon sinks in global ecosystems (which includes wood waste, of which conversion to biochar is a solution), and carbon capture, utilization, and storage technologies—Wang et al. (61) declared that biochar occupied a special position within the production of green cement and concrete. Furthermore, the present shortage of natural aggregates in construction (gravel and sand in some parts of the world) offers yet another reason to examine the use of biochar for both cement and aggregate substitution (62).

Biochar can be made from a variety of materials, from food waste to wood waste, with variations in carbon storage and strength when used in concrete. Gupta et al. (63) found that biochar from mixed food waste, rice waste, and wood waste can all be used as carbon-sequestering additives in mortar, though the carbon content varies, being highest in mixed-wood saw dust and lowest in rice waste. The addition of 1–2 wt% of mixed food-waste biochar or rice waste biochar resulted in a similar mechanical strength as the control mix which was without biochar. The best results in terms of mechanical strength and permeability were seen with mixed-wood saw dust-derived biochar. For that biochar, there were increases in compressive and tensile strength by up to 20% and reduction in water penetration depth by 60% and reduction in sorptivity by 38%. Thus, non-wood-waste sources can indeed be used for biochar, but the carbon storage and strength properties will not be as great as with wood waste biochars.

If biochar is to be used with accelerated carbonation curing, it is important to note that the retained water within biochar will speed up the rate of ACC. The optimal relative humidity for carbonation is 50–75% (64), which the biochar helps to maintain over a longer period.

Significant carbon footprint reductions are possible due to the use of biochar in building materials, along with associated improvements in mechanical, physical, and chemical properties. However, much more research is required in this area concerning the biochar use in building materials for climate change mitigation. Legan et al. (65) described performing the first systematic literature search on biochar-containing building materials for use in climate change mitigation; unfortunately, this only yielded 13 English-language articles for their final review. Clearly, there is an opportunity for further work in this field.

2.2.3.2 Alternative Concretes

This section describes alternative concretes which, in some cases, can also employ biochar for improved carbon storage and strength.

LC3 concrete: Pradhan et al. (66) examined how chloride resistance impacts the service life estimation of concrete mixtures since chloride is the major cause of corrosion of the steel reinforcement. Their paper also covered limestone calcined clay cement (LC3) concrete benefits, which will be more advantageous as the gradual decline in the supply of quality fly ash and ground-granulated blast furnace slag (GGBS) continues. This is another reason why biochar is so promising, given that organic waste is much more plentiful. LC3 concrete had better resistance to chloride penetration compared to fly ash- and GGBS-incorporated concrete due to having more-refined pores (due to the secondary hydration of pozzolanic materials, which reduces the diffusion of chloride ions with time), as well as a 3–12% lesser CO_2 footprint than fly ash-blended concrete of the same strength and similar chloride resistance. It also had a much longer service life (56.7 years vs. 16.0 years for the control) than any of the other tested concrete types (fly ash- and GGBS-containing). Furthermore, according to Pradhan, Poh, and Qian (66) the reduction in global warming potential (GWP) of different concrete mixes with respect to the control mix for a cradle-to-grave system boundary condition was 84% for LC3 concrete, 62% for fly ash-containing concrete FA30, and 59% for a ground-granulated blast furnace slag-containing concrete GGBS50. The LC3 concrete had the least environmental impact and highest service life of all three of these mixes.

Alkali-activated geopolymer concrete: Geopolymers are inorganic materials consisting of a network of AlO_4 and SiO_4 tetrahedra (67). A cementing material (source of aluminosilicates) and an alkaline activator (alkaline hydroxides and salts) are used in combination. Piccolo, Andreola, Barbieri, and Lancellotti (67) found that biochar can be used in alkali-activated geopolymer materials and at a very high percentage of 70 vol% (not wt%). This aggregate material had an increase in pore area and total porosity but a decrease in the dimensions of pores.

Lime–hemp concrete: Jami et al. (68) describe the advantages and disadvantages of this material, with the chief disadvantage being that it cannot be used as a load-bearing material due to inadequate compressive strength. Still, it is a good example of a sustainable concrete whose carbon storage properties are highly desirable. Lime–hemp concrete (LHC), hemp concrete, or hempcrete are all names for this cellulose aggregate concrete. Hemp is used as the aggregate and a lime-based material is the binder. It is possible to use many other plants as a cellulose source, but hemp has a dry matter yield of 7–34 tonnes/ha/yr while being easy to grow and having a high operating margin. Hemp concrete is carbon-negative, lightweight, low-density, buffers moisture well, has a low thermal conductivity, and provides acoustic insulation. The standard types of supplementary cementitious materials can be added to hemp concrete (fly ash, GGBS, metakaolin, silica fume). Concrete made with ordinary Portland cement (OPC) has a typical density around 2400 +/− 50 kg/m^3, whereas hempcrete has widely varying densities, from 270 kg/m^3 to 850 kg/m^3. Jami et al. (68) then describe how the compressive strengths for the hempcrete samples are also very low, varying from 0.10 MPa to 4.74 MPa, largely due to high aggregate flexibility and high porosity. Strength improves when cement is added to it, but this defeats the purpose of using less cement. Strength can also be increased significantly by compaction, which reduces the porosity. On carbon content, hemp aggregate is typically 45% carbon and 1 m^3 of hemp concrete can sequester 307.26 kg CO_2; when made into a wall of concrete blocks, −48.36 kg CO_2-eq/m^3 was demonstrated. However, hempcrete walls are not immune to rain—they must be covered to prevent dampness and mass run-off. It can, however, be made into lightweight wall insulation panels in most low-rise construction.

Magnesia-containing concrete: Lippiatt, Ling, and Pan (11) describe how magnesia cements produce more CO_2 per tonne during production, are weaker than CaO cements, and do not naturally recarbonate, unlike CaO cements. Thus, MgO cements have a larger GWP than CaO cements. However, these disadvantages can be offset by the use of CO_2 curing and biochar incorporation. Wang et al. (69) described how, in magnesia cement (MC)- and magnesia cement–Portland binary cement (MP)-based pastes, biochar incorporation promoted the generation of hydration products due to the internal curing effect. The use of CO_2 curing also accelerated the carbonation of pastes. The CO_2-cured MC pastes preferentially formed hydrated magnesium carbonates, while the CO_2-cured MP pastes preferentially formed $CaCO_3$. This study found that the synchronous use of biochar and CO_2 curing significantly enhanced mechanical strength of the resulting blocks. This was thought to be due to the ability of the porous biochar to provide channels for CO_2 diffusion and intensive carbonation. In comparison, PC (Portland cement)-based composites require less water for hydration than MC-based composites.

2.3 Performance Expectations for Carbon-Neutral Concrete

2.3.1 Carbon Storage Characteristics of Biochar and Calcium Carbonate

The use of biochar as a lightweight aggregate for construction has been identified as a future direction to investigate (70), with its potential benefits for carbon storage. This is because, depending on the preparation condition and the biomass source, biochar itself can reduce net GHG emissions by 870 kg CO_2-eq per tonne dry feedstock (−870 kg CO_2-eq/tonne) (71). Kua et al. (72) describe how biochar-containing building materials can capture CO_2 directly from air. This takes place in the biochar pores; biochar-coated plaster pellets were found to absorb CO_2 at a rate of 8 to 4000 ppm/min with a CO_2 adsorption of 0.033 mmol CO_2/g biochar. Legan, Gotvajn, and Zupan (65) showed that biochar-containing building material could capture CO_2 from the air with a capacity of 0.138 mmol CO_2/g biochar, although calculated biochar CO_2 adsorptions around 1.67 mmol CO_2/g biochar were also reported. Another added benefit of producing biochar is the elimination of CH_4 or N_2O release from the conventional management of waste biomass.

Construction aggregate is the single most produced material by weight in the world, with demand projected to more than double from 24 to 55 gigatonnes per year by 2060 (36). This increase, however, will also cause carbon emissions of approximately 350 gigatonnes CO_2 by 2050 (36). Although different types of feedstocks yield differing amounts of net CO_2 sequestration with biochar, from −0.1 for cardboard biochar to −3.5 kg CO_2-eq/kg biochar for Miscanthus grass-derived biochar (31), it is conceivable for the carbon sequestration ability of biochar to counteract these emissions, but only if biochar production can be appropriately scaled. The 350 gigatonnes of CO_2 associated with future aggregate production is equivalent to 95.4 Pg C. In comparison, there are 126 Pg C presently in deadwood (73 +/− 6 Pg C) and litter (43 +/− 3 Pg C) which will eventually re-enter the carbon cycle through near-term decomposition (73). This decomposition could be slowed by centuries to millennia if made into biochar (74), used as an aggregate replacement.

Locking biochar inside concrete will also help it to maintain long-term stability. This is important because questions about the permanence of biochar remain, even after the results of a recent meta-analysis of biochar permanence in soil. That study, performed on 57 studies, indicated that the longer the study duration (incubation time) for examining biochar stability in soil, the higher the permanence reported, shifting from years/decades for shorter tests to centuries and millennia for longer tests (74). Considering this result, the overall picture seems to suggest that biochar is a highly permanent form of carbon storage, and that if protected from exposure to decomposition by being locked inside concrete, this would only help improve its long-term stability.

In contrast to biochar, which is a product of relatively recent human origin, calcium carbonate has had a history of billions of years of use as a natural carbon storage medium. Mineral carbonates such as $CaCO_3$ or $MgCO_3$ have been shown to be the most stable forms of carbon from a thermodynamic perspective, which means these would allow for long-term CO_2 storage when CO_2 is reacted with alkaline minerals (75).

Separately, both biochar and calcium carbonate have been used as carbon storage media. This raises the question of whether both can be used together with cement as a hybrid carbon storage medium. If so, what might be the compressive strength of the resulting composite? Conducting research into this would help with the future storage of CO_2 emissions by this system and the possibility of its use as a construction material.

2.3.2 Compressive Strength Characteristics of Biochar and Calcium Carbonate

This section explores literature on the compressive strength of biochar and calcium carbonate, respectively, when used with cement, to provide insight on possible compressive strengths for a mixture of biochar–calcium carbonate–cement in concrete. Standard concrete, a composite of Portland cement, sand, aggregate, and water, is essential in construction due to its high compressive strength and is an area of focus due to its ubiquity. However, this section will also cover variations on standard concrete, such as cement mortars and ultra-high-performance concrete.

Biochar has been shown to improve the compressive strengths of both cement mortars as well as standard concrete. In cement mortar, a 1–2 wt% addition of biochar from wood waste has been shown to improve compressive strength (76). Biochar prepared from wood waste at 500 °C and used as a 5 wt% cement replacement also demonstrates the filler effect (77) —the filling in of pores that is chiefly responsible for compressive strength enhancements. Han (78) also described how increases in water-cured cement mortar compressive strength at 28 days were found for 1% and 3% peanut biochar, which were similar to increases found in wood waste biochar. In concrete, the addition of greater amounts of biochar are possible while still resulting in compressive strength increases. For example, a study reported that the addition of 5% rice husk biochar and 5% bagasse biochar (for a total of 10% biochar) to concrete resulted in a 55% higher compressive strength than the control concrete (79). This strength increase was concluded to be dependent on the high surface area of the biochar used, with bagasse biochar having the higher surface area of the two types. The specific surface area was determined using the BET method (Brunauer–Emmett–Teller N_2 sorption) and values were reported in m2/g: the bagasse biochar was 52.3 and rice husk biochar was 37.5, compared to 0.32–0.38 for Portland cement. If other types of biochar can be made with similar specific surface areas, it might be possible to reproduce similar increases in compressive strength.

An examination of the benefits of pre-soaking biochar on the properties of the cement mortar containing it was made by Gupta and Kua (80). The authors found that pre-soaking biochar improves moisture retention and hydration, allowing for an increase in mechanical strength in the resulting mortar under wet and dry curing conditions. Pre-soaking biochar made from mixed-wood saw dust at 300 °C and 500 °C offered 40–50% higher compressive strength at 28 days than plain mortar, especially when being air-cured. Although pre-soaking is not an option when using ready-mix concrete, it is an option during the manufacture of precast concrete products as well as during the preparation of mixes for concrete 3D printing.

Biochar has also been shown to be usable with ultra-high-performance concrete (UHPC), which differs from standard concrete in having extremely high compressive strengths. A study of biochar in UHPC, otherwise made from a combination of ordinary Portland cement, silica fume, quartz powder, silica sand, and a polycarboxylate-based superplasticizer, demonstrates what is achievable for compressive strength despite the strength reductions associated with high degrees of biochar used as cement replacement in UHPC (40). In this study, smaller particle sizes of sawdust-derived biochar (<125 µm) were found to yield higher compressive strengths than larger particle sizes at each of 1, 7, and 28 days of curing for the concrete.

Regardless of size, all samples were lower in compressive strength than the control which contained no biochar. However, at no time between 1 and 28 days did any of the samples have lower than a 40 MPa compressive strength, and at the end of 28 days the sample of lowest compressive strength, an 8% cement replacement sample, tested at 105.1 MPa. Additionally, fine biochar (<125 µm) at a 5% cement replacement rate was comparable in compressive strength (144 MPa) to the control mix (150 MPa) when measured at 28 days. This finding, that biochar can be used with UHPC to yield compressive strengths greater than those of standard concrete made with Portland cement, raises an important possibility. That is, a hybrid of UHPC and a high-biochar Portland cement might be made to preserve the material properties of standard concrete while maintaining high carbon storage. Using biochar in such high-performance concretes has already been suggested to reduce the demand for both Portland cement and silica fume (77). However, replacing sand in cement mortars with biochar at 10, 20, and 40 wt% sand replacement rates has been found to reduce compressive strength from 43 MPa (control) down to 34, 30, and 25 MPa, respectively (81). This was explained by the addition of water during composite production, which increases the porosity as more biochar is added, thus decreasing compressive strength (81).

Calcium carbonate, by comparison, has a rather low compressive strength, but is still able to find good use in concrete in the form of "whiskers" (82), needle-like single crystals of calcium carbonate that improve compressive, tensile, and flexural strength (83), akin to the mechanical advantages offered by trabecular bone [(84), (85)]. As an example of these improvements, an addition of just 1.5% calcium carbonate whisker which can be produced at a cost of USD 236 per ton (USD 214 per tonne) led to a 12.60% increase in compressive strength of a cement mortar (86). Adding such whiskers to cement mortars also improves compressive strength by providing high temperature stability, though only up to a maximum temperature of about 800 °C. That is because this is the temperature at which calcium carbonate starts to decompose; at this temperature, calcium carbonate whisker degradation inside a cement mortar creates pores that then causes a decrease in compressive strength (35).

In aggregate form, calcium carbonate also improves compressive strength under high temperatures. Concrete compressive strength in general suffers at high temperature, but this depends on the type of aggregates used, with limestone aggregate concrete faring better than standard siliceous aggregate concrete until 800 °C, at which temperature concrete of both aggregate types deteriorates irreversibly (87).

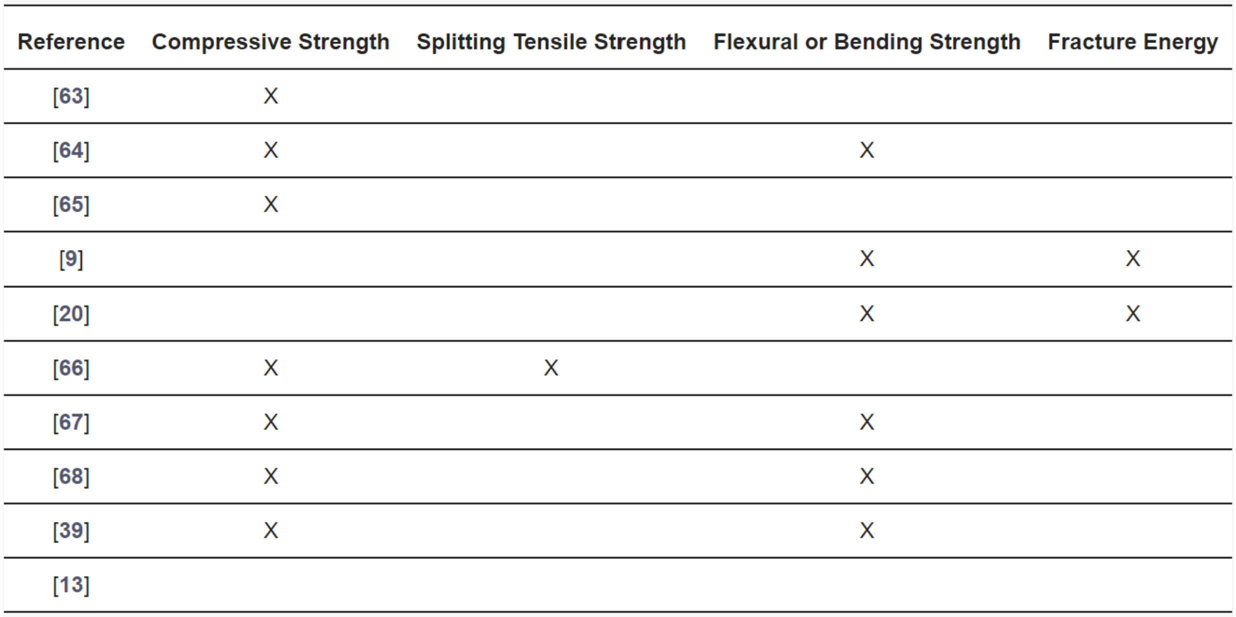
Calcium carbonate in different size ranges can also have different effects on concrete. While particles above 1 mm grain size act primarily as inert filler and can be counted as aggregates, particles below 1 mm grain size affect the hydration process, mechanical properties, and durability through four effects: filler, dilution, nucleation, and chemical (87). Furthermore, if limestone powder is to be added to a cement mixture, the presence of some nano-calcium carbonate seems to enhance compressive strength, as evidenced by a 15% limestone powder mixture exhibiting lower compressive strength than a 14% limestone powder and 1% nano-calcium carbonate mixture (88).

The literature has described how both biochar and calcium carbonate, when used separately with cement, are able to offer high compressive strength. Therefore, using both biochar and calcium carbonate with cement as a carbon storage medium and subsequently using it as concrete replacement material for construction would be worth exploring.

2.3.3 Additional Performance Characteristics of Biochar and Calcium Carbonate

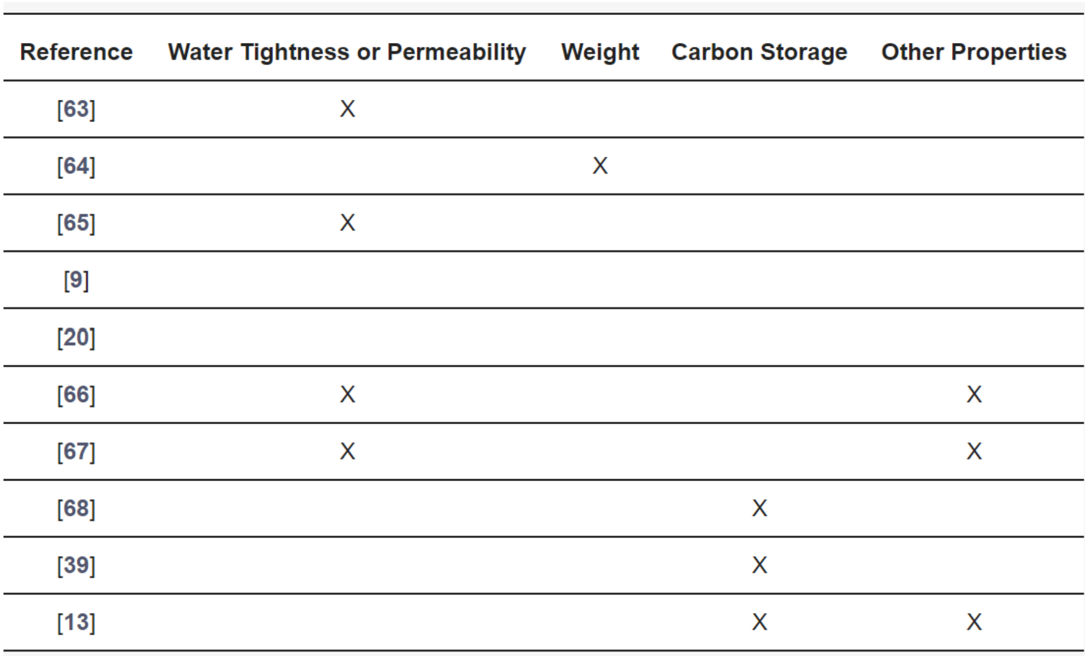
This section goes beyond compressive strength to offer a look at other performance characteristics when biochar and calcium carbonate are used in cement mortars and concretes. These include additional strength measurements, fracture resistance, water tightness/permeability, weight, and other properties such as albedo, thermal impacts, and electrical resistivity. The findings are summarized in Table 1 and Table 2 and are described next.

Table 1. Strength performance characteristics of biochar and calcium carbonate.



Reference	Compressive Strength	Splitting Tensile Strength	Flexural or Bending Strength	Fracture Energy
[63]	X			
[64]	X		X	
[65]	X			
[9]			X	X
[20]			X	X
[66]	X	X		
[67]	X		X	
[68]	X		X	
[39]	X		X	
[13]				

Table 2. Additional performance characteristics of biochar and calcium carbonate.



Reference	Water Tightness or Permeability	Weight	Carbon Storage	Other Properties
[63]	X			
[64]		X		
[65]	X			
[9]				
[20]				
[66]	X			X
[67]	X			X
[68]			X	
[39]			X	
[13]			X	X

Wood waste biochar findings: Gupta, Kua, and Pang (89) reported that adding 0.5 to 1% biochar from wood waste pyrolyzed at 500 °C increased concrete compressive strength at 7 and 28 days compared to the control by 15–20%. This was due to the filler effect as well as a reduction in the effective water–cement ratio from the biochar. At elevated temperatures, addition of 1–2 wt% of this biochar leads to lower damage to the concrete microstructure and a 22–25% higher residual strength and water tightness compared to the control mix. Sirico et al. (38) described how, for wood waste biochar made at 700 °C, the addition of 2 wt% biochar was the most suitable for use as filler in cement paste mixtures, improving flexural strength and fracture energy by acting as a micro-reinforcement in the cement paste that deflects the trajectory of fractures and creates multiple fractures instead. Additionally, for mortars, 2.5 wt% biochar was found to be optimal; anything more hindered the casting process and required a greater amount of superplasticizer than recommended. Suarez-Riera, Restuccia and Ferro (49) examined using 2% wood waste biochar (with respect to cement weight) as a filler and cement substitute. This yielded a flexural strength increase of >15% and a fracture energy > 150% at 7 days.

Water curing: Kovács, Pokorný, Šál, and Ševčík (90) reported on the underwater curing of cement pastes containing biochar. For cement pastes cured underwater for 27 days, a gradual decrease in bending and compressive strength with the increasing replacement of Portland cement (up to 20 wt%) was observed, alongside significant lightening in the mass of the produced pastes. For a 5 wt% incorporation of biochar, compressive and bending strength were reduced only slightly compared to the reference sample (a reduction of 5 MPa in compressive strength and a reduction of 2 MPa in bending strength). Additionally, Mrad and Chehab (91) found that when biochar is cured in water instead of air at 28 days, there was a significant drop in compressive strength. This was because the biochar continued to absorb excessive amounts of water, taking it away from the mortar. Under air-curing conditions, the biochar was only partially saturated prior to its inclusion within the mix. This allowed water to be taken up. Compressive strength decreases slightly as biochar content rises to 10 wt%. Both 5% and 10 wt% biochar worked similarly.

Pervious concrete: Qin, Pang, Tan, and Bao (92) studied how pervious concrete (a highly porous material allowing water to pass through directly for runoff reduction and water purification) sees an increased level of water absorption as biochar content increases. It is feasible to replace up to 6.5% of cement with biochar without suffering declines in compressive and splitting tensile strength. The use of 6.5% biochar in the cement paste can also decrease the albedo by 0.05. The result at 6.5% biochar is an albedo comparable to an aged asphalt pavement. Under sunlight at noon, this 0.05 drop (from 0.168 to 0.119) could make biochar-containing concrete about 1.0 °C hotter than conventional pavements, though this was deemed acceptable by the paper. The albedo was found to decrease linearly with the biochar content. Additionally, Tan, Qin, and Wang (93) found that for pervious concrete, a 1–3 wt% addition of biochar will improve the compressive and flexural strength, but these strengths will be compromised at higher percentages. The water absorption capacity of pervious concrete gradually increases with increasing biochar content. Furthermore, although there is more solar radiation absorption due to albedo, this heating can be offset by the extra absorbed water via evaporative cooling. Pervious concrete containing biochar has a max temperature reduction of 10 °C due to evaporative cooling.

Carbon content: In Falliano et al. (94), the percentage of biochar in 3D-printable cement mortars varied from 5 to 22% of the cement weight. Superplasticizer was also used, not to obtain a low-viscosity concrete but to reduce the water/cement ratio in the presence of biochar. The superplasticizer amount varied from 0 to 12% of the cement weight. Tap water varying from 27 to 51% of the cement weight was also used. It was possible to reduce the carbon footprint by 43% while maintaining mechanical strength at very high values (compressive strengths > 60 MPa and flexural strengths > 8 MPa). Legan, Gotvajn, and Zupan (65) concluded that biochar dosages from 0.5 to 24% increased the strength of cementitious materials, but a higher content of biochar up to 40% decreased flexural strength. Furthermore, replacing sand with biochar in concrete resulted in decreased compressive strength. Mortars with CO_2-unsaturated biochar had better mechanical and physical properties than mortars with CO_2-saturated biochar. Additionally, Haque, Khan, Ashraf, and Pendse (42) found that, due to the high carbon content (~80 wt%) of their super-hydrophobic carbonaceous biochar-containing powder, the electrical conductivity of their mortar samples increased by 23%. This made the mortar piezoresistive—the resistivity and applied stresses were linearly correlated. This opens the possibility of being able to perform real-time monitoring of the stresses in the material through electrical-resistance measurements.

2.3.4 Potential Benefits of Both Materials in a Carbon Storage System

The interaction between biochar and calcium carbonate with cement has not been well explored, despite the reported co-occurrence of biochar and calcium carbonate in other studies not involving cement. One of these studies is an article on a calcium-based magnetic biochar, using calcium carbonate as the calcium source (23). Another is the use of calcium carbonate to stabilize biochar for longer residence times in soil (95). This latter article points to the possibility that calcium carbonate and biochar together might result in greater long-term stability of carbon storage. It also indicates how both materials, when used together in cement, might result in a composite with improved properties compared to the single materials alone. One paper does suggest that the carbon storage and compressive strength of cement can be improved through the combination of biochar and calcium carbonate (96). Notably, it features the addition of biosilica, a biologically derived form of silica which is a UHPC ingredient. The paper demonstrated that a combination of 15 wt% biosilica, 5 wt% biochar, and 15 wt% of calcium carbonate in OPC improved the performance of cement. This provides evidence that a hybrid concrete with biochar, calcium carbonate, and UHPC ingredients might also permit the compressive strength and fatigue properties of standard concrete to be maintained while significant carbon storage is added.

Such a hybrid concrete appears to be a possibility given available published data. The highest three points below belong to UHPC mixtures with low rates of cement substitution with biochar (40). The lowest point belongs to a carbon-negative standard concrete with a high rate of aggregate substitution (30 wt%) from biochar (37). All four points denote 28-day strength, and the four points appear to have a linear relationship as shown in Figure 4.

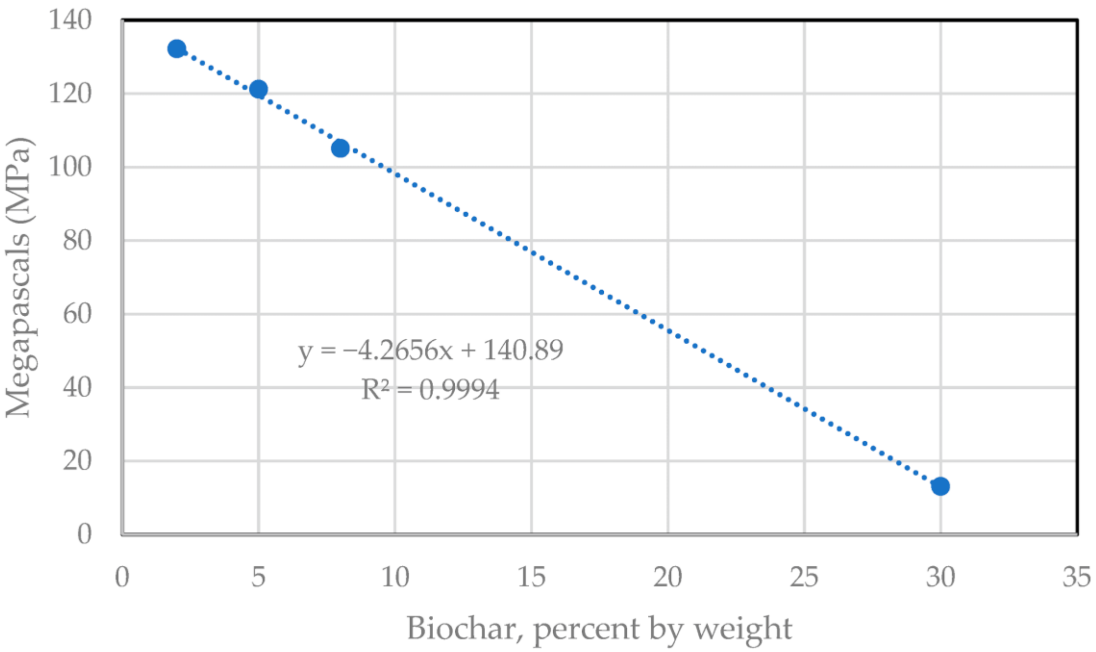


Figure 4. Data from two studies describing 28-day compressive strength variation with biochar wt% in a UHPC.

If a linear relationship is indeed present after collecting additional data, it could be that carbon neutrality might be achievable with a structurally useful compressive strength of approximately 34 MPa. A starting point for such a mixture would be 25 wt% biochar, 20 wt% Ordinary Portland Cement (OPC), and 10 wt% supplementary cementitious material (SCM). This estimate is based on LCA results reporting that 30 wt% OPC emits 408 kg CO_2/tonne, and that 10 wt% biochar can sequester 119 kg CO_2/tonne (37). This also assumes that SCMs are responsible for no more than 25.5 kg CO_2/tonne; if this is not the case, carbon neutrality will be reachable at a compressive strength lower than 34 MPa.

2.4 Obstacles to Scaling the Use of Carbon-Neutral Concrete

Scaling the use of carbon-neutral concrete might be the most important and cost-effective strategy at our disposal to meet our climate goals. Kelemen et al. (97) describe how it will be essential to permanently sequester about 10 gigatonnes of CO_2/year by mid-century, and roughly twice that amount each year by 2100. Unfortunately, the cost of ex situ carbon mineralization using minerals such as olivine is 10× higher than in situ methods such as CO_2 injection and sequestration into subsurface reservoirs (97). Given that geologic storage for CO_2 is neither widely located in all geographies nor plentiful, it would be beneficial to focus attention on CO_2 storage forms that are plentiful, such as concrete. Another benefit of the widespread use of carbon-neutral concrete is its ability to help create a cleaner cement and construction industry without a dependence on the simultaneous growth of the carbon capture, utilization, and storage (CCUS) industry. Tanzer et al. (98) describe how direct CO_2 emissions from the cement industry from fossil sources were 2.3 gigatonnes in 2019, while the status of CO_2 capture in that industry was still in demonstration stage, only capturing up to 75 kilotonnes/year. Demonstration plants capturing 400–600 kilotonnes CO_2/year were under development, but clearly there is a shortfall in CCUS capability.

This section covers four obstacles to scaling the use of carbon-neutral concrete: (1) a lack of sufficient architectural codes and standards addressing carbon footprint reduction through the use of carbon-negative materials such as biochar within concrete; (2) a resistance to change caused by uncertainties and delays; (3) the availability of necessary materials; and (4) cost.

2.4.1 Revising Architectural Codes and Standards

Architectural codes and standards govern which materials can be used by the construction industry, and how; these are presently in great need of revision to incorporate carbon-neutral concrete. Presently, contractors and engineers must use conventional concrete to abide by engineering codes and ethics (99). An important prerequisite for updating these codes to include carbon-neutral concrete is a simple, reliable definition of a building's carbon footprint, which is needed to measure the impact of using a carbon-neutral concrete. However, there has been difficulty in doing this.

Cabeza et al. (100) describe a difficult element in calculating a building's carbon footprint: embodied energy. They define embodied energy as the energy used during all processes of production, on-site construction, and final demolition/disposal. They also define operating energy as the energy used to maintain the inside environment (heating/cooling, lighting, operating expenses). Together, the sum of embodied energy and operating energy equals the total life-cycle energy. Although this is clear, the relationship between embodied energy and carbon footprint of a building is less so. Furthermore, they describe how embodied energy is difficult to quantify and how there is no generally accepted methodology for its measurement or calculation.

In cases where agreement can be reached on the calculation method of embodied energy and embodied carbon, it is then possible to compare different methods and to draw conclusions about construction methods likely to lower a building's carbon footprint. Minunno et al. (101) examined the embodied energy and carbon of concrete structures compared to timber and steel construction and found that concrete structures are preferable over timber and steel structures from an embodied energy standpoint. Specifically, timber structures ranged from 2.3 to 5.5 GJ/m^2, steel structures ranged from 1.4 to 6.5 GJ/m^2, and concrete structures ranged from 0.3 to 8.4 GJ/m^2, though most of the concrete structures examined fell within 1.1–4.6 GJ/m^2. For embodied carbon, timber was found to be the more environmentally friendly material (−445.6 to 333.5 kg CO_2-eq/m^2), with a negligible difference between concrete and steel structures regarding embodied carbon.

Despite the successful use of GJ/m^2 for embodied energy and kg CO_2-eq/m^2 for embodied carbon, the authors in (101) suggested new functional units for embodied energy and carbon that effectively divide the above units by the specific strength of the material. The resulting new units are MJ/(kN*m) for embodied energy, and for embodied carbon, kg CO_2-eq/(kN*m). While there are advantages to the new units, they may be less intuitive given that the denominator is no longer associated with a building's total floor area.

2.4.2 Uncertainties and Delays Create Resistance to Change

Habert et al. (102) describes several key obstacles to scaling the use of CO_2 storage in concrete used within building materials:

(1) Legal issues in determining which stakeholder will have to carry the risk associated with CO_2 storage. Such an uncertainty can greatly delay large-scale implementation of carbon-neutral concrete.

(2) Lack of incentive for adoption. If specifications are based on material formulations or recipes (the most popular approach in standards worldwide) or on technical performance (strength and fluidity) and not on environmental performance, there will be no incentive for concrete producers to propose environmentally friendly mix designs.

(3) Lack of incentive for optimization. Without a request from clients or national/regional policies to require materially efficient structural designs, design teams have no incentive to optimize their structure.

(4) Lack of supply chain education and communication. Time constraints, fragmented supply chains, and lack of awareness were also cited as barriers for implementation.

2.4.3 Material Availability

Most biochar is presently used in soil applications, but this may change as biochar use in carbon-neutral concrete begins to scale. There have been studies indicating that biochar application within soil can increase CO_2 emissions from the application site (103). In one such study, a statistically significant increase of 28% in CO_2 emissions was found, calling into question the ability of the applied biochar to sequester carbon. Notably, this increase was attributed to the ratio of biochar C to soil organic carbon (SOC) and the albedo impact of biochar. When $C/SOC > 2$, a significant increase in CO_2 emissions was observed, but not when the ratio was less than 2. Such a problem does not exist in cement mortar. This is a reason why the use of biochar in carbon-neutral concrete might be prioritized over its use in soil.

2.4.4 Cost

The use of carbon-neutral concrete must make strong economic sense before it can scale; the added value must outweigh the costs. Carbon-neutral concretes can be designed with high performance in mind, offering greater value with respect to cost. For example, Makul (104) describes the advantages and drawbacks of RPC, which has the same elements as UHPC (cement, sand, quartz, and silica fume) but in an advanced state, along with superplasticizer and steel fibers. Average compressive strengths range from

200 to 800 MPa, offering great value. However, its cost is high because traditional concrete's less expensive constituents are substituted or completely removed in favor of more expensive ingredients (sand vs. aggregate, silica fume vs. cement). The cost of a carbon-neutral RPC could be lowered by replacing expensive ingredients such as silica fume with less expensive ingredients, ideally biochar.

Roberts, Gloy, Joseph, Scott, and Lehmann (71) describe how the primary costs of biochar production are feedstock collection and pyrolysis. Transport and biochar applications have relatively small contributions during production. For transportation, at 1000 km the net GHG emission reductions decrease by 28% to −626 kg CO_2-eq/tonne dry feedstock. Thus, biomass sources with a need for waste management (such as yard waste and tree cutting waste) will have the highest economic profitability potential, limited by the transportation distance for feedstock (71).

Another problem is that the production of different feedstocks will create widely variable prices for biochar, making it difficult to settle on one price for use in carbon-neutral concrete. Mensah et al. (45) describe how it costs USD 266 to produce a tonne of poultry litter biochar. However, they also quoted the market price of biochar at 184 USD/tonne. Adding transportation and application costs for biochar caused the price/tonne to range from USD 222–584. This variation depended on the pyrolysis scale and the quantity of feedstock consumed.

2.5 Research Directions

The study of biochar and calcium carbonate in carbon-neutral concrete and how it can scale to meet climate goals is still a very new field worthy of further research. Of all the carbon dioxide removal (CDR) areas discussed in the 2021 critical review by Terlouw et al. (105), there was only one mention, under "other promising CDR technologies", about the use of infrastructure to store CO_2. Timber use and concrete carbonation were both cited as examples, but not the use of carbon-negative materials such as biochar within concrete infrastructure. This ignores the finding that if less than 1% of biochar by weight of concrete were included in concrete materials, 0.5 gigatonnes of CO_2 could be realistically sequestered every year by the modified concrete, an amount equivalent to ~20% of the annual total emissions of CO_2 produced by the cement-based industries (70). In China alone, where most of the Earth's concrete is manufactured, Yang et al. (106) found that over 920 kg CO_2-eq could be sequestered through the conversion of 1 tonne of crop residues into biochar. Based on crop residue availability for China in 2014, the estimated annual carbon sequestration potential in China could be as high as 0.50 gigatonnes CO_2-eq from this method alone. A difference with the use of biochar in concrete is that there is no crop yield for the trapped biochar to promote. Thus, the following figure of −870 kg CO_2-eq/tonne dry feedstock from Roberts et al. (71) derived from corn stover and yard waste biochar might be more accurate since they did not incorporate the promoting effect of this biochar on crop yield.

The key areas of further research within this section are as follows: 1) a thorough exploration of the material properties of biochar–calcium carbonate–cement composites and their impact on compressive strength and carbon storage, 2) creating a comprehensive model featuring the properties of individual materials within carbon-neutral concrete and their interactions, 3) examining long-term durability of carbon-neutral concretes in a variety of harsh conditions, 4) drawing upon life-cycle assessments for use in concrete mix optimization, 5) exploring enhancements to biochar's CO_2-adsorbent ability through functionalization, and 6) developing strategies to overcome economic and social obstacles to scaling the use of carbon-neutral concrete. Additionally, Akinyemi and Adesina (70) highlight the following research efforts which will be rather useful: 1) regulating pyrolysis conditions, 2) developing biochar aggregates to make a more lightweight concrete, 3) developing a nano-biochar to enhance cement composites, 4) understanding durability of biochar–concrete composites, and 5) using biochar for accelerated carbonation given its CO_2 adsorption capability.

2.5.1 Continued Exploration of Composite Material Properties

There are many factors that can affect the properties of composite materials such as carbon-neutral concrete, and such factors are worthy of continued exploration. According to Restuccia et al. (107), there is not currently an ideal mix design for the use of biochar, since it comes from different raw materials and production plants with different characteristics. Furthermore, the curing conditions of the cement-based specimens influence the benefits of incorporating biochar. Lastly, any treatment of the biochar particles (sieving, grinding, pre-soaking) prior to their addition to the cement/concrete can also lead to different results. This was realized in their study—the percentages of biochar addition that led to the best results for flexural strength and fracture energy were not the percentages found in previous studies, perhaps because of the different production processes for different biochars as well as different biomass sources. This variation in performance can be challenging when it comes to broad adoption within ready-mix concrete where the mix is periodically changed for specific concrete jobs. Consistency is extremely important for ready-mix plants and therefore the use of standardized biochar–calcium carbonate concrete mix formulations is critical.

If carbon-neutral concrete is to be fiber-reinforced, the following studies can provide insight on the best means of doing so, as well as provide suggestions for additional research directions. Gupta, Kua, and Cynthia (64) explored using biochar as a coating on polypropylene (PP) fibers to improve the mechanical properties and permeability of mortar. The biochar was from wood saw dust pyrolyzed at 300 °C, with or without being saturated with CO_2 prior to applying it as a coating. The fresh biochar coating offered the best performance in terms of a significant improvement in compressive and flexural strength of mortar. Coating fresh biochar on PP fibers makes the surface hydrophilic rather than hydrophobic, and thus the PP fibers were more stable in the wet mix. This reduced the agglomeration of fibers, which is a factor in reducing the strength of fiber-reinforced cementitious composites. The biochar coating also roughened the PP fiber surface, improving the anchoring of fibers in the mortar matrix. CO_2-saturated biochar, on the other hand, added as a coating lowered both the 7- and 28-day compressive strength. This was due to carbonation induced by the CO_2 molecules adsorbed by the pores of the biochar particles. The CO_2 reacted with the portlandite or C-S-H, compromising the bonding of fibers. Carbonation is typically very slow, but it was observed quickly since the CO_2 source was coming from inside the mortar (i.e., the saturated biochar) rather than from the atmosphere. Furthermore, Kua et al. (108) showed that when polypropylene (PP) fibers used in reinforcement were coated with CO_2-dosed biochar, there was a 13 and 16% reduction in compressive and flexural strength. Fibers not saturated with CO_2 had an improvement of 19% for both compressive and flexural strength when compared to control samples containing PP fibers not coated with biochar. This was suggested to be due to the filler effect, strengthening the bond between the PP fiber surface and the mortar matrix. This paper also highlighted the potential usefulness of biochar as a carbon sink as well as a strength enhancement for cement mortar.

Further research can also be conducted on the chemical modification of carbon-neutral concrete. For example, Haque, Khan, Ashraf, and Pendse (42) describe how chemo-mechanically modified biochar (using stearic acid) was used to create a super-hydrophobic carbonaceous powder (SHCP) that could partially replace (up to 15 wt%) OPC in paste and mortar samples. This caused up to a 70% reduction in the rate of water absorption while accelerating cement hydration due to the fine particle size distribution of the SHCP. However, most chemical modifications cannot be performed without affecting one or more material properties through a number of possible interactions. The next research direction below will cover this in greater detail.

2.5.2 Important Material Properties and Interactions to Model

This section describes 16 reported interactions between material properties, many of which contain multiple interactions between multiple properties. If each property is represented as a node, edges can be drawn between them, one for each interaction between respective properties. The result would be a graph network that can be weighted according to the number of sources found for each interaction/edge. Such a graph network could be used as the backbone of a comprehensive model for predicting the compressive strength and carbon storage of carbon-neutral concretes.

Other modeling methods exist and can be employed alongside the above. For example, Liu et al. (109) described a pore-connectivity-changing model to predict how carbon capture ability would improve in biochar-containing cementitious composites. This model works with water-to-cement ratios of 0.25–0.4 and demonstrates improvements of biochar on carbon capture ability from 10% to 148%. A layered structure compared to an even structure also leads to a 44% increase in compressive strength and a 28% increase in three-point flexural strength when a W/C ratio of 0.25 is used. Such a layered structure may be good for improving compressive strength, but it is likely unworkable for ready-mix applications, except for possibly the 3D printing of concrete. Pre-cast applications might be able to take advantage of this. Lastly, Boumaaza et al. (110) developed ANN (artificial neural network) and RSM (response surface method) models designed to provide much useful information with the least amount of test mixtures—these have been effective in predicting flexural strength, displacement, and flexural modulus. Between the two, the ANN model outperformed RSM by an R^2 of 0.9980 (110). It would be ideal to apply this or other models to the data in Table 1 of (111) to better understand what improvement in CO_2 storage might be expected when including biochar-based CO_2 adsorbents in concrete.

The 16 reported interactions between material properties which can be investigated in future research work are as follows:

Concrete Shrinkage vs. Expansion—Effects on Carbon Storage and Strength: Ye et al. (112) describe a balance between shrinkage and expansion that affects both carbonation capacity as well as strength performance of the concrete. There is typically a shrinkage during carbonation in mortars made with plain OPC. However, there is an expansion in OPC with alkali enrichment. Thus, a volume change in OPC due to carbonation can occur, a balance of shrinkage induced by dissolution and expansion induced by crystallization.

Pyrolysis Temperature, Volatile Matter, and Carbon Storage: Mensah et al. (45) demonstrate that higher pyrolysis temperatures were found to decrease the amount of volatile matter in the pores, leaving behind the carbon. Figure 1 of (45) shows that for wood, straw, green waste, and dry algae, volatile matter content, which is at 70–80 wt% at 350 °C, drops to 20–30 wt% at 450 °C and continues to drop, but not as quickly, when 600 °C and 800 °C are reached.

Pyrolysis Temperature, Porosity, Moisture Retention, and Concrete Shrinkage: Wang et al. (21) created biochar blocks produced at 500 °C and 700 °C, and the higher temperature one had larger pores (due to removal of volatile matter) and higher specific surface area to facilitate increased bonding due to increased matrix infiltration. However, this also increased the moisture retention ability of the mortar, which can reduce the risk of concrete shrinkage.

Cement and Water Content, Aggregate Packing/Shape, Porosity, Additives, Admixtures, Carbon Storage: Javadabadi and Baghban (113) elaborate on the importance of optimizing concrete mix design for the development of sustainable concrete. Important components to such a design are the amount of cement, water-to-binder ratio, aggregate packing, additives, and admixtures. As the amount of water increases, particles move more easily but too much water will lead to density stratification, with heavier/larger particles falling to the bottom. Aggregate packing is also important—if there are too few fine aggregates and too many coarse aggregates, there is a larger void fraction in the concrete mix. Aggregate shape is also important—rounded grains will slide more easily onto another, but angular grains tend to stick to each other, reducing mass movement and workability. With good aggregate packing, the amount of cement can be reduced; its use is to bind the aggregates together and fill voids, so fewer voids = less cement = less CO_2 emissions.

Compressive Strength, Cumulative Heat of Hydration, Water Content: Gupta and Kashani (114) found strong positive correlations (R2 = 0.96 and 0.94 at 3-day and 7-day ages, respectively) between compressive strength development and cumulative heat of hydration (J/g of binder). This finding suggests that a higher rate of hydration in biochar–cement pastes contributes substantially to compressive strength development; however, this may only be applicable to high water–binder ratio (W/B > 0.40) cementitious composites because there, the total heat evolution is consistent as W/B increases. Lower W/B composites would have a lower heat release at later ages due to self-desiccation and less space for hydration products.

Particle Size, Porosity, Pore Structure Connectivity, and CO_2 Adsorption: Liu, Xiao, Guan, Zhang, and Yao (109) describe how biochar particles offer a filler effect while coarser biochar particles allow resulting building materials to have a higher porosity and pore structure connectivity. The larger size of biochar particles, coupled with the larger pores in the larger-sized biochar, helps explain why larger biochar sizes improve CO_2 capture.

Water and Pozzolan Content; Aggregate Size/Texture/Shape/Roughness/Porosity: Mrad and Chehab (91) describe how the additional water offered by biochar over the curing process promotes pozzolanic reactions where the aggregates and cement paste meet, thus strengthening the bond between the two interfaces. Important properties governing bond strength between these interfaces are the size, texture, shape, roughness, and porosity of the aggregates.

Particle Size, Water Permeability, Hydrophobicity, Durability, Compressive Strength, and Carbon Storage: Haque, Khan, Ashraf, and Pendse (42) found that a low permeability improves the resistance of the composites against chemical attack by detrimental ions, and thus improves the durability of the composite. This was likely due to the fine particle size and the super-hydrophobic nature of the particles (SHCP) they used in their study, which served to block pores in the mortar to reduce the moisture permeability. However, the lower permeability came at the cost of performance: incorporation of SHCP caused gradual decreases in both compressive and flexural strength upon increasing SHCP addition from 2.5 to 15%. The addition of 2.5% SHCP did not have any significant effect on the mortar compressive strength and was associated with an embodied CO_2 reduction in the binder mix (OPC + SHCP) by 10%.

Pyrolysis Temperature, Surface Area, Chemical Stability, Low Flammability, and Carbon Storage: Akinyemi and Adesina (70) examine how pyrolysis temperatures affect chemical stability. Chemical stability of biochars in cementitious materials is likely enhanced using fast pyrolysis at 800 °C due to higher carbon contents, aromaticity of the feedstock, and increased surface area needed for sorption while reducing reactive oxygen and hydrogen volumes. Reducing these reactive zones leads to better chemical stability and minimizes the occurrence of destructive chemical reactions when mixed with cementitious materials. This finding points out a tradeoff for the use of biochar-containing concrete in buildings. Low flammability is desirable (115) but so are higher carbon content and higher CO_2 sequestration. However, higher temperatures are needed to deliver the higher carbon content, which also uses more fuel, which reduces CO_2 sequestration.

CO_2 Adsorption, Surface Area, Pyrolysis Temperature/Rate, Pressure, Porosity, Quantity of Biochar Produced: Gupta and Kua (116) indicate that CO_2 adsorption capability is determined by the structure of biochar, particularly its total surface area. This is affected by pyrolysis temperature, pyrolysis rate, and pressure. Temperature is important since it affects volatile release, formation of the carbon skeleton, formation of pores, and widening of pores. Pyrolysis rate and pressure govern the mass transfer of volatiles at a particular temperature. However, at higher temperatures, biochar does undergo a secondary reaction increasing the yield of gas and liquid and decreasing the actual proportion of biochar. For example, in pine undergoing slow pyrolysis at 300 °C a 58% char yield is possible. At 450 °C under the same conditions, the char yield is 26%. Corn stover biochar made at 500 °C has a char yield of only 16.80.

Pyrolysis Temperature, Surface Area, Porosity: Gupta and Kua (116) found that too-high a pyrolysis temperature can cause a loss of structural complexity—this happens in a pronounced manner when the pyrolysis temperature is the same as the ash melting point of the feedstock. For pine, a decrease in biochar surface area was found at a pyrolysis temperature of 1000 °C. This is likely due to pore widening/coalescence with neighboring pores, and perhaps softening and melting.

Pyrolysis Temperature/Rate, Carbon Storage, Quantity of Biochar Produced: Gupta and Kua (116) also describe how the pyrolysis process not only affects the carbon content of different biochars but also the net amount of solid char produced instead of liquid or gaseous byproducts. In fast pyrolysis, the heating rate ranges from 100 to 1000 °C/s, causing thermal cracking, but produces about 15–25% biochar, with the rest being liquids and gases. In slow pyrolysis, there is a low heating rate (10 °C/min) between 300 and 700 °C. This produces more char, but the longer vapor residence time and lower heating rate provide an improved environment for secondary reactions. Fast pyrolysis biochars have lower carbon content and higher oxygen content compared to those produced by slow pyrolysis.

Low Flammability, Pyrolysis Temperature/Rate: Zhao, Enders, and Lehmann (115) describe how, although biochar does not qualify as flammable according to UN criteria, it can support a propagating combustion front of about 200 mm, which is important when it comes to the use of biochar-containing concrete in buildings, The presence of a propagating combustion front was much more likely for biochars made using fast pyrolysis (5 of 7 samples) than those made with slow pyrolysis (5 of 24 samples). More short-term flammability was also observed in biochar produced at higher pyrolysis temperatures compared with those produced at lower temperatures, but this short-term flammability reduced to negligible levels within hours, likely due to the removal of free radicals through reaction with air and the reordering of the carbon structure. Both reduce flammability.

Hydration, Porosity, Compressive and Flexural Strength: An advantage of biochar-containing concrete is the ability to use internal curing, as described by Mrad and Chehab (91). Internal curing consists of supplying a well-dispersed, water-saturated material throughout the hydrating Portland cement paste to increase the degree of hydration over time. This is as opposed to conventional curing, where the surface of the concrete is wetted after it is placed, allowing water to penetrate only a few millimeters down. High-porosity aggregates are most favorable for internal curing, and internal curing improves compressive and flexural strength of mortar, particularly at later stages. This occurs because the additional water offsets the empty matrix pore spaces created during the shrinkage that takes place at the early stages of hydration.

Heat of Hydration, Workability, Setting Time, Strength, Shrinkage, Permeability, Chemical Resistance, Serviceability, Sustainability: Al-Mansour, Chow, Feo, Penna, and Lau (60) also discuss ternary vs. binary concrete systems. In a ternary system, the goal is to obtain the most benefits out of each material and overcome the shortfalls of each material. Properties of concern are properties while fresh (workability, setting time, heat of hydration), when hardened (strength, shrinkage, permeability, resistance to sulfate attack), serviceability, and sustainability. The paper described some ternary systems with OPC and observations of how properties varied in those systems.

Carbon Storage, Hydration, and Compressive Strength: Gupta, Kashani, Mahmood, and Han (41) concluded that adding biochar to cement mortar has a positive influence on rapid carbonation and subsequent carbon sequestration. There is an initial loss in compressive strength after 7 days due to higher initial moisture loss from carbonation, but after 28 days, increased carbonate mineralization and a reduced depth of carbonation lead to a 24% improvement in compressive strength.

2.5.3 Examination of Long-Term Durability

There is already a relatively good understanding of the short-term (<180 days) mechanical performance of biochar-containing concretes, but there is very little literature on how these will perform when exposed to harsh environments with high salinity, high alkalinity, freeze–thaw conditions, high temperature, or high sulfates. Thus, Tan, Wang, Zhou, and Qin (50) have pointed out the need for additional studies examining the long-term durability of biochar-containing concretes. For example, any CO_2 captured in biochar could cause later concrete carbonation, which could cause corrosion problems for reinforced concrete. This and other interactions between biochar and other concrete admixtures also remain unknown.

In contrast to the potential detrimental effects of biochar on reinforced concrete in the long term, Gupta and Kua (117) found that sorptivity was also reduced by about 70% after 28 days, demonstrating how the addition of biochar can play a key role in promoting the durability and strength of concrete infrastructure. Furthermore, there are many undeniable short-term benefits: similar to many other papers, the authors report how up to a 4% cement replacement by biochar can yield a slight compressive strength improvement due to the fine particle size and microfiller effect of biochar. When both the short- and long-term benefits of biochar-containing concrete are examined, which include reduced vulnerability to damage and fewer repairs over its lifespan, it becomes clear how such concrete can promote the economic and environmental sustainability of buildings.

The incorporation of other materials besides biochar can also affect long-term durability. Rostami et al. (118) describe how shrinkage in fiber-reinforced mortars (and thus susceptibility to crack formation) can be counteracted by the use of superabsorbent polymers. A reduction in plastic shrinkage by 30–75% and a reduction in autogenous shrinkage by 30–124% occurred when superabsorbent polymers (SAP) were added. Furthermore, de Souza et al. (119) examined the effects on durability of incorporating graphene, a form of carbon-like biochar, into concrete. Graphene-based nanosheets (GNS) include graphene, graphene oxide, reduced graphene oxide, and graphene nanoplatelets. A very small addition of GNS (0.01–0.05% of the weight of the Portland cement) can impart >80% increases in compressive/tensile strength and >500% improvements in water-penetration resistance to the cementitious material. Though the total cost of graphene oxide-reinforced concrete might be ~2–7% higher than a reference concrete mix, the compressive strength/cost per m^3 was increased by 25–40%. This enhanced durability must also be factored in since this will lengthen the service life of the concrete, ultimately lowering costs over that service life.

2.5.4 Enhancing the Use of Life-Cycle Assessments (LCA) in Concrete Mix Optimization

The wider use of LCA may very well drive improvements in the way embodied energy and carbon are defined, measured, and ultimately used when revising architectural codes and standards for carbon-neutral concrete. Santos et al. (120) describe how LCA is crucial for optimizing mortars, which have many applications in modern construction and that are used throughout the service life of buildings. Using improved mortars can significantly reduce the embodied energy and embodied carbon in buildings. LCA aids such optimization by allowing users to research and select the best materials for their mortar mix, whether based on embodied energy, embodied carbon, or other environmental data. For example, Table 1 of Adesina (99) provides the embodied carbon for concrete constituents and indicates that, by far, the constituent with the highest embodied carbon is Portland cement at 0.83 kg CO_2/kg. Through the use of LCA software with such data, a user can design a carbon-neutral mix.

There are many software programs to aid in the performance of LCA; these will not be reviewed here except to mention how extensive their capabilities and data extents can be. An example of what goes into developing such a program is offered by Kim et al. (121), which discusses the development of a software program to assess GHG emissions incurred over the life cycle of a concrete product. Data collection, maintenance, and the frequency of updates are key to ensuring accurate LCA results.

System scope is also critical for performing an accurate and meaningful LCA, as demonstrated by the following example. Feiz et al. (122) examined the CO_2 performance of different ways of producing cement, in cooperation with the cement-producing company CEMEX. They found that cement products containing a large proportion of byproducts (such as GGBS from the iron/steel industry) had the lowest unit emissions of CO_2-eq. However, the authors also mentioned that the LCA results did not include any allocation of the impact from the iron/steel industry via the GGBS to the cement products.

2.5.5 Functionalizing Biochar with CO_2 Adsorbent Capability to Enhance Carbon Negativity

Biochar-based CO_2 adsorbents can improve carbon storage and minimize the amount of biochar needed to achieve carbon neutrality, which may be advantageous from a cost perspective depending on the balance of other ingredients within the concrete mix. There are four ways of activating biochar for CO_2 adsorption, as reported in (103): (1) physical, (2) chemical, (3) surface functionalization, and (4) heteroatom doping and metal/metal oxide impregnation. These can either be used alone or in combination. Examples of achievable increases in CO_2 adsorption after activation range from 1.9 to 4.4 mmol/g at 25 °C and 1 bar, with the maximum being 6.78 mmol/g at 30 °C and 1 bar for biochar impregnated with copper oxide (103).

Given the wide variety of biochar feedstocks, pyrolysis temperatures, surface areas, and CO_2 adsorption capacities possible, it is desirable to improve the understanding of how biochar-based adsorbents could be used for CO_2 capture. This was addressed by (111), which also indicated a good performance measure for CO_2 adsorption: the oxygen/carbon ratio (O/C). Both low H/C and O/C ratios (≤0.2) suggest a high amount of aromaticity and fixed carbon, which are chemically stable. White oak biochar had a very low O/C of 0.051, which was associated with high hydrophobicity, low polarity, and enhanced CO_2 capturing capability of biochar. Hydrophobicity and non-polar characteristics were also suggested as facilitators of improved CO_2 adsorption capacity due to lowering the competition of H2O molecules for the CO_2 adsorbing sites (111).

Another strong determinant of CO_2 adsorption capacity appears to be the closeness in biochar pore size to the kinetic diameter of CO_2 molecules. There are many routes to achieving this desired pore size, and a fruitful research direction would be to enumerate these and determine how these may interact. For example, Gupta and Kua (116) describe how biochar can be treated with potassium or sodium hydroxide to create a very high surface area useful for enhancing CO_2 adsorption. They also describe how treating biochar with low oxygen at 3–5% at a temperature range of 550–650 °C can produce micropores conducive for CO_2 capture under ambient conditions. The selectivity of those micropores is yet another factor for improving CO_2 adsorption. To make biochar select for CO_2 more than water vapor or nitrogen, the isosteric heat of adsorption for CO_2 must be much higher than that of N_2. A narrow pore distribution with diameters closer to the molecular diameter of CO_2 will do this. A doubling of the isosteric heat of adsorption for CO_2 over that of N_2 will make CO_2 adsorption dominant at room temperature and pressure. A CO_2 adsorption of 4.80 mmol/g at 25 °C was recorded for a KOH-to-biochar ratio of 2, yielding many narrow micropores (<1 nm diameter) at an activation temperature of 600 °C. During that 2-minute adsorption time, N2 adsorption was only 0.89 mmol/g, much lower than the CO_2 adsorption, which implies high CO_2 selectivity.

CO_2 adsorption can decrease at higher activation temperatures, likely due to reduced pore filling, as found by Gupta and Kua (116). Although higher temperatures yield higher surface areas, it may also produce pores that are larger than optimal. The kinetic diameter of CO_2 molecules is 0.33 nm and CO_2 adsorption by pore filling is reduced when pore diameters are much larger or smaller than this. With bamboo-derived biochar, a CO_2 adsorption of 7 mmol/g was measured. Additionally, four reuse cycles were performed at 25 °C with no regeneration loss. Further research might be performed on the effects of activation temperature and pore size on CO_2 adsorption.

2.5.6 Overcoming Economic and Social Obstacles to Scaling Carbon-Neutral Concrete

Reaching consensus on guidelines for CO_2 storage within concrete is important to promote the spread of carbon-neutral concrete. Habert, Miller, John, Provis, Favier, Horvath, and Scrivener (102) provide examples of such benchmarks from Europe that can help scale-up the use of concrete CO_2 storage. These include the following. For cement producers: tonnes CO_2/tonnes clinker < 0.7. For concrete producers: <3.5 kg clinker/m3/MPa for a standard 30–50 MPa concrete mix. For engineering offices designing concrete structures: <250 kg CO_2/m^2 floor area for the concrete allocated to the structure. For construction companies: <500 kg CO_2/m^2 floor area for the whole building.

Other future directions have been described by Adesina (99): (1) a high use of alkali-activated binders in developing countries due to abundant aluminosilicate precursors at those locations; (2) the use of more demolition and construction wastes in concrete to create a more circular economy; (3) standards development supporting the use of waste materials in concrete; (4) designing new concrete mixtures that use low cement; (5) significant use of alternative fuels such as biomass to offset the heavy use of coal and pet coke at present; (6) developing a carbon-neutral concrete construction process involving such techniques as CO_2 curing; (7) CO_2 management; (8) stricter policies regarding carbon footprints (environmental taxes, approval delays); and (9) incentives for green concrete use (grants, tax rebates, lower development fees).

Finally, since there is much more ocean on Earth than land, coastal and oceanic applications for carbon-neutral concrete are much more plentiful and thus worthy of further investigation. Pradhan, Poh, and Qian (66) suggest an important point if such concrete is to be used for seawater applications: the salinity of seawater is approximately 3.5%, translating into a 0.6 M NaCl solution. Thus, chloride tests should be conducted using similar concentrations of NaCl to determine the effects on long-term durability of carbon-neutral concrete used at sea.

2.6 Conclusions

Carbon storage has become a key aspect of dealing with greenhouse gases such as CO_2. Currently, many solutions are being explored to reduce the greenhouse effect caused by CO_2, with one being carbon capture and storage. In view of this, there is a need to develop higher-density, highly permanent forms of carbon storage, to reduce the volume required for storing captured CO_2.

A literature review was performed on production methods for carbon-neutral concrete, performance expectations, obstacles to scaling its use, and promising research directions for developing and scaling carbon-neutral concrete. Within this review, a focus was maintained on two high-density, highly permanent forms of carbon storage: biochar and calcium carbonate. These were considered separately in cementitious composites, and both were shown to perform with high compressive strength. The results of this literature review offer confidence that exploring a combination of biochar–calcium carbonate–cement for use within carbon-neutral concrete will be worthwhile.

The benefits of a successful exploration of a biochar–calcium carbonate–cement composite would be considerable. Not only might such a concrete-based carbon storage system be capable of holding all the CO_2 needed to be stored by carbon dioxide removal systems this century, assuming current trends in urban growth and development, but such a system would help reduce cement usage. This would reduce the need for clinker in cement manufacturing, thus directly reducing CO_2 emissions that result from limestone calcination during clinker manufacturing. Another benefit of this composite carbon storage system is in enabling the construction of structures with positive environmental and social impact. Even if a hybrid concrete is not used and the compressive strength is lower than the required standard for concrete, the material can still be explored for alternative structures which can still be of social benefit. It is therefore beneficial to research this composite material further with the goal of developing and scaling improved carbon-neutral concretes.

2.7 Research Impact

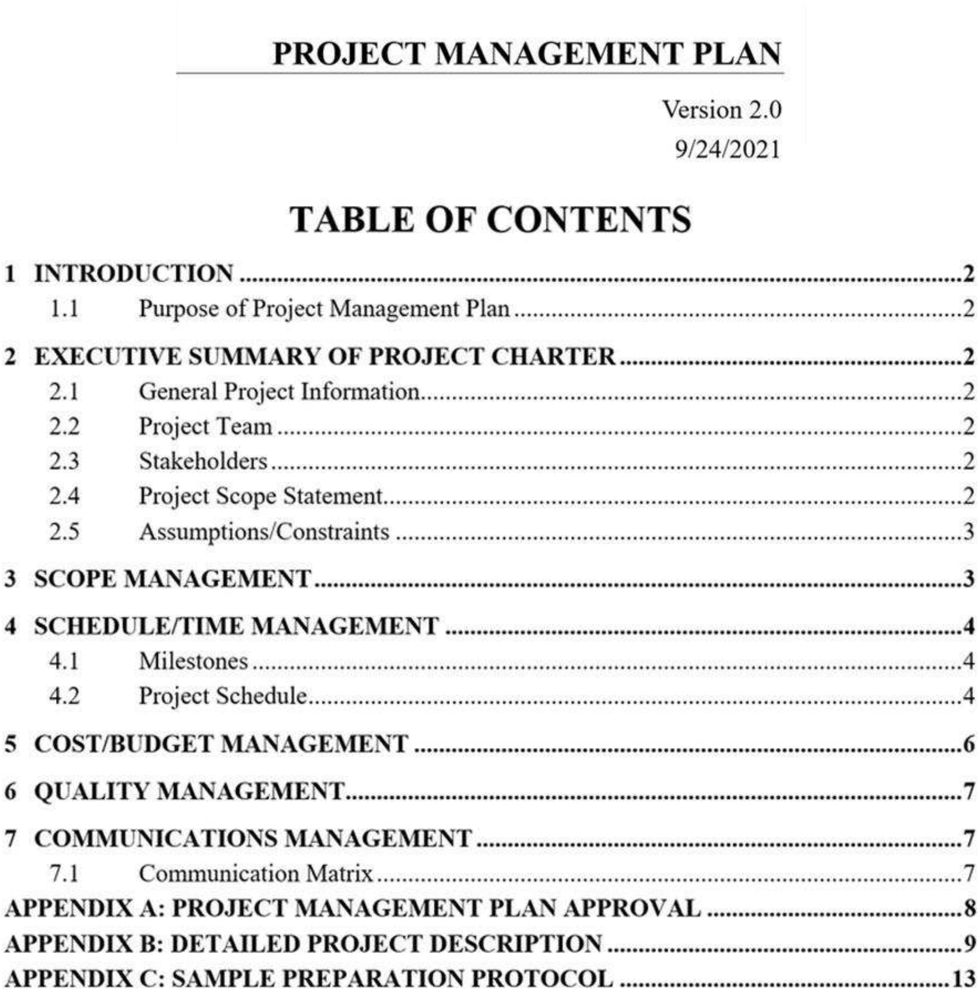
The literature review presented in this chapter was conducted in spring 2022 with findings published that April (16), having had as of today (October 28, 2024) 24 citations and 10,503 views. This review was cited within research on the mechanical performance of $CaCO_3$-containing ternary Portland cements (123), the use of AI models for compressive strength estimation of green concrete (124), the recycling of waste into green concrete in Poland (125), biochar from Saudi agricultural waste in Saudi Arabia to improve the strength and durability of concrete (126), in dynamics simulations studying carbonate mineralization (127), for the use of biochar and recycled carbon fibers in lowering the electrical impedance while raising the compressive and tensile strength, water absorption, carbonation, and chloride resistance of concrete, the latter which is useful for marine applications (128), the use of biochar to replace fine aggregates at 10, 20, and 30 vol% where aggregates make up about 70-75% of the volume, yielding higher compressive strength with or without CO_2 curing at any of the three biochar replacement levels (129). The CCUS potential of biochar-enriched cementitious systems is rather high give that the addition of 1% biochar yields a 42% increase in CO_2 uptake, while carbonated biochar mortars have a 64% increase in toughness due to the mineralization of calcium carbonate, leading to a denser and stronger cement matrix (130). These are only the first 9 citations. Research has continued to evolve to define what is possible in cement-based carbon storage systems.

CHAPTER 3: RESEARCH METHODS AND RESULTS FOR CEMENT–BASED COMPOSITES

The goal of this study was to characterize a cement-based carbon storage system that incorporated varying quantities of biochar and calcium carbonate and how its properties and potential uses might vary in different settings and applications due to the relationship found between compressive strength and carbon storage capacity. Such a study would be valuable toward predicting the strength and carbon storage attributes of carbon neutral concrete, even if the study focused on a cement-biochar-calcium carbonate composite without significant biochar or calcium carbonate for replacing sand and/or aggregate. This chapter describes the methods behind the research I conducted between mid-2021-early 2022 with Dr. Steven Simske and now Drs. Kwaku Boakye and Kevin Fenton. I performed the experimental design, sample preparation, data analysis, and report preparation on the findings. Testing was performed by Boakye at a Lehigh-Hanson laboratory. The results are shared at the end of this chapter.

3.1 Project Management and Experimental Design/Planning

A project management plan (Figure 5) was prepared along with a chain of custody form to enable sample preparation, testing, and subsequent analysis of results to be performed efficiently and with quality assurance by the project participants. The experimental design was determined using the Taguchi method to reduce the number of trials needed to determine and subsequently to quantify the variables of importance. Orthogonal arrays describing the amounts of components to be included in mixtures were obtained from the software, representing the experimental configurations to be used. Each of these configurations would contain a different amount of each of the three components for the BC+$CaCO_3$+cement composites, to be molded, allowed to cure over three different time periods, then tested for compressive strength. These configurations included the following 5 levels for each of the 3 components: 0, 1, 2, 3, and 4 wt% for BC, 0, 1.5, 3.0, 4.5, and 6.0 wt% for $CaCO_3$, and 0.3, 0.4, 0.5, 0.6, and 0.7 for the water-to-composite ratio. This was originally the water/cement ratio, but it was recognized that for testing, water needed to be added to the entirety of dry mix once the samples were shipped to the testing site, something that would need to be done for a ready mix for actual construction uses as well. The water-to-composite ratio is the amount of water to the amount of dry mix by weight. Higher than typical values for the water/cement ratio were chosen and used for the water-to-composite ratio below to provide sufficient water given its absorption by biochar. Sufficient water was verified before testing by pre-mixing these samples and testing for workability.



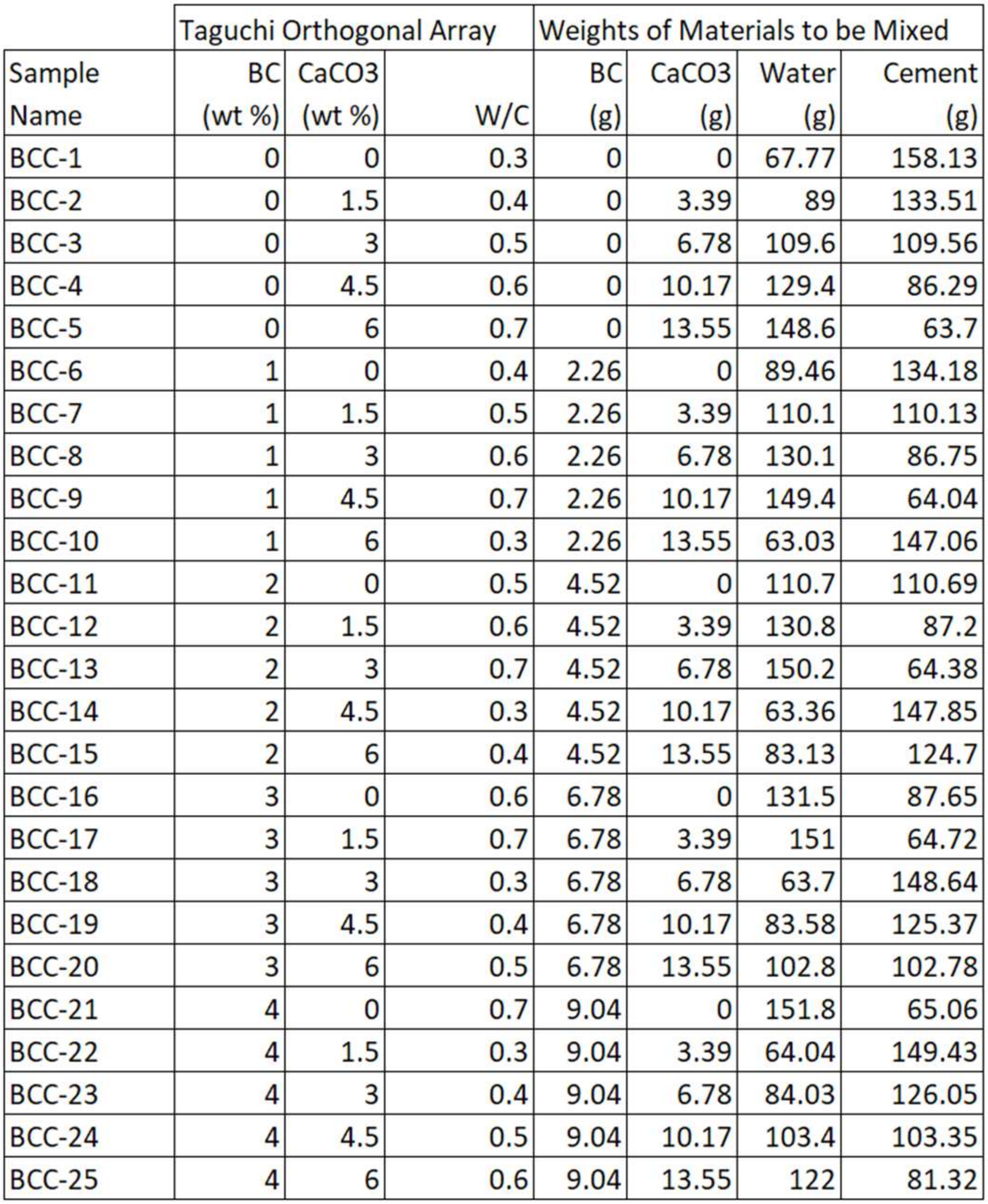
PROJECT MANAGEMENT PLAN

Version 2.0
9/24/2021

TABLE OF CONTENTS

Figure 5. The cover of the project management plan prepared.

Table 3. Samples made with the BC and CaCO3 wt%, and WC ratios identified in the orthogonal arrays specified by the Minitab software as best for employing the Taguchi method to identify and quantify the variables with the greatest influence on compressive strength. The corresponding weights of the materials to be mixed are given in the last four columns, with all components except water added to form a single dry mix for each sample.



	Taguchi Orthogonal Array			Weights of Materials to be Mixed			
Sample Name	BC (wt %)	CaCO3 (wt %)	W/C	BC (g)	CaCO3 (g)	Water (g)	Cement (g)
BCC-1	0	0	0.3	0	0	67.77	158.13
BCC-2	0	1.5	0.4	0	3.39	89	133.51
BCC-3	0	3	0.5	0	6.78	109.6	109.56
BCC-4	0	4.5	0.6	0	10.17	129.4	86.29
BCC-5	0	6	0.7	0	13.55	148.6	63.7
BCC-6	1	0	0.4	2.26	0	89.46	134.18
BCC-7	1	1.5	0.5	2.26	3.39	110.1	110.13
BCC-8	1	3	0.6	2.26	6.78	130.1	86.75
BCC-9	1	4.5	0.7	2.26	10.17	149.4	64.04
BCC-10	1	6	0.3	2.26	13.55	63.03	147.06
BCC-11	2	0	0.5	4.52	0	110.7	110.69
BCC-12	2	1.5	0.6	4.52	3.39	130.8	87.2
BCC-13	2	3	0.7	4.52	6.78	150.2	64.38
BCC-14	2	4.5	0.3	4.52	10.17	63.36	147.85
BCC-15	2	6	0.4	4.52	13.55	83.13	124.7
BCC-16	3	0	0.6	6.78	0	131.5	87.65
BCC-17	3	1.5	0.7	6.78	3.39	151	64.72
BCC-18	3	3	0.3	6.78	6.78	63.7	148.64
BCC-19	3	4.5	0.4	6.78	10.17	83.58	125.37
BCC-20	3	6	0.5	6.78	13.55	102.8	102.78
BCC-21	4	0	0.7	9.04	0	151.8	65.06
BCC-22	4	1.5	0.3	9.04	3.39	64.04	149.43
BCC-23	4	3	0.4	9.04	6.78	84.03	126.05
BCC-24	4	4.5	0.5	9.04	10.17	103.4	103.35
BCC-25	4	6	0.6	9.04	13.55	122	81.32

3.2 Materials and Composition Testing

Biochar that had been produced from softwood chips and sieved to a fine grade (intermediate between coarse and powder) was obtained from Biochar Now in Berthoud, CO. Calcium carbonate from ground limestone was obtained alongside Quikrete Portland cement. Each of the 25 mixtures were prepared as dry mixes sealed in plastic bags for transport in a single shipment to the testing site.

	BC (g)	CaCO3 (g)	Cement (g)	Water (g)	Total (g)
BCC-1	0.00	0.00	105.00	45.00	150.00
BCC-10	1.50	9.00	97.65	41.85	150.00
BCC-14	3.00	6.75	98.18	42.08	150.00
BCC-18	4.50	4.50	98.70	42.30	150.00
BCC-22	6.00	2.25	99.23	42.53	150.00

Figure 6. Validation of workability using the lowest water-to-composite (WC) ratio of 0.3 with other components of various amounts from BCC-1 (control), 10, 14, 18, and 22. Workability was confirmed in each. The lowest water-to-composite ratio was chosen since all mixtures would have greater workability than these.

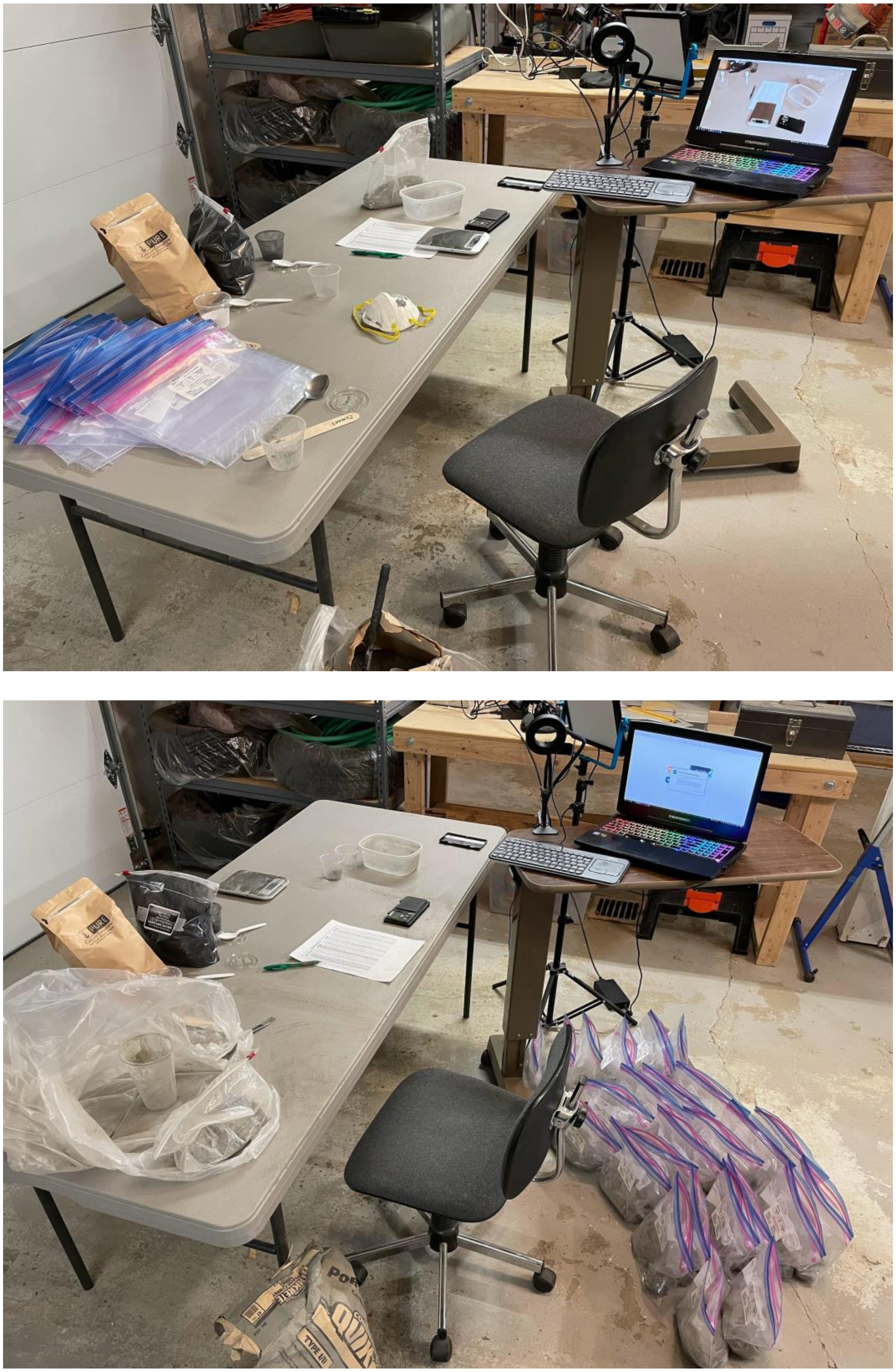


Figure 7. Layout of workspace before and after preparing the 25 samples in bags (lower right).

BCC-1 800 g (for 25 samples)

Biochar (BC) wt %	CaCO3 wt %	Water/Cement Ratio (W/C)
0	0	0.3

Project: Cement Sample Testing
Location: Lehigh-Hanson Union Bridge

Sender:	**Recipient:**
Dahl Winters 1152 Stagecoach Blvd Evergreen, CO 80439 dwint@colostate.edu	Kwaku Boakye 874 Amherst Ln Westminster, MD 21158 kboakye@colostate.edu

Figure 8. Twenty-five sample bags, labeled with the composition and being prepared for shipment.

Figure 9. Sample bags packaged into 4 large bags to fit within a box to ship to Boakye for testing.

Shipment was accomplished within a 3-day time window. At the testing site, each mix's chemical and physical properties would be measured according to a bank of 13 tests. These included 5 oxide tests: Silicon Dioxide (SiO_2), Aluminum Oxide (Al_2O_3), Iron Oxide (Fe_2O_3), Calcium Oxide (CaO), and Magnesium Oxide (MgO) to help describe the minerals present, followed by 4 more tests for Sulfuric Anhydride (SO_3), Alite (Tricalcium Silicate, C_3S), Tricalcium Aluminate (C_3A), and Free Lime Content (FCaO). Alite (C_3S) is highly reactive and develops early strength in concrete as its major phase. C_3A leads to the rapid initial hydration of cement and is typically less than 10% of the total composition (131). The last 4 tests were for Limestone Percentage (LS%), Blaine (Fineness), LAlpine, and 45-micron residue (ASTM C430). The limestone percentage (LS%) is typically up to 5% for Portland cement but can be as high as 10-12% for Portland limestone cement. We can see the LS% increases for each BC wt% accordingly with $CaCO_3$ wt% as expected from its addition, remaining within the limits of Portland limestone cement (28). The Blaine value represents a specific surface area of the cement, a description of its fineness. The higher the value, the finer the cement and the higher the rate of reaction. The LAlpine test specifies the use of an Alpine E200-LS connecting with a type L industrial vacuum cleaner to perform air jet sieving down to 20 microns (132). The 45-micron residue test indicates how finely the clinker has been ground; about 95% of cement particles are smaller than 45 microns. The higher the value, the fewer the number of particles larger than 45 microns.

Once these 13 tests were performed, non-chlorinated water was then added according to the water-to-composite ratio (WC) specified by the Taguchi method for each sample. The mixtures were then molded into sample containers for curing over either 3, 7, and 28 days prior to testing via a compressive testing machine. After compressive strength testing was complete and results were obtained, Minitab software was used to quantify through Taguchi analysis how much each of the 3 factors of BC content, $CaCO_3$ content, and WC influenced the compressive strength of each cured mix.

3.3 Results

This section presents the results from experiments planned, performed, and with data analyzed between mid-2021 and early 2022, using the methods described earlier in this chapter. These results serve to characterize the relationship between compressive strength of BC+$CaCO_3$+cement composites and their wt% which reflects the quantities of these components possible, thus the overall carbon storage of the composite. Curves of biochar wt% vs. compressive strength as well as $CaCO_3$ wt% vs. compressive strength will be presented, as well as results describing whether the combination of BC+$CaCO_3$ has improved the compressive strength of its cement composite more than biochar alone. The mix ratio of cement+BC+$CaCO_3$ that yields a suitable compressive strength while offering a good quantity of carbon storage will also be given in this section.

3.3.1 Results of Composition Testing

Table 4. Sample Compositions - Oxides: Silicon Dioxide, Aluminum Oxide, Iron Oxide, Calcium Oxide, Magnesium Oxide

Sample Name	BC (wt %)	CaCO3 (wt %)	W/C	SiO$_2$	Al$_2$O$_3$	Fe2O$_3$	CaO	MgO
BCC-1	0	0	0.3	19.22	4.22	3.27	62.79	1.014
BCC-2	0	1.5	0.4	18.81	4.11	3.21	63.05	0.994
BCC-3	0	3	0.5	18.71	4.08	3.2	63.27	0.992
BCC-4	0	4.5	0.6	18.04	3.91	3.11	63.67	0.959
BCC-5	0	6	0.7	17.79	3.86	3.08	63.51	0.936
BCC-6	1	0	0.4	19.1	4.18	3.26	62.43	1.008
BCC-7	1	1.5	0.5	18.72	4.08	3.2	62.69	0.988
BCC-8	1	3	0.6	18.57	4.04	3.18	62.82	0.979
BCC-9	1	4.5	0.7	18.23	3.9	3.11	63.29	0.949
BCC-10	1	6	0.3	17.64	3.8	3.06	63.47	0.93
BCC-11	2	0	0.5	18.85	4.17	3.25	61.93	0.99
BCC-12	2	1.5	0.6	18.64	4.13	3.22	62.34	0.985
BCC-13	2	3	0.7	18.26	4.02	3.17	62.54	0.961
BCC-14	2	4.5	0.3	18.21	4	3.16	62.59	0.959
BCC-15	2	6	0.4	17.69	3.87	3.09	62.87	0.952
BCC-16	3	0	0.6	18.61	4.09	3.24	61.29	0.963
BCC-17	3	1.5	0.7	18.45	4.09	3.22	61.97	0.972
BCC-18	3	3	0.3	17.99	3.97	3.16	61.17	0.956
BCC-19	3	4.5	0.4	17.73	3.88	3.12	62.19	0.931
BCC-20	3	6	0.5	17.45	3.82	3.08	62.66	0.917
BCC-21	4	0	0.7	18.51	3.99	3.24	60.7	1.002
BCC-22	4	1.5	0.3	18.13	3.99	3.21	61.48	0.981
BCC-23	4	3	0.4	17.49	3.83	3.14	61.45	0.924
BCC-24	4	4.5	0.5	17.33	3.78	3.1	61.89	0.918
BCC-25	4	6	0.6	17.13	3.74	3.07	62.14	0.905

Table 5. Sample Compositions: Sulfuric Anhydride (SO_3), Alite (Tricalcium Silicate, C_3S), Tricalcium Aluminate (C_3A), Free Lime Content (FCaO)

Sample Name	BC (wt %)	CaCO3 (wt %)	W/C	SO_3	C_3S	C_3A	FCaO
BCC-1	0	0	0.3	3.4	65.52	2.59	0.94
BCC-2	0	1.5	0.4	3.38	64.82	2.59	1
BCC-3	0	3	0.5	3.39	63.12	2.59	0.91
BCC-4	0	4.5	0.6	3.24	60.13	2.81	0.87
BCC-5	0	6	0.7	3.2	60.35	2.33	0.8
BCC-6	1	0	0.4	3.42	65.17	2.65	0.73
BCC-7	1	1.5	0.5	3.37	64.33	2.79	0.87
BCC-8	1	3	0.6	3.34	63.36	2.45	0.88
BCC-9	1	4.5	0.7	3.24	61.24	2.41	0.91
BCC-10	1	6	0.3	3.25	60.86	2.82	0.78
BCC-11	2	0	0.5	3.42	63.27	2.39	0.68
BCC-12	2	1.5	0.6	3.38	62.31	2.68	0.78
BCC-13	2	3	0.7	3.37	62.92	3.04	0.6
BCC-14	2	4.5	0.3	3.36	62.31	2.86	0.71
BCC-15	2	6	0.4	3.25	59.87	2.6	0.78
BCC-16	3	0	0.6	3.37	62.68	2.73	0.91
BCC-17	3	1.5	0.7	3.38	63.11	2.53	0.91
BCC-18	3	3	0.3	3.37	63.07	2.59	0.94
BCC-19	3	4.5	0.4	3.28	61.73	2.73	0.77
BCC-20	3	6	0.5	3.25	59.23	2.44	0.72
BCC-21	4	0	0.7	3.37	63.79	2.19	0.73
BCC-22	4	1.5	0.3	3.44	62.86	2.66	0.89
BCC-23	4	3	0.4	3.3	62.1	2.75	0.86
BCC-24	4	4.5	0.5	3.28	59.17	2.42	0.67
BCC-25	4	6	0.6	3.28	58.68	2.52	0.81

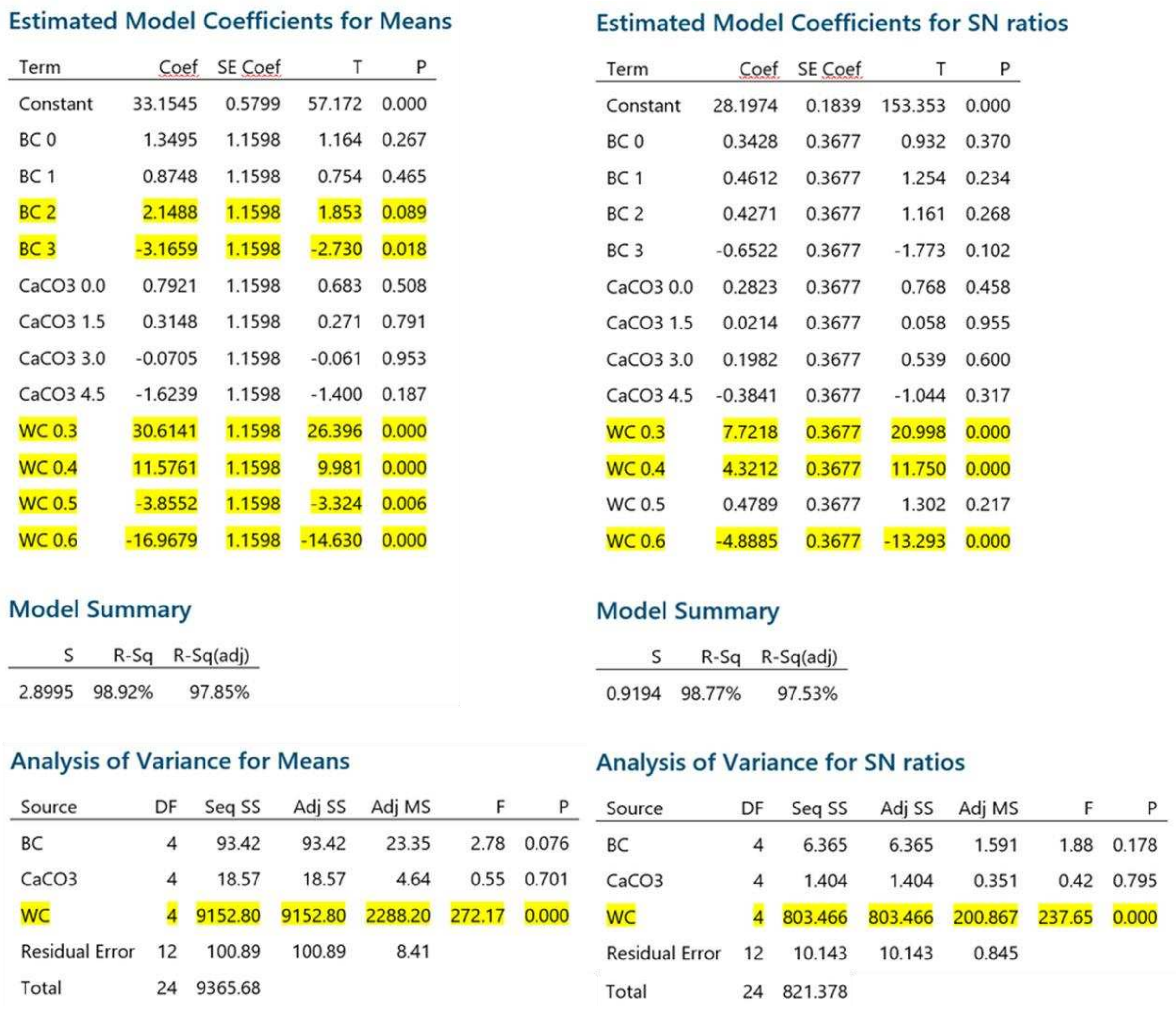
Table 6. Sample Compositions: Limestone Percentage (LS%), Blaine (Fineness), LAlpine, 45 micron residue (ASTM C430)

Sample Name	BC (wt %)	CaCO3 (wt %)	W/C	LS%	Blaine	LAlpine	45 microns
BCC-1	0	0	0.3	4.23	423	5.36	97.57
BCC-2	0	1.5	0.4	5.39	435	4.6	96.88
BCC-3	0	3	0.5	6.16	440	4.45	97.64
BCC-4	0	4.5	0.6	8.04	462	4.51	97
BCC-5	0	6	0.7	10.38	468	4.53	96.12
BCC-6	1	0	0.4	4.5	429	5.24	95.67
BCC-7	1	1.5	0.5	6.04	462	5.2	96.03
BCC-8	1	3	0.6	6.44	445	5.22	96.77
BCC-9	1	4.5	0.7	8.12	476	5.1	97
BCC-10	1	6	0.3	11.32	488	5.05	96.25
BCC-11	2	0	0.5	4.84	449	5.53	96.06
BCC-12	2	1.5	0.6	6.15	455	5.48	94.8
BCC-13	2	3	0.7	6.91	474	5.07	95.39
BCC-14	2	4.5	0.3	7.96	480	5.6	94.18
BCC-15	2	6	0.4	10.39	494	5.65	98.2
BCC-16	3	0	0.6	4.97	402	6.51	95.57
BCC-17	3	1.5	0.7	5.71	455	6.12	91.71
BCC-18	3	3	0.3	7.58	480	6.47	95.79
BCC-19	3	4.5	0.4	8.24	472	6.28	94.81
BCC-20	3	6	0.5	9.76	470	6.08	94.25
BCC-21	4	0	0.7	5.07	440	6.92	92.83
BCC-22	4	1.5	0.3	5.11	423	6.85	92.64
BCC-23	4	3	0.4	8.61	436	7.43	90.45
BCC-24	4	4.5	0.5	9.95	447	6.25	91.85
BCC-25	4	6	0.6	11.31	462	6.7	92.89

3.3.2 Results for Compressive Strength and Carbon Storage

Curves are planned to be developed following Taguchi method analysis that would describe the variation of biochar wt% vs. cement mortar compressive strength as well as $CaCO_3$ wt % vs. compressive strength, from which the relationship between compressive strength and carbon storage could be determined. Analytical support was planned for assessing whether the combination of BC+$CaCO_3$ can improve the compressive strength of its cement mortar composite more than BC alone, and under what ranges of BC and $CaCO_3$ wt% this might be so. This information could then provide justification of a mix ratio of cement+BC+$CaCO_3$ in terms of wt% that yields both a favorable compressive strength and high quantity of carbon storage. The methods to be described are to test the hypothesis that despite a much lower wt% of biochar being possible to include in cement than concrete, the addition of calcium carbonate due to its fine particle size and void-filling capability might favorably contribute to increasing compressive strength compared to the same wt% of biochar alone up to an optimal value. If biochar wt% increases further beyond such an amount, it is hypothesized that compressive strength will continue to decline due to too much cement replacement.

The combined results at 3, 7, and 28 days for compressive strength vs. the variables of biochar (BC), calcium carbonate ($CaCO_3$), and water-to-composite content (WC) are indicated in Figure 10. The yellow highlights indicate where p-values were significant, meaning the component has enough influence on compressive strength to merit a closer look at its relevance. It is the case that WC has much larger estimated model coefficients than BC, suggesting its greater importance as an explanatory variable for compressive strength than the amounts of biochar tested. However, BC of 2 and 3% were also significant and suggests that 2% biochar improves compressive strength while 4% reduces it.



Estimated Model Coefficients for Means

Term	Coef	SE Coef	T	P
Constant	33.1545	0.5799	57.172	0.000
BC 0	1.3495	1.1598	1.164	0.267
BC 1	0.8748	1.1598	0.754	0.465
BC 2	2.1488	1.1598	1.853	0.089
BC 3	-3.1659	1.1598	-2.730	0.018
CaCO3 0.0	0.7921	1.1598	0.683	0.508
CaCO3 1.5	0.3148	1.1598	0.271	0.791
CaCO3 3.0	-0.0705	1.1598	-0.061	0.953
CaCO3 4.5	-1.6239	1.1598	-1.400	0.187
WC 0.3	30.6141	1.1598	26.396	0.000
WC 0.4	11.5761	1.1598	9.981	0.000
WC 0.5	-3.8552	1.1598	-3.324	0.006
WC 0.6	-16.9679	1.1598	-14.630	0.000

Model Summary

S	R-Sq	R-Sq(adj)
2.8995	98.92%	97.85%

Analysis of Variance for Means

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BC	4	93.42	93.42	23.35	2.78	0.076
CaCO3	4	18.57	18.57	4.64	0.55	0.701
WC	4	9152.80	9152.80	2288.20	272.17	0.000
Residual Error	12	100.89	100.89	8.41		
Total	24	9365.68				

Estimated Model Coefficients for SN ratios

Term	Coef	SE Coef	T	P
Constant	28.1974	0.1839	153.353	0.000
BC 0	0.3428	0.3677	0.932	0.370
BC 1	0.4612	0.3677	1.254	0.234
BC 2	0.4271	0.3677	1.161	0.268
BC 3	-0.6522	0.3677	-1.773	0.102
CaCO3 0.0	0.2823	0.3677	0.768	0.458
CaCO3 1.5	0.0214	0.3677	0.058	0.955
CaCO3 3.0	0.1982	0.3677	0.539	0.600
CaCO3 4.5	-0.3841	0.3677	-1.044	0.317
WC 0.3	7.7218	0.3677	20.998	0.000
WC 0.4	4.3212	0.3677	11.750	0.000
WC 0.5	0.4789	0.3677	1.302	0.217
WC 0.6	-4.8885	0.3677	-13.293	0.000

Model Summary

S	R-Sq	R-Sq(adj)
0.9194	98.77%	97.53%

Analysis of Variance for SN ratios

Source	DF	Seq SS	Adj SS	Adj MS	F	P
BC	4	6.365	6.365	1.591	1.88	0.178
CaCO3	4	1.404	1.404	0.351	0.42	0.795
WC	4	803.466	803.466	200.867	237.65	0.000
Residual Error	12	10.143	10.143	0.845		
Total	24	821.378				

Figure 10. The combined results at 3, 7, and 28 days for compressive strength vs. the variables of biochar (BC), calcium carbonate ($CaCO_3$), and water-to-composite content (WC)

The following plots produced in Minitab provide a visual representation of the magnitude of influence of each of the three components BC, $CaCO_3$, and WC on the compressive strength.

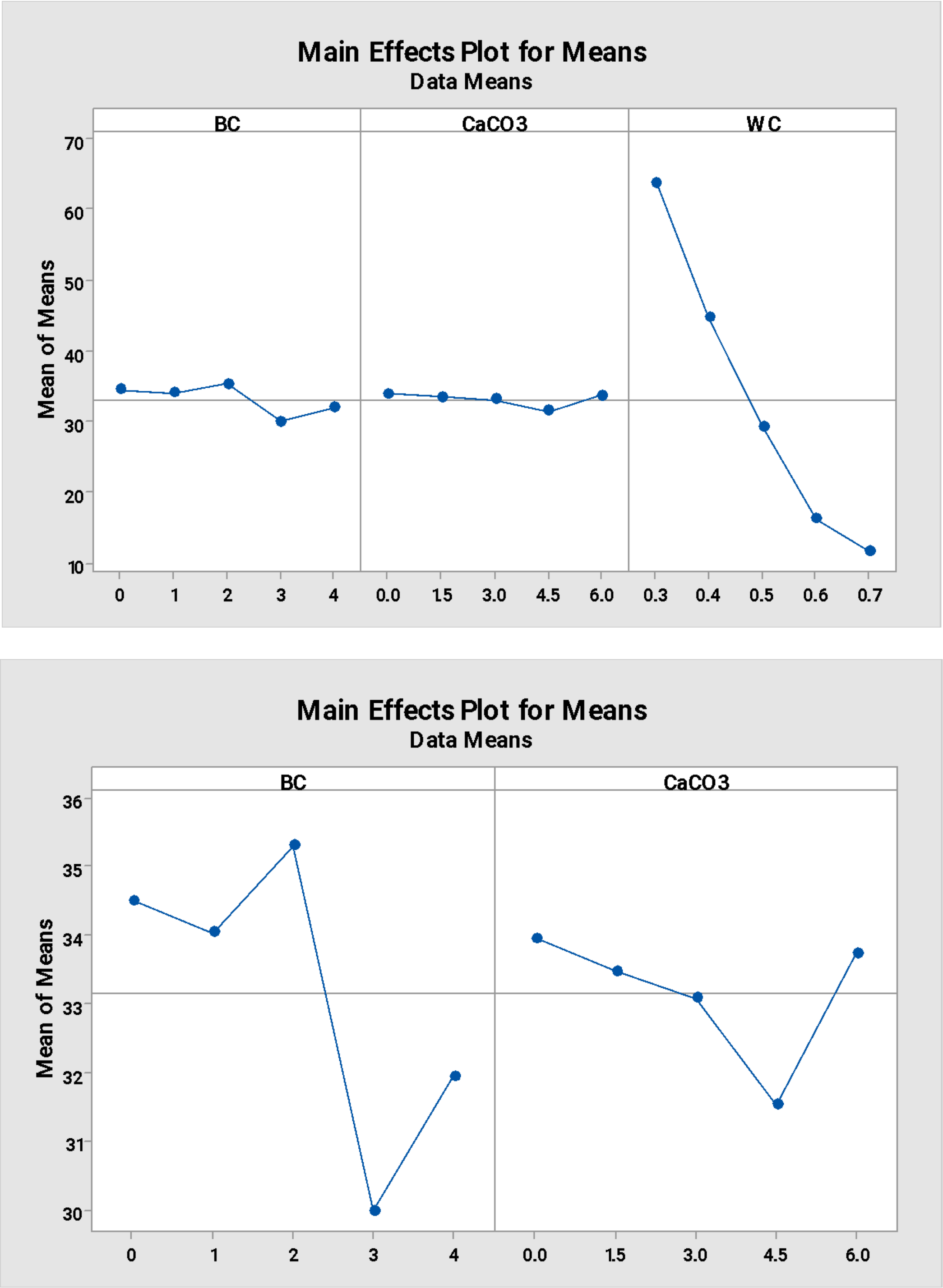


Figure 11. Top: Along the y-axis, the mean of means of compressive strength in MPa is plotted for the amounts of each component on the x-axis. The WC ratio is the most important, with a strong negative relationship - as the amount of water relative to the amount of composite increases, compressive strength decreases. Biochar has the second greatest effect, positive at and below 2% but negative at and greater than 3%. $CaCO_3$ has a positive effect below 3% and negative at 4.5%, but the results were not significant for $CaCO_3$ at 28 days. Bottom: A closeup of just the BC and $CaCO_3$ plots.

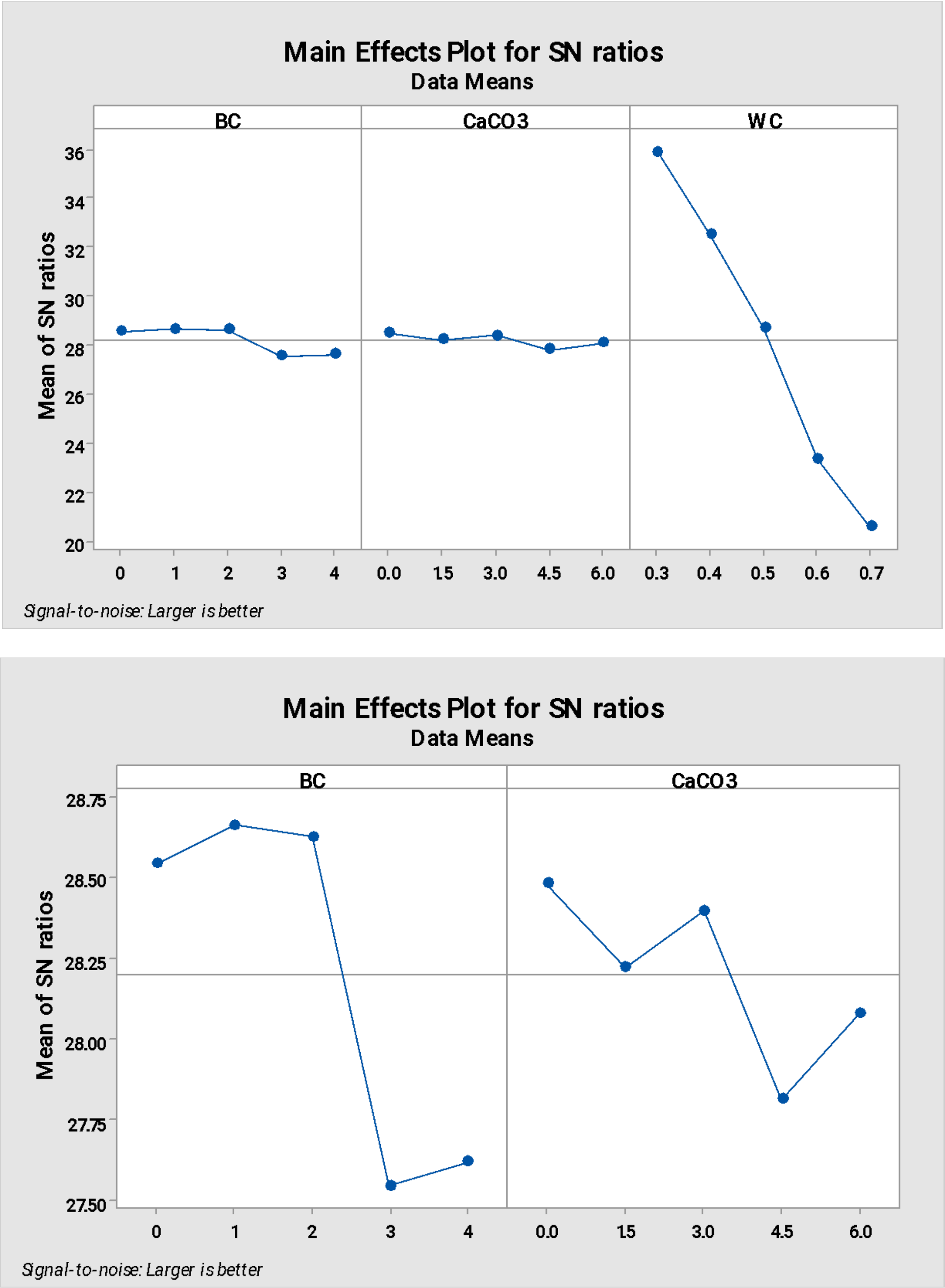


Figure 12. Along the y-axis, the means of the signal-to-noise (SN) ratios are plotted in MPa of compressive strength. A decrease in compressive strength is associated with higher biochar amounts of 3% and above and higher calcium carbonate amounts of 4.5% and above. These decreases are small compared to the greater impact of the water-to-composite ratio on compressive strength, but those for biochar are significant. Those for calcium carbonate have not been.

3.3.3 Compressive Strength vs. Carbon Storage with Biochar and Calcium Carbonate

After the composition tests of the dry mixes were performed, water was added according to the water-to-composite (WC) ratios specified for each sample. Samples were molded into composites in triplicate such that cured samples from each could be tested for compressive strength at 3, 7, and 28 days after mixing with water occurred. Results were returned and a Taguchi linear model analysis was done to determine how compressive strength varied with the wt% of BC, $CaCO_3$, and WC. Plots for the means and signal-to-noise (SN) ratios vs. the wt% of BC and $CaCO_3$ and WC were obtained and analyses of variance for both the SN ratios and means were also performed. Results were compiled into a preliminary report. The top 4 compressive strengths for each of the three tests at 3, 7, and 28 days are indicated by the gray and yellow highlights in the following table. Observation 1 (yellow) was the control at 0 wt% biochar, Observation 10 (yellow) had 1 wt% biochar, Observation 14 (gray) had 2 wt% BC, and Observation 22 (yellow) had 4 wt% BC. All four of these mixtures had a 0.3 WC (water-to-composite ratio) but varied in BC and $CaCO_3$ wt%. The low WC was expected to be associated with higher compressive strength as is generally the case when concrete made with less water is allowed to cure. However, the strength of the effect of WC compared to that of BC or $CaCO_3$ was unknown in such a composite before this research. This was a reason the Taguchi method was employed, to help answer which variables might have the strongest effects in this cement-based carbon storage system.

If seeking to maximize strength only, Observation 1 (the control) performed the best. Without any additional BC or $CaCO_3$, it had the largest fraction of cement of all samples and thus would be expected to have the highest compressive strength because of this. Observation 14 is highlighted in a different color than the others (gray) because it demonstrated the second highest strength after the control and also contained 2% biochar. The key finding for this research was demonstrated by Observation 22, having only a slightly lower strength but able to contain 4 wt% BC with the addition of only 1.5 wt% $CaCO_3$. Observation 22 was able to maximize both the carbon storage and strength of cement pastes at 28 days.

The series number below is the observation number from the previous data table. Observation 1 is the control, without BC or $CaCO_3$ and is the strongest at 28 days. Observation 14, however, is the highest at 7 days and the second highest at 28 days. This is a mixture of 2% BC, 4.5% $CaCO_3$, and 0.3 WC. Observations 10 and 22 are the other two with high compressive strength in all 3 tests, with Observation 22 having the highest amount of carbon storage of all four observations.

Table 7. Compressive Strength (MPa) vs. Carbon Storage by Component over 3, 7, and 28 Days

				Compressive Strength (MPa) at Day		
Observation	**BC**	**CaCO3**	**WC**	**3**	**7**	**28**
1	0	0	0.3	59.59	63.09	77.41
2	0	1.5	0.4	36.39	48.03	52.92
3	0	3	0.5	22.98	34.36	39.85
4	0	4.5	0.6	13.08	13.47	20.83
5	0	6	0.7	8.68	10.4	16.48
6	1	0	0.4	38.62	40.44	54.57
7	1	1.5	0.5	22.42	28.32	40.79
8	1	3	0.6	12.61	17.21	25.08
9	1	4.5	0.7	9.56	11.98	16.11
10	1	6	0.3	59.73	59.3	73.7
11	2	0	0.5	21.88	30.89	37.63
12	2	1.5	0.6	11.56	14.81	21.32
13	2	3	0.7	8.01	11.33	17.29
14	2	4.5	0.3	58.91	66.24	74.65
15	2	6	0.4	44.4	53.1	57.53
16	3	0	0.6	13.47	16.3	22.21
17	3	1.5	0.7	8.16	9.86	15.85
18	3	3	0.3	51.35	52.11	68.84
19	3	4.5	0.4	35.94	24.13	49.65
20	3	6	0.5	21.69	25.9	34.37
21	4	0	0.7	8.38	10.32	14.4
22	4	1.5	0.3	56.14	61.74	73.73
23	4	3	0.4	36.48	45.61	53.15
24	4	4.5	0.5	19.66	25.51	33.24
25	4	6	0.6	8.93	12.29	19.63

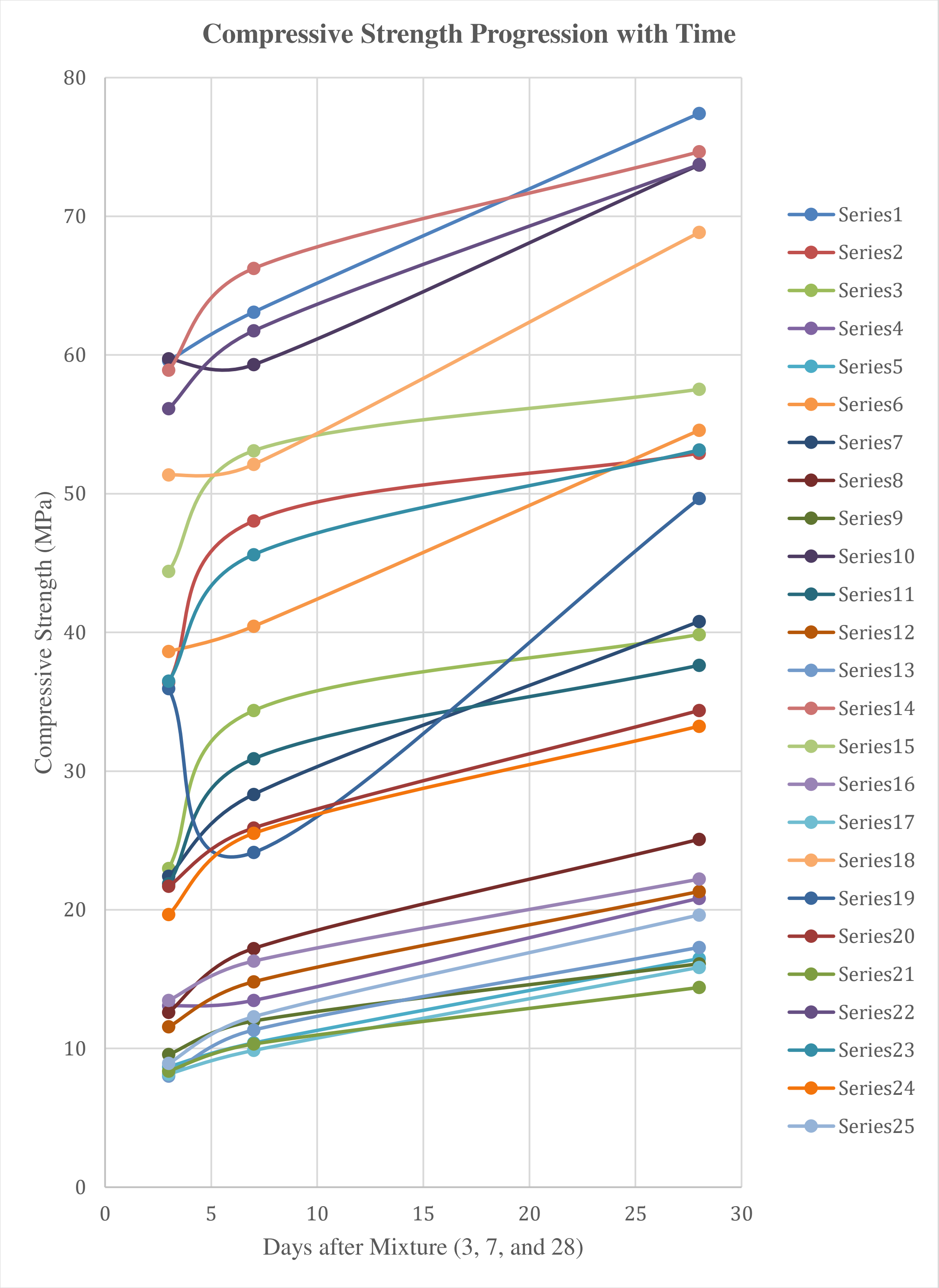


Figure 13. Compressive Strength (MPa) vs. Carbon Storage Over Time: Aside from Series 19 (BCC-19) that did not test well at 7 days, graphing the data from the preceding table indicates all other samples increased in compressive strength on day 7 than on day 3. Notably, higher increases between 7 to 28 days occurred for those samples that already had a higher compressive strength at 7 days (the four samples near the top of the plot, previously highlighted) than those lower on the plot.

3.3.4 Summary of Results

The mixture that optimizes **compressive strength only** at 28 days, Observation 14, is only slightly lower in compressive strength than the control at 77.41 MPa. Observation 14 (74.65 MPa) contains 2% BC, 4.5% $CaCO_3$, and 0.3 WC (water-to-composite mixture ratio). The mixture that optimizes both **carbon storage and strength** at 28 days, Observation 22, is slightly less strong, a 1.2% reduction. Observation 22 (73.73 MPa) contains 4% BC, 1.5% $CaCO_3$, and 0.3 WC. The literature has previously pointed to **1-2% BC** by weight as being possible to add to cement without a significant compressive strength reduction. We obtained **4% BC** with only a 1.2% reduction in strength by also adding 1.5% $CaCO_3$.

CHAPTER 4: DISCUSSION OF RESULTS

This chapter discusses the results from experiments planned, performed, and with data analyzed between mid-2021 and early 2022, using the methods described in Chapter 3. These results serve to characterize the relationship between compressive strength of BC+$CaCO_3$+cement composites and their wt% which reflects the quantities of these components possible, thus the overall carbon storage of the composite. Curves of biochar wt% vs. compressive strength as well as $CaCO_3$ wt% vs. compressive strength will be presented, as well as results describing whether the combination of BC+$CaCO_3$ has improved the compressive strength of its cement composite more than biochar alone. The mix ratio of cement+BC+$CaCO_3$ that yields a suitable compressive strength while offering a good quantity of carbon storage will also be given in this chapter.

4.1 Toward the Predictive Modeling of Compressive Strength and Carbon Storage of Concrete Made with Biochar and Calcium Carbonate

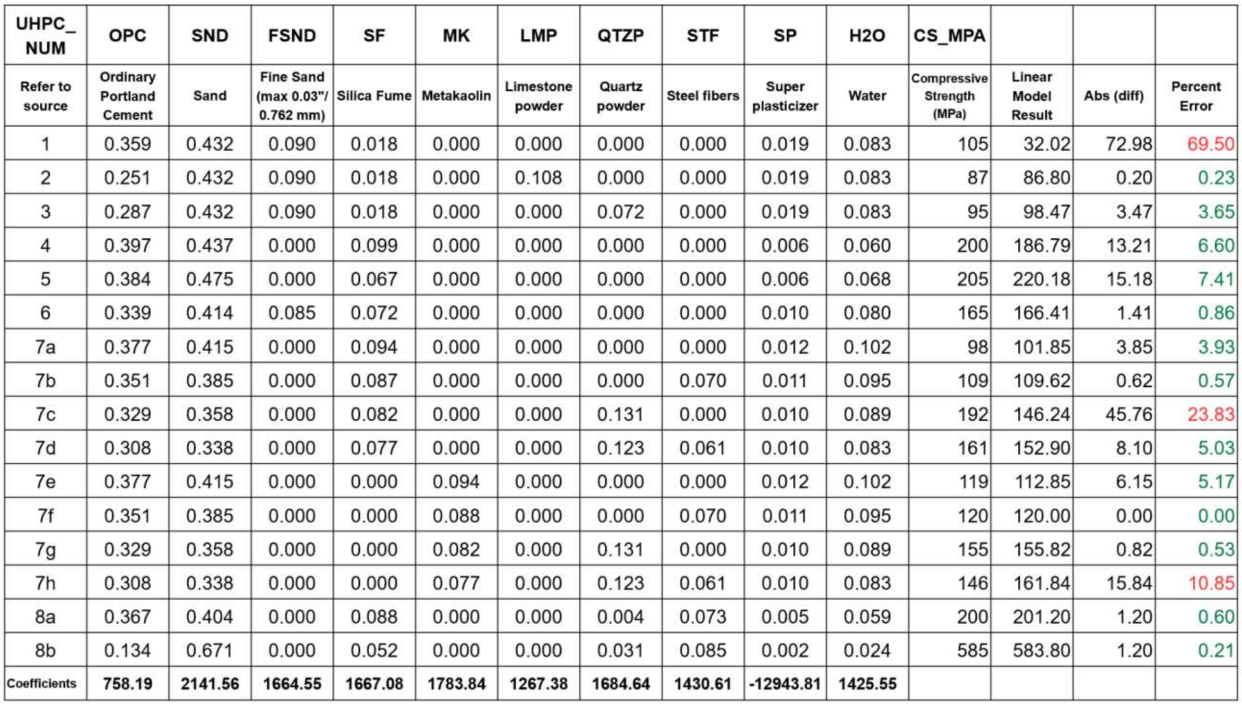
4.1.1 Modeling Compressive Strength vs. Carbon Storage from a UHPC: Literature Review

On February 24, 2022, I submitted my review paper on carbon-neutral concrete and began investigating a predictive model for carbon-neutral concrete. The review paper featured the plot in Figure 4, provided in Chapter 2. It was a key finding for the paper, though only from experiments performed in 2 studies, indicating a linear variation in compressive strength at 28 days with an increasing biochar wt% in a UHPC. UHPC do not usually contain biochar; as their name suggests, these are specialty concretes used for ultra-high-performance applications where high strength is necessary. The strongest UHPC is known to have a compressive strength near 800 MPa, over 10 times that of the highest compressive strengths achieved from the work of the last chapter. However, understanding how compressive strength develops in a UHPC, with or without biochar, would offer significant usefulness in engineering cement-based carbon storage systems able to support higher compressive strength, perhaps also compensating for the losses that additional biochar incorporation brings.

4.1.2 A Comparison of the Linear Model Results With a 10 Variable UHPC Model

The research I performed, described in Chapter 3, indicated that a mixture of 4 wt% BC, 1.5 wt% $CaCO_3$, and a water/cement ratio of 0.3 maximizes both the carbon storage and compressive strength of BC-$CaCO_3$-cement composites at 28 days. The data collected have provided support for a 3 variable linear model of compressive strength and carbon storage in such composites, the three variables being biochar, calcium carbonate, and the water-to-composite ratio. After that research and the publication of the literature review in Chapter 2, I then researched a model of compressive strength and carbon storage in a UHPC to better understand how compressive strength varied and perhaps could be increased in such composites to enable greater carbon storage of this system over a wider range of applications. Data from 5 papers (below) were used to create a 10-variable model of UHPC compressive strength using an Excel spreadsheet that does not include biochar but does include $CaCO_3$. The reason for not including biochar but $CaCO_3$ instead is that biochar is not often used in UHPC; at least literature was difficult to find. Whereas $CaCO_3$ has had many more uses alongside ordinary Portland cement such as Portland limestone cement and within LC_3 concrete. A table was first created, where values are reported are dimensionless density fractions defined as the ingredient's density (in kg/m_3) divided by the sum of densities of all UHPC ingredients (in kg/m_3).

Table 8. The 10 variables of the model, with high percent errors (red) for only a few data sources.



UHPC_NUM	OPC	SND	FSND	SF	MK	LMP	QTZP	STF	SP	H2O	CS_MPA			
Refer to source	Ordinary Portland Cement	Sand	Fine Sand (max 0.03"/ 0.762 mm)	Silica Fume	Metakaolin	Limestone powder	Quartz powder	Steel fibers	Super plasticizer	Water	Compressive Strength (MPa)	Linear Model Result	Abs (diff)	Percent Error
1	0.359	0.432	0.090	0.018	0.000	0.000	0.000	0.000	0.019	0.083	105	32.02	72.98	69.50
2	0.251	0.432	0.090	0.018	0.000	0.108	0.000	0.000	0.019	0.083	87	86.80	0.20	0.23
3	0.287	0.432	0.090	0.018	0.000	0.000	0.072	0.000	0.019	0.083	95	98.47	3.47	3.65
4	0.397	0.437	0.000	0.099	0.000	0.000	0.000	0.000	0.006	0.060	200	186.79	13.21	6.60
5	0.384	0.475	0.000	0.067	0.000	0.000	0.000	0.000	0.006	0.068	205	220.18	15.18	7.41
6	0.339	0.414	0.085	0.072	0.000	0.000	0.000	0.000	0.010	0.080	165	166.41	1.41	0.86
7a	0.377	0.415	0.000	0.094	0.000	0.000	0.000	0.000	0.012	0.102	98	101.85	3.85	3.93
7b	0.351	0.385	0.000	0.087	0.000	0.000	0.000	0.070	0.011	0.095	109	109.62	0.62	0.57
7c	0.329	0.358	0.000	0.082	0.000	0.000	0.131	0.000	0.010	0.089	192	146.24	45.76	23.83
7d	0.308	0.338	0.000	0.077	0.000	0.000	0.123	0.061	0.010	0.083	161	152.90	8.10	5.03
7e	0.377	0.415	0.000	0.000	0.094	0.000	0.000	0.000	0.012	0.102	119	112.85	6.15	5.17
7f	0.351	0.385	0.000	0.000	0.088	0.000	0.000	0.070	0.011	0.095	120	120.00	0.00	0.00
7g	0.329	0.358	0.000	0.000	0.082	0.000	0.131	0.000	0.010	0.089	155	155.82	0.82	0.53
7h	0.308	0.338	0.000	0.000	0.077	0.000	0.123	0.061	0.010	0.083	146	161.84	15.84	10.85
8a	0.367	0.404	0.000	0.088	0.000	0.000	0.004	0.073	0.005	0.059	200	201.20	1.20	0.60
8b	0.134	0.671	0.000	0.052	0.000	0.000	0.031	0.085	0.002	0.024	585	583.80	1.20	0.21
Coefficients	**758.19**	**2141.56**	**1664.55**	**1667.08**	**1783.84**	**1267.38**	**1684.64**	**1430.61**	**-12943.81**	**1425.55**				

Below are the five papers whose studies pertained to each UHPC plot (UHPC_NUM) in Table 8.

Table 9. The 5 papers that informed the 10 variable UHPC model.

UHPC_NUM	**Source**
1-3	Mix design and properties evaluation of Ultra-High Performance Fibre Reinforced Concrete (UHPFRC) (133)
4, 8a-8b	Reactive Powder Concrete: Durability and Applications (134)
5	Development of Thermoplastic Composite Reinforced Ultra-High-Performance Concrete Panels for Impact Resistance (135)
6	UHPC compressive strength test specimens: Cylinder or cube? (136)
7a-7h	Metakaolin in the formulation of UHPC (137)

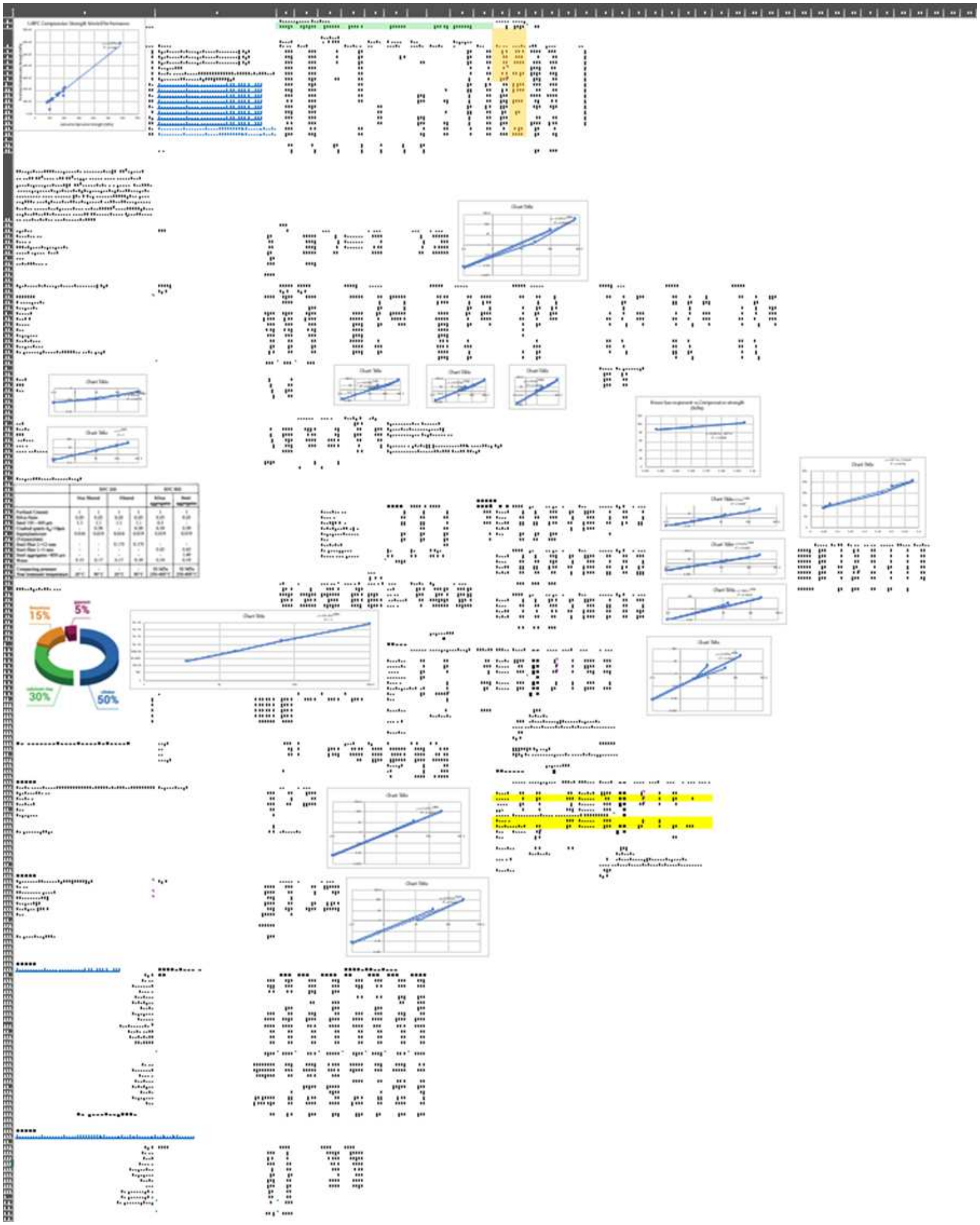


Figure 14. A screenshot of the spreadsheet showing the layout of data from each UHPC_NUM and their plots, to be used in developing a linear model of UHPC strength according to the values of ten variables.

The results from each paper were used to determine important variables to include in the 10-variable model. By representing each variable with a coefficient and using Excel Solver to find a solution minimizing the percent error across all variables, a model with coefficients given in the previous table was found that yielded the plot in Figure 15. UHPC compressive strength is represented on both axes since this is a graph of predicted vs. actual values obtained from the literature of compressive strength. The line drawn is that due to using the 10-variable linear model for UHPCs to predict compressive strength, and the R^2 is a reflection of how close the prediction came to what was measured. Biochar as mentioned is not one of the variables. Removing the one distant point (8b, RPC800, a UHPC with 500-800 MPa compressive and 45-140 MPa tensile strength) still yields an R^2 of 0.9759.

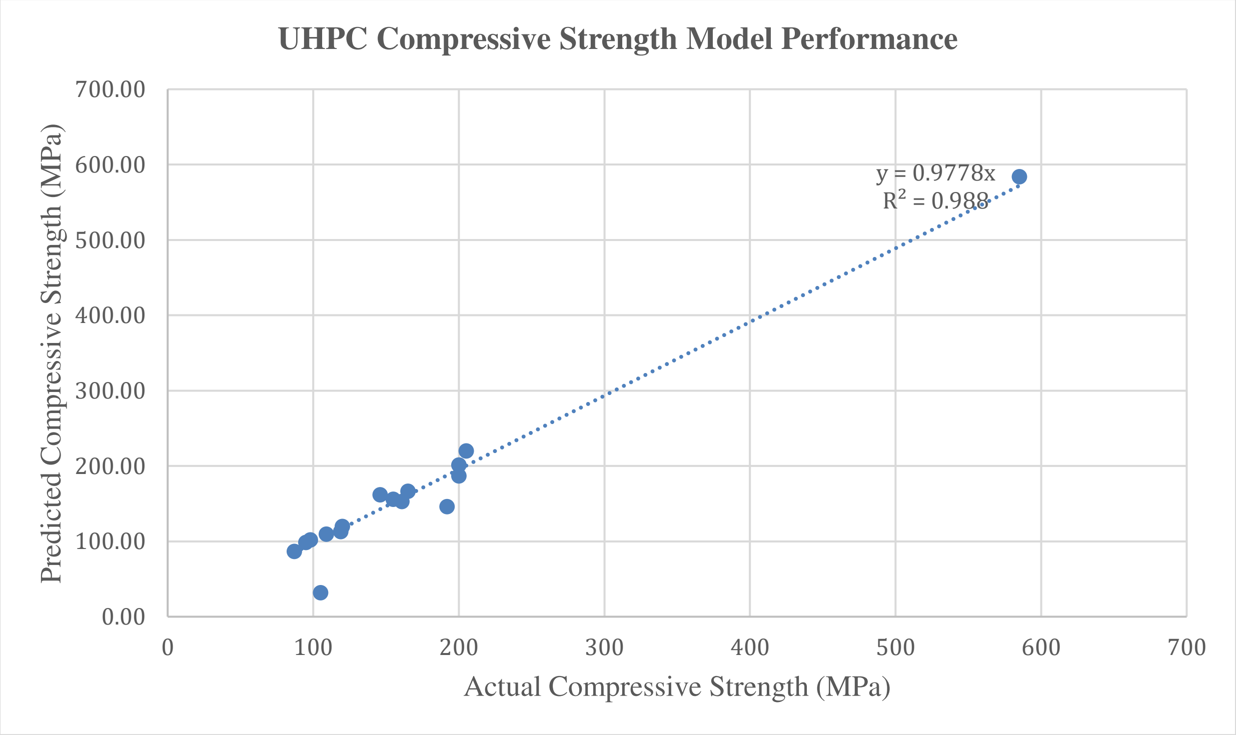


Figure 15. Predicted vs. actual compressive strength for the 10-variable UHPC model.

4.2 Consideration of Tensile Strength and Requirements for Tetrapod Construction

Tetrapods may offer great carbon storage capacity within their interior. However, a stiffer exterior without good tensile strength over a core with less compressive strength will be prone to crack formation. To improve the tensile strength of concrete tetrapods for a longer useful life, rebar and fibers are both options. Rebar takes up internal space and is difficult to separate for recycling concrete demolition waste. Steel fibers also have such difficulties. Both steel fibers and rebar also have the added problem of the intrusion of saltwater combined with any steel fibers or rebar causing corrosion, eventually leading to much faster failure of the tetrapod's concrete structure than otherwise. Carbon fibers have the advantage of being resistant to corrosion while performing better than rebar at resisting cracks and later failure (138). These can be recycled and would complement the use of biochar in concrete for carbon storage. Basalt fiber is an alternative to carbon fiber that is lower cost (139) and offers the potential for additional carbon storage given the use of basaltic rocks for carbon mineralization when water with high levels of dissolved CO_2 (soda water) is allowed to react with such rocks. This is the chemistry behind Carbfix's method of subsurface carbon mineralization (12) at the Climeworks Orca plant in Iceland (140).

Adding fibers (steel or fiber-reinforced polymers (FRP) such as fiberglass, carbon fiber, or basalt fiber) increases tensile strength and compressive strength by a smaller amount, as described in Table 2 of (138), due to reduced crack formation which is a precursor to failure. For steel fibers, (141) described how 0.5 to 1.5% fiber could increase concrete's compressive strength, inherent tensile strength, and peak flexural load capacity by 7–27 %, 11–47 %, and 3–124 %, respectively.

4.3 Impacts of This Research on Cement Industry Decarbonization and Climate Change

The supply and use of nanoscale calcium carbonate ($CaCO_3$) as a cement replacement instead of fly ash in concrete is worthy of further exploration, given that gigatonne-scale CO_2 emissions reductions have been estimated to be possible from the cement industry if all cement plants integrated 2% nano-$CaCO_3$ (142). CO_2 emissions could be captured and stored as nano-$CaCO_3$. The possibilities of clinker reduction using nano $CaCO_3$ are considered in this section, as well as the prospects for its increased manufacture through carbon mineralization. The content presented in this section was published in a recent book co-authored with Kwaku Boakye, Olurotimi Oguntola, Kevin Fenton, and Steve Simske (143). Within the cement industry, possible pathways to achieving net zero by 2050 are included in Figure 16.

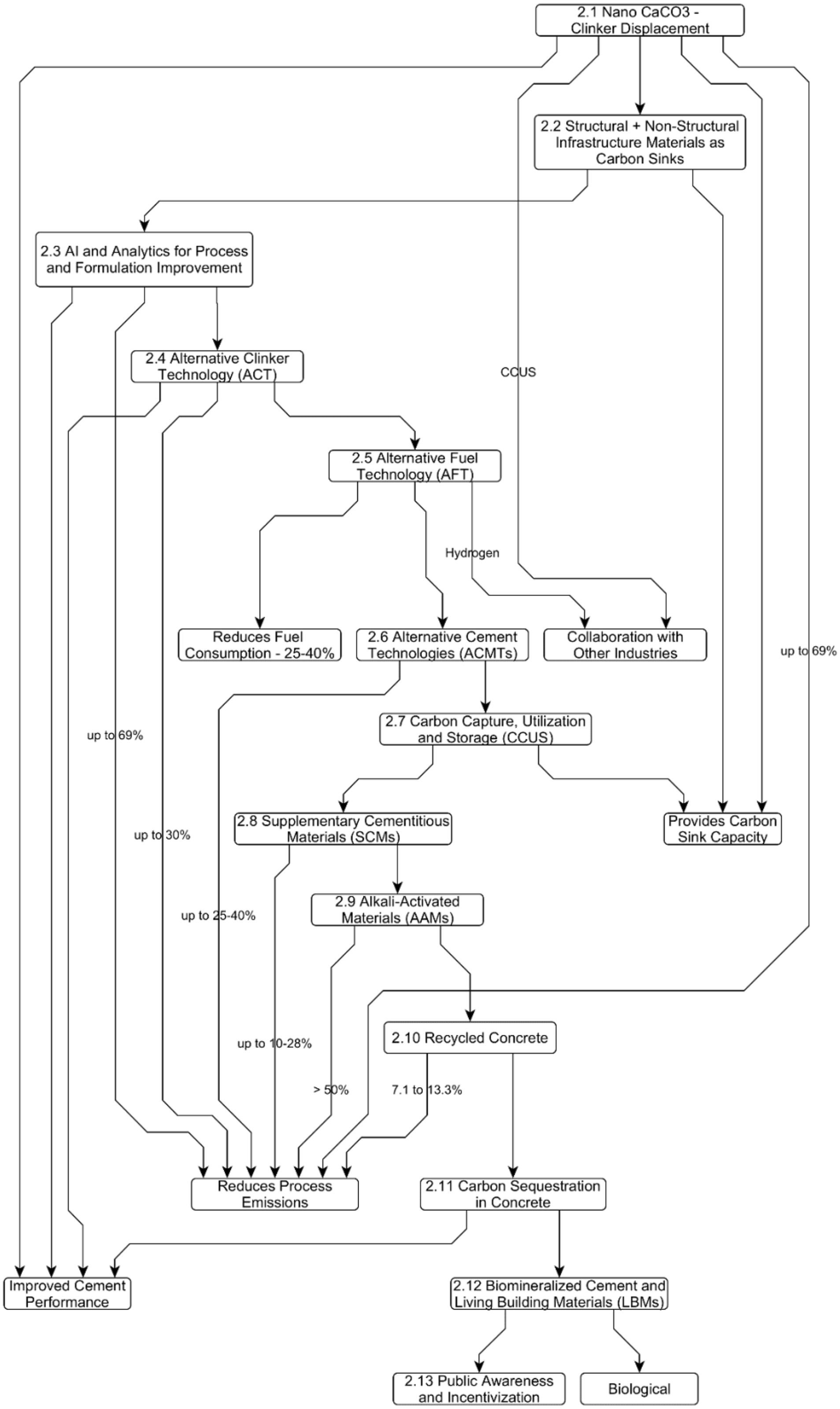


Figure 16. Possible pathways to achieving net zero by 2050.

Of note is the production of nanoscale calcium carbonate (NCC), having the potential to help the industry achieve gigatonne-scale decarbonization. NCC is comprised of calcium carbonate particles smaller than a micron, ranging from 15-35 nm to 400 nm (144). Typically produced as precipitated calcium carbonate (PCC), they present diverse applications across various industries such as adhesives, sealants, food, pharmaceuticals, paints, coatings, paper, and construction materials. Producing higher-value polymorphs of calcium carbonate, like calcite, instead of aragonite or vaterite, can help offset the costs associated with carbon capture, utilization, and storage (CCUS) (145). Lastly, PCC can also be generated from $Ca(OH)_2$ using ultrasound (146). Boyjoo et al. (147) offer additional synthesis approaches for both micro and nano-sized calcium carbonate, organizing these first into the CO_2 bubbling method, which sees the most industrial use. Calcite is the primary synthesized polymorph, with NCC more likely than micro and nano-sized particles. Biomimetic approaches involve precipitation and reverse emulsion, separated into spontaneous precipitation and slow carbonation reactions.

NCC in the form of PCC can be made with surfactants with concomitant changes in size, shape, and other properties (144). These particles can also be sourced from carbon mineralization activities designed to remove CO_2 from point sources or the atmosphere. PCC can also be made with nano-silica using microbes (148) and by using $CaCl_2$ from Solvay process wastewater to remove CO_2 (149). Liu et al. (148) describe the precautions for managing adverse health outcomes such as silicosis from breathing in nano-silica (150). The Solvay wastewater carbonation route's scalability depends on wastewater calcium concentration, flow rate, and CO_2 concentration, and has been commercially advanced for carbonating subsurface mineral brines. Displacing clinker is how NCC offers a significant decarbonization potential. According to Batuecas et al. (142), 2% of NCC promises to displace enough clinker to eliminate 69% of global greenhouse gas emissions from the global cement industry. This would be without altering the performance of the resulting cement in terms of its compressive strength or other properties. This potential may be lowered in the case of NCC made from nano-silica and microbes, as described by Liu et al. (148), due to the nutrient input required for microbial growth. Nutrient production in microbial NCC requires energy, increasing carbon footprint. Obtaining nutrients from food waste reduces LCA impact but introduces contamination concerns. Sterilization reduces LCA but requires energy. McDonald et al. (151) describe their carbon-negative manufacturing process for their admixture, PCC-A, as sequestering between 100 and 350 kg CO_2 per tonne of their PCC-A produced. Compressive strength peaks at 10 wt% PCC-A, but workability declines, requiring more water. Still, a significant emissions reduction is the result, which is 27-30%, depending on the alkali used.

Improved performance characteristics suggest value in the use of NCC. These include compressive strength and other performance properties of cement containing NCC, as well as studies demonstrating the viability of NCC in cement production (142). NCC offers additional routes to decarbonization beyond use in the cement industry. One of those is in improving soil nutrient availability, as demonstrated in fields that grow winter wheat. Another involves its deposition onto nanocellulose to make a flexible material that can make up most paper (152). NCC is already a bright white compound ideal for the color of paper, and its use would reduce the number of new trees needed. It may even enable the use of more recycled paper materials that could be coated with NCC to remove non-uniformities in color, thus providing higher value.

Market acceptance and regulatory considerations offer significant hurdles to more widespread adoption. Changing the cement composition has an even higher risk of successful hurdles to adoption. Even with tests showing improvements, representation in databases used by structural engineers allowing for selection by architects on new construction is needed for structural use. Using any new composition can carry significant risks if testing is improperly done - structural failures due to poor quality cement have happened. It is crucial to identify these as project risks that have more to do with the validation and verification of proper manufacture and use of the NCC-containing cement rather than arising from the NCC itself.

CHAPTER 5: RECOMMENDATIONS, FUTURE RESEARCH, AND CONCLUSION

5.1 Recommendations for Scaling Cement-Based Carbon Storage Systems

5.1.1 Costs vs. Benefits

To examine the costs vs. benefits of scaling cement-based carbon storage systems more accurately, life cycle assessments (LCA) can be performed. Their results will vary by geography given that the percent of renewable energy available, distances from material sources to areas of use, the distribution of GHG emissions from various types of sources, and the scale-up of biochar and calcium carbonate from carbon capture, all vary by geography. The availability of biochar from waste biomass and calcium carbonate from mineralization are limiting factors for scaling cement-based carbon storage. Biochar cementitious composites can be produced today at up to 33% BC content, demonstrating a similar minor increase in compressive strength at 28 days compared to a control with no biochar, but with a 118-172% increase in cost (153). This is lowered for a 20% BC, 40% fly ash mix given that biochar is compatible with fly ash as a cement replacement, but carbon storage is also lowered as well. For high strength integration, milling of the biochar alongside use of biochar with high available sorption capacity, low O/C (oxygen-carbon ratio), and a high soluble silicon content is recommended (154).

Table 10. Costs of biochar carbon storage in a cement composite, adapted from (153).

Mix	OPC $150/mt	Biochar $275-$750/mt	Fly Ash $80/mt	Cost/yd $275/mt biochar	Cost/yd $500/mt biochar	Cost/yd $750/mt biochar	Cost compared to base	Strength compared to base
Base	100%	--	--	$71.90	$71.90	$71.90	100%	100%
33% BC	67%	33%	--	$84.80	$103.30	$123.90	118-172%	101%
20% BC, 40% FA	40%	20%	40%	$70.45	$81.70	$94.20	98-131%	tbd

For calcium carbonate sourced from the capture and mineralization of CO_2, carbon capture, utilization, and storage (CCUS) technologies such as direct CO_2 capture (155) and oxyfuel combustion have been identified as having significant potential for use in the cement sector for emissions reduction (156), and GHG emission reduction calculations have been calculated for CCUS technology in the cement industry that would be useful for life cycle assessments (7) to project the impact of industrial decarbonization efforts more accurately. The availability of carbon-free energy remains a key limiting factor; there has been research pointing out limitations of CCUS for cement industry decarbonization. Ravikumar et al (2021) suggested that the net CO_2 benefit of concrete made with CCU was negative in their experimental datasets (157) and to improve the CO_2 reduction via CCU, the amount of electricity needed for carbon curing needed to be reduced. Reducing electricity in this case was not suggested for reasons of cost, but because most electricity needed for power or heat is still not carbon-free. The largest sector of GHG emissions is from heat and power generation, comprising 25% of global GHG emissions (158), followed by agriculture, forestry and land use (24%), industries (21%), transportation (14%), other energy industries (10%) and building exhausts (6%). Hence, life cycle assessments to account for the emissions of the energy mix used in cement-based carbon storage systems will be essential in every location where scale-up and scale-out are planned.

5.1.2 Locations

NOAA's Sea Level Rise Viewer (159) was used to provide the following maps of mean highest high water (MHHW), showing areas estimated to be in need of flooding protection by certain times shown in blue. For sea level rise that has occurred as of today, impacted areas include the Seattle-Tacoma area of Washington, the Gulf Coast area around New Orleans, the coasts off Florida, North Carolina, the Chesapeake Bay, the Mid-Atlantic, as well as Maine. These are areas where beach erosion is likely, and where tetrapods might be integrated as part of a wetland restoration plan further inland to regrow wetlands capable of dealing with future storm surges.

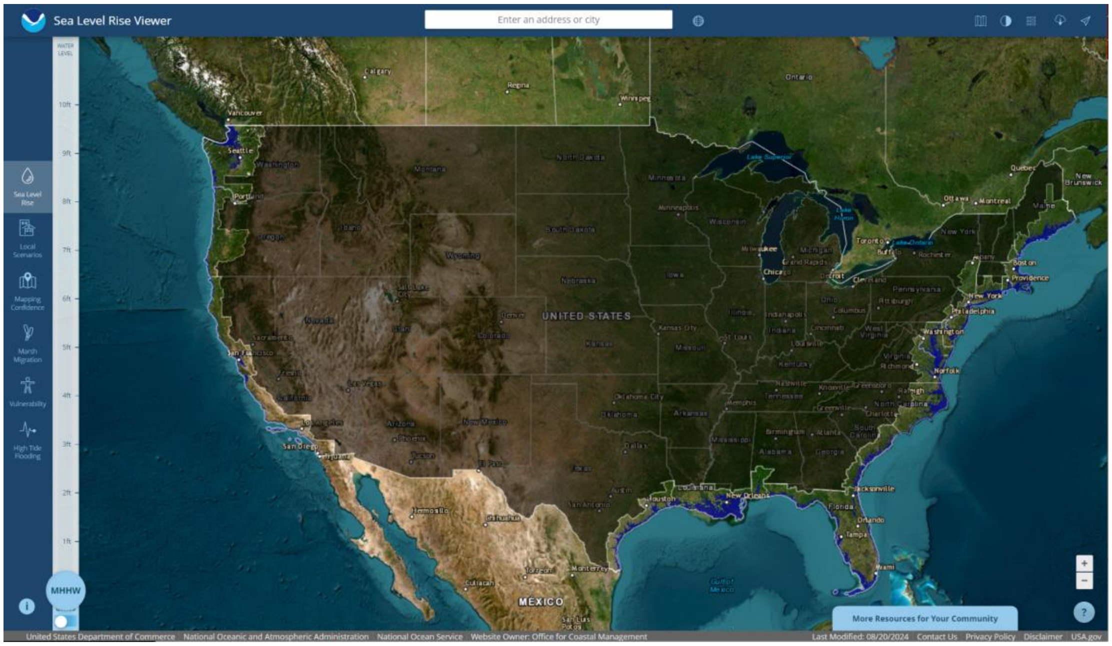


Figure 17. Current map of mean highest high water (MHHW).

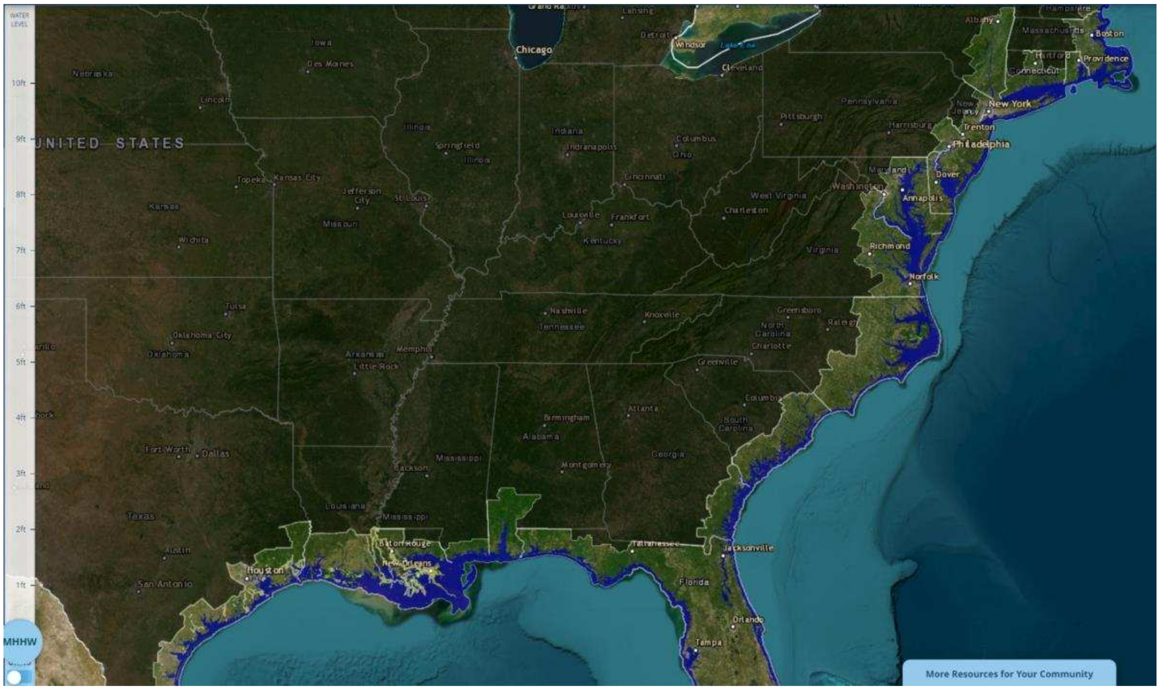


Figure 18. Eastern and southeastern US, current MHHW.

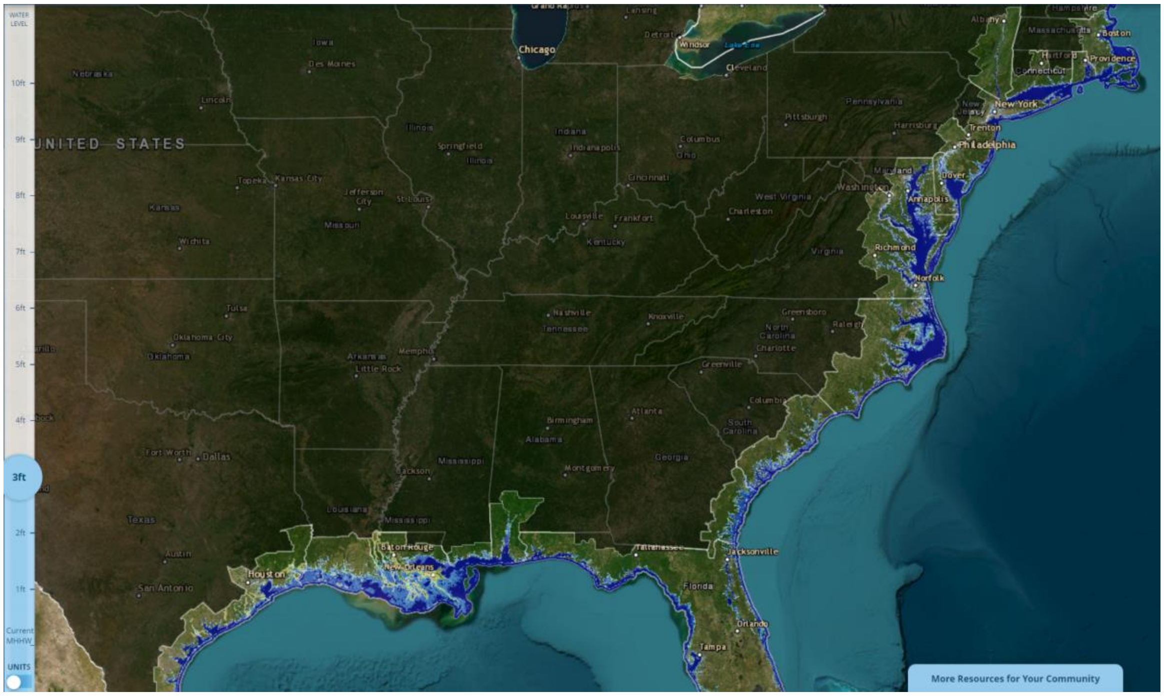


Figure 19. Eastern and southeastern US under the 3 ft of sea level rise projected for 2050. Every coastal state has extensively impacted shorelines.

As we scale out cement-based carbon storage systems, as with any technology, it is important to recognize that there are methods to minimize the conflicts that will arise between development priorities and the protection of nature. The necessary renewable energy infrastructure, biochar production facilities, and carbon storage sites at gigatonne scale necessitates a meticulous approach to avoid unintended consequences for ecosystems, biodiversity, and critical habitats. This is key for ensuring that as we strive to undo the harm caused by our past actions, our solutions do not inadvertently create new problems. There exist tradeoffs between renewable energy development, potential greenhouse gas emissions from land-use change, and ecosystem preservation that are vital to understand for informed decision-making. Rigorous research and modeling can guide the development of strategies that balance our energy needs with ecological sustainability. This involves evaluating the costs and benefits of different land-use scenarios and identifying optimal solutions that minimize environmental impact while maximizing renewable energy generation and carbon sequestration potential. Through thoughtful policy and regulatory controls, we can navigate a path that allows us to decarbonize without compromising our overall sustainability goals.

Balancing the need for clean energy with the preservation of natural habitats is crucial for achieving a truly sustainable future. Recommendations include:

1. Evaluating the environmental impacts of biochar and calcium carbonate production and use in concrete: Spatial externalities and environmental impacts provide important constraints on the location of carbon storage sites. For cement-based carbon storage where storage is achieved through biochar or calcium carbonate the latter of which would require either CCUS or direct air capture technologies. The environmental impacts of both must be considered along with the benefit of storing carbon. Both biochar production and carbon mineralization will have spatially explicit impacts on the environment as with any other land use. The minimization of those impacts, perhaps through co-location of another land use providing the opposite impact, is important to ensure such projects yield a net ecosystem benefit. Without attention paid to not just a benefit but a net benefit, ecosystem degradation in an area cannot be halted, only slowed.

2. Regional planning and impact assessments of key technologies and their life cycle activities to identify optimal locations for each in their supply networks: From the perspective of spatial economics, *land availability and land use zoning* plays a key role. Land must be available for carbon storage and preferably close enough to sites of sequestration to minimize energy needs for transportation and increased costs for both that would arise with greater distances traveled. What land is available will also depend on the zoning regulations governing land use in the area. Areas where biochar production may be favorable, such as agricultural lands where crop residues such as corn stover may be produced, may be different from areas suitable for carbon storage. The type of carbon storage is also an important factor since structural concrete will most often be used in/near urban areas. Non-structural concrete for uses such as in tetrapods controlling beach erosion, these will require proximity to beaches. Geologic carbon sequestration is dependent on the identification of suitable subsurface geology and biomass carbon sequestration depends on the many factors that affect net primary production in ecosystems. Where favorable land is available and permitted by zoning, economic factors such as land prices, proximity to transportation networks, and other land use policies may still influence decisions about where to locate biochar production facilities or carbon mineralization sites. Regional planning and impact assessments should be conducted to identify optimal locations and supply networks for biochar and calcium carbonate production, cement and concrete production, CCUS, and the renewable energy to support cradle-to-cradle life cycle activities for each. For example, an assessment might include an examination of where Portland cement-based concrete is used, what the demand for such concrete construction might look like over the next few years, and a determination of the potential for concrete carbon storage under different conditions for biochar used as a cement replacement (at 2 wt%), as an aggregate (at 20 wt%), and for calcium carbonate used as a cement replacement (at 2 wt%, nanoscale size) and as an aggregate (see if 20 wt% might be possible). Scenarios of low, moderate, and high construction growth could be included, as well as deployment of tetrapods for beach erosion due to storms and sea level rise as an important nonstructural use.

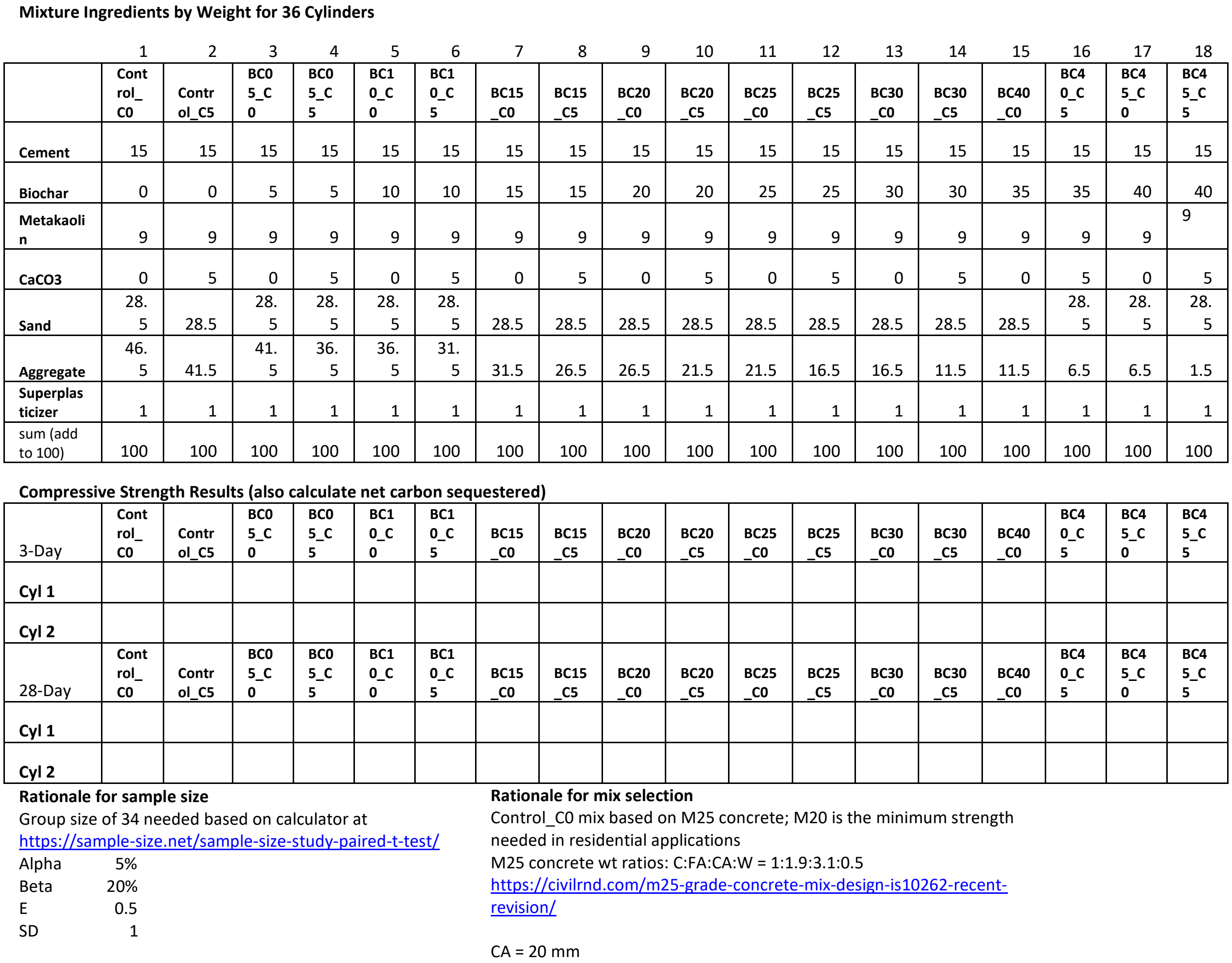
3. Create robust markets and supportive policy frameworks to incentivize the use of biochar and calcium carbonate in construction: There are significant financial challenges as well as opportunities associated with the large-scale deployment of carbon storage systems. Addressing financial and infrastructure challenges is key to unlocking investment to enable such a scale-out. By leveraging innovative financing mechanisms, promoting the benefits of these technologies, and addressing barriers to investment, we can accelerate the transition to a sustainable future.

4. Advance technologies together: the important role of technological advancements in sustainable energy and carbon management: Continuous technological advancements are crucial for the successful and widespread deployment of renewable energy and carbon management solutions. By addressing financial barriers, fostering collaboration, and prioritizing research and development, we can unlock the transformative potential of these technologies and pave the way for a sustainable future.

5. Separate emissions from heating to reduce the carbon footprint of cement production: CO_2 can be isolated from the calcination process by heating limestone indirectly (through a wall) to separate emissions from heating from emissions from the limestone. The emissions from limestone are nearly pure; since these do not require much further processing, this would reduce the cost of CCUS. The LEILAC 1 and 2 projects (in Lixhe, Belgium, and Hanover, Germany, respectively) are trialing this; LEILAC 2 captures about 20% of a cement plant's process emissions, which is around 100,000 tonnes/year (155).

5.2 Future Research

It would be of engineering relevance to better understand what amounts of biochar and calcium carbonate could be useful for different concrete applications, especially within UHPC systems, and how compressive strength and carbon storage varied within such systems. An experiment has been proposed to test variations in compressive strength and carbon storage in UHPC (Figure 20).



Mixture Ingredients by Weight for 36 Cylinders

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	Control_C0	**Control_C5**	**BC05_C0**	**BC05_C5**	**BC10_C0**	**BC10_C5**	**BC15_C0**	**BC15_C5**	**BC20_C0**	**BC20_C5**	**BC25_C0**	**BC25_C5**	**BC30_C0**	**BC30_C5**	**BC40_C0**	**BC40_C5**	**BC45_C0**	**BC45_C5**
Cement	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Biochar	0	0	5	5	10	10	15	15	20	20	25	25	30	30	35	35	40	40
Metakaolin	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
CaCO3	0	5	0	5	0	5	0	5	0	5	0	5	0	5	0	5	0	5
Sand	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5
Aggregate	46.5	41.5	41.5	36.5	36.5	31.5	31.5	26.5	26.5	21.5	21.5	16.5	16.5	11.5	11.5	6.5	6.5	1.5
Superplasticizer	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
sum (add to 100)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Compressive Strength Results (also calculate net carbon sequestered)

3-Day	**Control_C0**	**Control_C5**	**BC05_C0**	**BC05_C5**	**BC10_C0**	**BC10_C5**	**BC15_C0**	**BC15_C5**	**BC20_C0**	**BC20_C5**	**BC25_C0**	**BC25_C5**	**BC30_C0**	**BC30_C5**	**BC40_C0**	**BC40_C5**	**BC45_C0**	**BC45_C5**
Cyl 1																		
Cyl 2																		
28-Day	**Control_C0**	**Control_C5**	**BC05_C0**	**BC05_C5**	**BC10_C0**	**BC10_C5**	**BC15_C0**	**BC15_C5**	**BC20_C0**	**BC20_C5**	**BC25_C0**	**BC25_C5**	**BC30_C0**	**BC30_C5**	**BC40_C0**	**BC40_C5**	**BC45_C0**	**BC45_C5**
Cyl 1																		
Cyl 2																		

Rationale for sample size

Group size of 34 needed based on calculator at https://sample-size.net/sample-size-study-paired-t-test/

Alpha	5%
Beta	20%
E	0.5
SD	1

Rationale for mix selection

Control_C0 mix based on M25 concrete; M20 is the minimum strength needed in residential applications

M25 concrete wt ratios: C:FA:CA:W = 1:1.9:3.1:0.5

https://civilrnd.com/m25-grade-concrete-mix-design-is10262-recent-revision/

CA = 20 mm

Figure 20. Screen capture of an experiment to test compressive strength and carbon storage in UHPC similar to the 10-variable model, except including biochar.

It would be of interest to compare UHPC results alongside those from our experimental results in a cement-based carbon storage system using biochar and calcium carbonate in concrete, to see which components from UHPC might be useful to improve strength development in carbon-neutral concrete having a larger percentage of biochar, calcium carbonate, or both than what was experimented with when forming BC+$CaCO_3$+cement mortar composites. Biochar of 30 wt% has been shown to be possible to incorporate into concrete by pre-soaking the biochar in alkaline water (80) to aid in internal curing, a step we could not do for two reasons: 1) the necessary performance of testing at a cement plant laboratory (Lehigh-Hanson, supervised by Boakye) meant that dry mixes needed to be shipped to lower transportation costs and 2) there is a desirability of having a ready-mix formulation more easily transported to construction or tetrapod manufacturing sites where local sources of water can be added as needed without transporting that water within the concrete. The internal curing and filler effects have since been described as important for the development of biochar-cement mortar strength, and the following four properties, the first two of which this research measured, are recommended for future biochar-cement composite studies: 1) Percentages of carbon, nitrogen, sulfur, hydrogen, and oxygen, 2) initial moisture content, 3) maximum liquid sorption capacity, and 4) deionized water soluble ion concentrations (154). $CaCO_3$ is another variable that can be incorporated as limestone powder in quantities as high as 25 wt% into ordinary Portland cement concretes, for other uses where the higher concentration is permissible (160).

Additional research might also seek to quantify the potential for not only tetrapods to serve as cement-based carbon storage systems, but also for these systems to be incorporated into a variety of non-structural forms such as interior insulation panels and exterior cladding given the fire resistance of such composite concretes. Lastly, the mapping of where demand might be highest for all such identified applications, not just for tetrapods for sea level rise in the US but perhaps worldwide across all buildings in need of both fire resistance and insulation for energy savings might prove valuable in quantifying this engineered carbon sink of significant potential.

REFERENCES

1. Yoro KO, Daramola MO. CO2 emission sources, greenhouse gases, and the global warming effect. Advances in carbon capture. Elsevier; 2020. p. 3–28.

2. Ke P, Ciais P, Sitch S, Li W, Bastos A, Liu Z, et al. Low latency carbon budget analysis reveals a large decline of the land carbon sink in 2023. Natl Sci Rev. 2024 Oct 22;

3. Kazlou T, Cherp A, Jewell J. Feasible deployment of carbon capture and storage and the requirements of climate targets. Nat Clim Chang. 2024 Sep 25;14(10):1047–55.

4. Zahasky C, Krevor S. Global geologic carbon storage requirements of climate change mitigation scenarios. Energy Environ Sci. 2020;13(6):1561–7.

5. Fuhrman J, Bergero C, Weber M, Monteith S, Wang FM, Clarens AF, et al. Diverse carbon dioxide removal approaches could reduce impacts on the energy–water–land system. Nat Clim Chang. 2023 Mar 9;

6. Dees JP, Sagues WJ, Woods E, Goldstein HM, Simon AJ, Sanchez DL. Leveraging the bioeconomy for carbon drawdown. Green Chem. 2023;25(8):2930–57.

7. Izumi Y, Iizuka A, Ho H-J. Calculation of greenhouse gas emissions for a carbon recycling system using mineral carbon capture and utilization technology in the cement industry. J Clean Prod. 2021 Aug;312:127618.

8. Elhacham E, Ben-Uri L, Grozovski J, Bar-On YM, Milo R. Global human-made mass exceeds all living biomass. Nature. 2020 Dec 9;588(7838):442–4.

9. Uratani JM, Griffiths S. A forward looking perspective on the cement and concrete industry: Implications of growth and development in the Global South. Energy Research & Social Science. 2023 Mar;97:102972.

10. NOAA. Nitrous oxide emissions grew 40 percent from 1980 to 2020, accelerating climate change - NOAA Research [Internet]. 2024 [cited 2024 Oct 28]. Available from: https://research.noaa.gov/2024/06/12/nitrous-oxide-emissions-grew-40-percent-from-1980-to-2020-accelerating-climate-change

11. Lippiatt N, Ling T-C, Pan S-Y. Towards carbon-neutral construction materials: Carbonation of cement-based materials and the future perspective. Journal of Building Engineering. 2020 Mar;28:101062.

12. Clark DE, Oelkers EH, Gunnarsson I, Sigfússon B, Snæbjörnsdóttir SÓ, Aradóttir ES, et al. CarbFix2: CO2 and H2S mineralization during 3.5 years of continuous injection into basaltic rocks at more than 250 °C. Geochim Cosmochim Acta. 2020 Jun;279:45–66.

13. Boakye K. Improving Kiln Feed Chemistry and Overburden Wasting through Controlled Consistent Quarry Material Mix: A Case Study at Union Bridge Cement Plant. CEBACOM. 2021 Oct 10;2(4):1–12.

14. Boakye K, Winters D, Simske S. Literature review and challenges for the adaptation, implementation of digitization, and data analytics for operational excellence in the cement and aggregate production industry. Salt Lake City, UT: SME; 2022. p. 1–6.

15. Oguntola O, Simske S. Continuous assessment of the environmental impact and economic viability of decarbonization improvements in cement production. Resources. 2023 Aug 9;12(8):95.

16. Winters D, Boakye K, Simske S. Toward Carbon-Neutral Concrete through Biochar–Cement–Calcium Carbonate Composites: A Critical Review. Sustainability. 2022 Apr 13;14(8):4633.

17. Center Of Inventions. How 100,000 Concrete Tetrapods / Xblocs Manufactured And Placed Along The Entire Coastline [Internet]. 2021 [cited 2024 Jul 3]. Available from: https://www.youtube.com/watch?v=7AWb2SQ14mI

18. Calculator | Xbloc [Internet]. [cited 2024 Oct 28]. Available from: https://www.xbloc.com/design/calculator

19. Giorcelli M, Khan A, Pugno NM, Rosso C, Tagliaferro A. Biochar as a cheap and environmental friendly filler able to improve polymer mechanical properties. Biomass and Bioenergy. 2019 Jan;120:219–23.

20. Gupta S, Kua HW, Low CY. Use of biochar as carbon sequestering additive in cement mortar. Cement and Concrete Composites. 2018 Mar;87:110–29.

21. Wang L, Chen L, Tsang DCW, Guo B, Yang J, Shen Z, et al. Biochar as green additives in cement-based composites with carbon dioxide curing. J Clean Prod. 2020 Jun;258:120678.

22. Matschei T, Lothenbach B, Glasser FP. The role of calcium carbonate in cement hydration. Cement and Concrete Research. 2007 Apr;37(4):551–8.

23. Wu J, Li Z, Huang D, Liu X, Tang C, Parikh SJ, et al. A novel calcium-based magnetic biochar is effective in stabilization of arsenic and cadmium co-contamination in aerobic soils. J Hazard Mater. 2020 Apr 5;387:122010.

24. Nehdi ML, Marani A, Zhang L. Is net-zero feasible: Systematic review of cement and concrete decarbonization technologies. Renew Sustain Energy Rev. 2024 Mar;191:114169.

25. Boakye K, Winters D, Oguntola O, Fenton K, Simske S. A review of strategies to achieve net zero targets in the cement and concrete sectors. Reducing Carbon Footprint - Microscale to Macroscale, Technical, Industrial and Policy Regulations [Working Title]. IntechOpen; 2024.

26. Food Waste FAQs | USDA [Internet]. [cited 2024 Oct 28]. Available from: https://www.usda.gov/foodwaste/faqs

27. Salah Uddin KM, Middendorf B. Reactivity of different crystalline surfaces of C3S during early hydration by the atomistic approach. Materials (Basel). 2019 May 9;12(9).

28. Ramezanianpour AA, Ghiasvand E, Nickseresht I, Mahdikhani M, Moodi F. Influence of various amounts of limestone powder on performance of Portland limestone cement concretes. Cement and Concrete Composites. 2009 Nov;31(10):715–20.

29. Dębska B, Rzeszow University of Technology, Krasoń J, Rzeszow University of Technology, Lichołai L, Rzeszow University of Technology. Application of Taguchi method for the design of cement mortars containing waste materials. BoZPE. 2020;9(1/2020):15–26.

30. van Vuuren DP, Stehfest E, Gernaat DEHJ, van den Berg M, Bijl DL, de Boer HS, et al. Alternative pathways to the 1.5 °C target reduce the need for negative emission technologies. Nat Clim Chang. 2018 May;8(5):391–7.

31. Alhashimi HA, Aktas CB. Life cycle environmental and economic performance of biochar compared with activated carbon: A meta-analysis. Resources, Conservation and Recycling. 2017 Mar;118:13–26.

32. Panwar NL, Pawar A, Salvi BL. Comprehensive review on production and utilization of biochar. SN Appl Sci. 2019 Feb;1(2):168.

33. Schmidt H, Kammann C, Hagemann N, Leifeld J, Bucheli TD, Sánchez Monedero MA, et al. Biochar in agriculture – A systematic review of 26 global meta-analyses. Glob Change Biol Bioenergy. 2021 Sep;

34. Ye L, Camps-Arbestain M, Shen Q, Lehmann J, Singh B, Sabir M. Biochar effects on crop yields with and without fertilizer: A meta-analysis of field studies using separate controls. Soil Use & Management. 2020 Jan;36(1):2–18.

35. Cao M, Li L, Yin H, Ming X. Microstructure and strength of calcium carbonate (caco3) whisker reinforced cement paste after exposed to high temperatures. Fire Technol. 2019 Mar 9;1–21.

36. Torres A, Simoni MU, Keiding JK, Müller DB, zu Ermgassen SOSE, Liu J, et al. Sustainability of the global sand system in the Anthropocene. One Earth. 2021 May;4(5):639–50.

37. Chen L, Zhang Y, Wang L, Ruan S, Chen J, Li H, et al. Biochar-augmented carbon-negative concrete. Chemical Engineering Journal. 2022 Mar;431:133946.

38. Sirico A, Bernardi P, Belletti B, Malcevschi A, Restuccia L, Ferro GA, et al. Biochar-based cement pastes and mortars with enhanced mechanical properties. Frattura ed Integrità Strutturale. 2020 Sep 23;14(54):297–316.

39. Danish A, Ali Mosaberpanah M, Usama Salim M, Ahmad N, Ahmad F, Ahmad A. Reusing biochar as a filler or cement replacement material in cementitious composites: A review. Constr Build Mater. 2021 Sep;300:124295.

40. Dixit A, Gupta S, Pang SD, Kua HW. Waste Valorisation using biochar for cement replacement and internal curing in ultra-high performance concrete. J Clean Prod. 2019 Nov;238:117876.

41. Gupta S, Kashani A, Mahmood AH, Han T. Carbon sequestration in cementitious composites using biochar and fly ash – Effect on mechanical and durability properties. Constr Build Mater. 2021 Jul;291:123363.

42. Haque MI, Khan RI, Ashraf W, Pendse H. Production of sustainable, low-permeable and self-sensing cementitious composites using biochar. Sustainable Materials and Technologies. 2021 Jul;28:e00279.

43. Khitab A, Ahmad S, Khan RA, Arshad MT, Anwar W, Tariq J, et al. Production of biochar and its potential application in cementitious composites. Crystals. 2021 May 10;11(5):527.

44. Maljaee H, Madadi R, Paiva H, Tarelho L, Ferreira VM. Incorporation of biochar in cementitious materials: A roadmap of biochar selection. Constr Build Mater. 2021 May;283:122757.

45. Mensah RA, Shanmugam V, Narayanan S, Razavi SMJ, Ulfberg A, Blanksvärd T, et al. Biochar-Added Cementitious Materials—A Review on Mechanical, Thermal, and Environmental Properties. Sustainability. 2021 Aug 20;13(16):9336.

46. Muthukrishnan S, Gupta S, Kua HW. Application of rice husk biochar and thermally treated low

silica rice husk ash to improve physical properties of cement mortar. Theoretical and Applied Fracture Mechanics. 2019 Dec;104:102376.

47. Restuccia L, Ferro GA. Influence of filler size on the mechanical properties of cement-based composites. Fatigue Fract Engng Mater Struct. 2018 Apr;41(4):797–805.

48. Sirico A, Bernardi P, Belletti B, Malcevschi A, Dalcanale E, Domenichelli I, et al. Mechanical characterization of cement-based materials containing biochar from gasification. Constr Build Mater. 2020 Jun;246:118490.

49. Suarez-Riera D, Restuccia L, Ferro GA. The use of Biochar to reduce the carbon footprint of cement-based materials. Procedia Structural Integrity. 2020;26:199–210.

50. Tan K-H, Wang T-Y, Zhou Z-H, Qin Y-H. Biochar as a partial cement replacement material for developing sustainable concrete: an overview. J Mater Civ Eng. 2021 Dec;33(12).

51. Yang X, Lin R-S, Han Y, Wang X-Y. Behavior of Biochar-Modified Cementitious Composites Exposed to High Temperatures. Materials (Basel). 2021 Sep 18;14(18).

52. Yang X, Wang X-Y. Hydration-strength-durability-workability of biochar-cement binary blends. Journal of Building Engineering. 2021 Oct;42:103064.

53. Nicoara AI, Stoica AE, Vrabec M, Šmuc Rogan N, Sturm S, Ow-Yang C, et al. End-of-Life Materials Used as Supplementary Cementitious Materials in the Concrete Industry. Materials (Basel). 2020 Apr 22;13(8).

54. D’Alessandro A, Fabiani C, Pisello AL, Ubertini F, Materazzi AL, Cotana F. Innovative concretes for low-carbon constructions: a review. International Journal of Low-Carbon Technologies. 2016 Oct 14;

55. Shi C, Tu Z, Guo M-Z, Wang D. Accelerated carbonation as a fast curing technology for concrete blocks. Sustainable and Nonconventional Construction Materials using Inorganic Bonded Fiber Composites. Elsevier; 2017. p. 313–41.

56. Kaliyavaradhan SK, Ling T-C. Potential of CO 2 sequestration through construction and demolition (C&D) waste—An overview. Journal of CO2 Utilization. 2017 Jul;20:234–42.

57. Pu Y, Li L, Wang Q, Shi X, Luan C, Zhang G, et al. Accelerated carbonation technology for enhanced treatment of recycled concrete aggregates: A state-of-the-art review. Constr Build Mater. 2021 May;282:122671.

58. Infante Gomes R, Brazão Farinha C, Veiga R, de Brito J, Faria P, Bastos D. CO2 sequestration by construction and demolition waste aggregates and effect on mortars and concrete performance - An overview. Renew Sustain Energy Rev. 2021 Dec;152:111668.

59. Suescum-Morales D, Fernández-Rodríguez JM, Jiménez JR. Use of carbonated water to improve the mechanical properties and reduce the carbon footprint of cement-based materials with recycled aggregates. Journal of CO2 Utilization. 2022 Mar;57:101886.

60. Al-Mansour, Chow, Feo, Penna, Lau. Green Concrete: By-Products Utilization and Advanced Approaches. Sustainability. 2019 Sep 20;11(19):5145.

61. Wang F, Harindintwali JD, Yuan Z, Wang M, Wang F, Li S, et al. Technologies and perspectives for achieving carbon neutrality. Innovation (Camb). 2021 Nov 28;2(4):100180.

62. Legan M, Zupan K, Gotvajn AŽ. Biochar-Containing Building Materials and Carbon Footprint Reduction. Bratislava, Slovakia: Slovak Society of Chemical Engineering; 2021 [cited 2024 Apr 22]. Available from: https://plus.cobiss.net/cobiss/adz/en/bib/COBIB/63636483

63. Gupta S, Kua HW, Koh HJ. Application of biochar from food and wood waste as green admixture for cement mortar. Sci Total Environ. 2018 Apr 1;619–620:419–35.

64. Gupta S, Kua HW, Tan Cynthia SY. Use of biochar-coated polypropylene fibers for carbon sequestration and physical improvement of mortar. Cement and Concrete Composites. 2017 Oct;83:171–87.

65. Legan M, Gotvajn AŽ, Zupan K. Potential of biochar use in building materials. J Environ

Manage. 2022 May 1;309:114704.

66. Pradhan S, Chang Boon Poh A, Qian S. Impact of service life and system boundaries on life cycle assessment of sustainable concrete mixes. J Clean Prod. 2022 Mar;342:130847.

67. Piccolo F, Andreola F, Barbieri L, Lancellotti I. Synthesis and Characterization of Biochar-Based Geopolymer Materials. Appl Sci. 2021 Nov 19;11(22):10945.

68. Jami T, Karade SR, Singh LP. A review of the properties of hemp concrete for green building applications. J Clean Prod. 2019 Dec;239:117852.

69. Wang L, Chen L, Poon CS, Wang C-H, Ok YS, Mechtcherine V, et al. Roles of Biochar and CO_2 Curing in Sustainable Magnesia Cement-Based Composites. ACS Sustain Chem Eng. 2021 Jun 28;9(25):8603–10.

70. Akinyemi BA, Adesina A. Recent advancements in the use of biochar for cementitious applications: A review. Journal of Building Engineering. 2020 Nov;32:101705.

71. Roberts KG, Gloy BA, Joseph S, Scott NR, Lehmann J. Life cycle assessment of biochar systems: estimating the energetic, economic, and climate change potential. Environ Sci Technol. 2010 Jan 15;44(2):827–33.

72. Kua HW, Ng MS, Ong K. Innovative uses of biochar as carbon sequestering building materials in wall plaster and pellets. Academic Journal of Civil Engineering. 2017;

73. Pan Y, Birdsey RA, Fang J, Houghton R, Kauppi PE, Kurz WA, et al. A large and persistent carbon sink in the world’s forests. Science. 2011 Aug 19;333(6045):988–93.

74. Leng L, Xu X, Wei L, Fan L, Huang H, Li J, et al. Biochar stability assessment by incubation and modelling: Methods, drawbacks and recommendations. Sci Total Environ. 2019 May 10;664:11–23.

75. Chang R, Kim S, Lee S, Choi S, Kim M, Park Y. Calcium carbonate precipitation for CO2

storage and utilization: A review of the carbonate crystallization and polymorphism. Front Energy Res. 2017 Jul 10;5.

76. Gupta S, Kua HW, Pang SD. Biochar-mortar composite: Manufacturing, evaluation of physical properties and economic viability. Constr Build Mater. 2018 Apr;167:874–89.

77. Gupta S, Krishnan P, Kashani A, Kua HW. Application of biochar from coconut and wood waste to reduce shrinkage and improve physical properties of silica fume-cement mortar. Constr Build Mater. 2020 Nov;262:120688.

78. Han T. Application of peanut biochar as admixture in cement mortar. IOP Conf Ser: Earth Environ Sci. 2020 Jul 1;531(1):012061.

79. Asadi Zeidabadi Z, Bakhtiari S, Abbaslou H, Ghanizadeh AR. Synthesis, characterization and evaluation of biochar from agricultural waste biomass for use in building materials. Constr Build Mater. 2018 Aug;181:301–8.

80. Gupta S, Kua HW. Effect of water entrainment by pre-soaked biochar particles on strength and permeability of cement mortar. Constr Build Mater. 2018 Jan;159:107–25.

81. Praneeth S, Saavedra L, Zeng M, Dubey BK, Sarmah AK. Biochar admixtured lightweight, porous and tougher cement mortars: Mechanical, durability and micro computed tomography analysis. Sci Total Environ. 2021 Jan 1;750:142327.

82. Saulat H, Cao M, Khan MM, Khan M, Khan MM, Rehman A. Preparation and applications of calcium carbonate whisker with a special focus on construction materials. Constr Build Mater. 2020 Mar;236:117613.

83. Li LI, Li Z, Cao M, Tang YI, Zhang ZHE. Nanoindentation and porosity fractal dimension of calcium carbonate whisker reinforced cement paste after elevated temperatures (up to 900∘c). Fractals. 2021 Mar;29(02):2140001.

84. Renders GAP, Mulder L, Langenbach GEJ, van Ruijven LJ, van Eijden TMGJ. Biomechanical

effect of mineral heterogeneity in trabecular bone. J Biomech. 2008 Sep 18;41(13):2793–8.

85. Keaveny TM, Hayes WC. A 20-year perspective on the mechanical properties of trabecular bone. J Biomech Eng. 1993 Nov;115(4B):534–42.

86. Cao M, Xu L, Zhang C. Rheology, fiber distribution and mechanical properties of calcium carbonate (CaCO 3) whisker reinforced cement mortar. Composites Part A: Applied Science and Manufacturing. 2016 Nov;90:662–9.

87. Cao M, Ming X, He K, Li L, Shen S. Effect of Macro-, Micro- and Nano-Calcium Carbonate on Properties of Cementitious Composites-A Review. Materials (Basel). 2019 Mar 7;12(5).

88. Yang H, Che Y, Shi M. Influences of calcium carbonate nanoparticles on the workability and strength of 3D printing cementitious materials containing limestone powder. Journal of Building Engineering. 2021 Dec;44:102976.

89. Gupta S, Kua HW, Pang SD. Biochar-concrete composite: manufacturing, characterization and performance evaluation at elevated temperature. Academic Journal of Civil Engineering. 2019;

90. Kovács P, Pokorný J, Šál J, Ševčík R. The influence of biochar addition on the strength and microstructural characteristics of cement pastes. IOP Conf Ser: Mater Sci Eng. 2020 Dec 1;960(4):042097.

91. Mrad R, Chehab G. Mechanical and Microstructure Properties of Biochar-Based Mortar: An Internal Curing Agent for PCC. Sustainability. 2019 Apr 28;11(9):2491.

92. Qin Y, Pang X, Tan K, Bao T. Evaluation of pervious concrete performance with pulverized biochar as cement replacement. Cement and Concrete Composites. 2021 May;119:104022.

93. Tan K, Qin Y, Wang J. Evaluation of the properties and carbon sequestration potential of biochar-modified pervious concrete. Constr Build Mater. 2022 Jan;314:125648.

94. Falliano D, De Domenico D, Quattrocchi S, Cosenza P, Ricciardi G, Restuccia L, et al.

Mechanical properties and carbon footprint of 3D-printable cement mortars with biochar additions. MATEC Web of Conferences. 2020;323:01017.

95. Zhang J, Wu C, Hou W, Zhao Q, Liang X, Lin S, et al. Biological calcium carbonate with a unique organic-inorganic composite structure to enhance biochar stability. Environ Sci Process Impacts. 2021 Nov 17;23(11):1747–58.

96. Sahibulla SMM, Jaisingh SJ. Pozzolanic biosilica, biochar, and egg shell in setting time, WVTR, and compression strength of biocement mortar: a Taguchi GRA validation. Biomass Conv Bioref. 2023 Aug;13(12):10475–82.

97. Kelemen P, Benson SM, Pilorgé H, Psarras P, Wilcox J. An overview of the status and challenges of CO2 storage in minerals and geological formations. Front Clim. 2019 Nov 15;1.

98. Tanzer SE, Blok K, Ramírez A. Decarbonising Industry via BECCS: Promising Sectors, Challenges, and Techno-economic Limits of Negative Emissions. Curr Sustainable Renewable Energy Rep. 2021 Dec;8(4):253–62.

99. Adesina A. Recent advances in the concrete industry to reduce its carbon dioxide emissions. Environmental Challenges. 2020 Dec;1:100004.

100. Cabeza LF, Barreneche C, Miró L, Morera JM, Bartolí E, Inés Fernández A. Low carbon and low embodied energy materials in buildings: A review. Renew Sustain Energy Rev. 2013 Jul;23:536–42.

101. Minunno R, O’Grady T, Morrison GM, Gruner RL. Investigating the embodied energy and carbon of buildings: A systematic literature review and meta-analysis of life cycle assessments. Renew Sustain Energy Rev. 2021 Jun;143:110935.

102. Habert G, Miller SA, John VM, Provis JL, Favier A, Horvath A, et al. Environmental impacts and decarbonization strategies in the cement and concrete industries. Nat Rev Earth Environ. 2020 Sep 22;

103. Arif M, Jan T, Riaz M, Fahad S, Adnan M, Amanullah, et al. Biochar; a remedy for climate change. In: Fahad S, Hasanuzzaman M, Alam M, Ullah H, Saeed M, Ali Khan I, et al., editors. Environment, climate, plant and vegetation growth. Cham: Springer International Publishing; 2020. p. 151–71.

104. Makul N. Modern sustainable cement and concrete composites: Review of current status, challenges and guidelines. Sustainable Materials and Technologies. 2020 Sep;25:e00155.

105. Terlouw T, Bauer C, Rosa L, Mazzotti M. Life cycle assessment of carbon dioxide removal technologies: a critical review. Energy Environ Sci. 2021;14(4):1701–21.

106. Yang Q, Mašek O, Zhao L, Nan H, Yu S, Yin J, et al. Country-level potential of carbon sequestration and environmental benefits by utilizing crop residues for biochar implementation. Appl Energy. 2021 Jan;282:116275.

107. Restuccia L, Ferro GA, Suarez-Riera D, Sirico A, Bernardi P, Belletti B, et al. Mechanical characterization of different biochar-based cement composites. Procedia Structural Integrity. 2020;25:226–33.

108. Kua HW, Gupta S, Tan C. Biochar as a bond enhancement in fiber-reinforced mortar. Academic Journal of Civil Engineering. 2017;

109. Liu R, Xiao H, Guan S, Zhang J, Yao D. Technology and method for applying biochar in building materials to evidently improve the carbon capture ability. J Clean Prod. 2020 Nov;273:123154.

110. Boumaaza M, Belaadi A, Bourchak M, Jawaid M, Hamid S. Comparative study of flexural properties prediction of Washingtonia filifera rachis biochar bio-mortar by ANN and RSM models. Constr Build Mater. 2022 Feb;318:125985.

111. Dissanayake PD, You S, Igalavithana AD, Xia Y, Bhatnagar A, Gupta S, et al. Biochar-based adsorbents for carbon dioxide capture: A critical review. Renew Sustain Energy Rev. 2020

Mar;119:109582.

112. Ye H, Radlińska A, Neves J. Drying and carbonation shrinkage of cement paste containing alkalis. Mater Struct. 2017 Apr;50(2):132.

113. Javadabadi MT, Kristiansen DDL, Redie MB, Baghban MH. Sustainable concrete: A review. IJSCER. 2019;126–32.

114. Gupta S, Kashani A. Utilization of biochar from unwashed peanut shell in cementitious building materials – Effect on early age properties and environmental benefits. Fuel Processing Technology. 2021 Jul;218:106841.

115. Zhao MY, Enders A, Lehmann J. Short- and long-term flammability of biochars. Biomass and Bioenergy. 2014 Oct;69:183–91.

116. Gupta S, Kua HW. Factors determining the potential of biochar as a carbon capturing and sequestering construction material: critical review. J Mater Civ Eng. 2017 Sep;29(9).

117. Gupta S, Kua HW. Biochar as a carbon sequestering construction material in cementitious mortar. Academic Journal of Civil Engineering. 2017;

118. Rostami R, Klemm AJ, Almeida FCR. Reduction of shrinkage by Superabsorbent polymers (SAP) in fibre reinforced mortars. Constr Build Mater. 2021 Jun;288:123109.

119. Basquiroto de Souza F, Yao X, Gao W, Duan W. Graphene opens pathways to a carbon-neutral cement industry. Sci Bull (Beijing). 2022 Jan;67(1):5–8.

120. Santos T, Almeida J, Silvestre JD, Faria P. Life cycle assessment of mortars: A review on technical potential and drawbacks. Constr Build Mater. 2021 Jun;288:123069.

121. Kim T, Lee S, Chae C, Jang H, Lee K. Development of the CO2 emission evaluation tool for the life cycle assessment of concrete. Sustainability. 2017 Nov 17;9(11):2116.

122. Feiz R, Ammenberg J, Baas L, Eklund M, Helgstrand A, Marshall R. Improving the CO2

performance of cement, part I: utilizing life-cycle assessment and key performance indicators to assess development within the cement industry. J Clean Prod. 2015 Jul;98:272–81.

123. Sanjuán MÁ, Menéndez E, Recino H. Mechanical Performance of Portland Cement, Coarse Silica Fume, and Limestone (PC-SF-LS) Ternary Portland Cements. Materials (Basel). 2022 Apr 18;15(8).

124. Khan K, Salami BA, Iqbal M, Amin MN, Ahmed F, Jalal FE. Compressive strength estimation of fly ash/slag based green concrete by deploying artificial intelligence models. Materials (Basel). 2022 May 23;15(10).

125. Osial M, Pregowska A, Wilczewski S, Urbańska W, Giersig M. Waste management for green concrete solutions: A concise critical review. Recycling. 2022 Jun 10;7(3):37.

126. Khan K, Aziz MA, Zubair M, Amin MN. Biochar Produced from Saudi Agriculture Waste as a Cement Additive for Improved Mechanical and Durability Properties-SWOT Analysis and Techno-Economic Assessment. Materials (Basel). 2022 Aug 3;15(15).

127. Prange MP, Mergelsberg ST, Kerisit SN. Structural water in amorphous carbonate minerals: ab initio molecular dynamics simulations of X-ray pair distribution experiments. Phys Chem Chem Phys. 2023 Mar 1;25(9):6768–79.

128. Mobili A, Cosoli G, Giulietti N, Chiariotti P, Bellezze T, Pandarese G, et al. Biochar and recycled carbon fibres as additions for low-resistive cement-based composites exposed to accelerated degradation. Constr Build Mater. 2023 May;376:131051.

129. Roychand R, Li J, Kilmartin-Lynch S, Saberian M, Zhu J, Youssf O, et al. Carbon sequestration from waste and carbon dioxide mineralisation in concrete – A stronger, sustainable and eco-friendly solution to support circular economy. Constr Build Mater. 2023 May;379:131221.

130. Mishra G, Danoglidis PA, Shah SP, Konsta-Gdoutos MS. Carbon capture and storage potential of biochar-enriched cementitious systems. Cement and Concrete Composites. 2023 Jul;140:105078.

131. Quennoz A. Hydration of C3A with Calcium Sulfate Alone and in the Presence of Calcium Silicate. Lausanne, EPFL. 2011;

132. Ibertest. Equipments for Cement and Mortars Testing [Internet]. Equipments for Cement and Mortars Testing. 2014 [cited 2024 Sep 11]. Available from: https://www.ibertest.es/wp-content/uploads/docs/fichas_producto/maquinas_ensayo/resistencia_cemento/IBERTEST-Cement-Testing-Equipment_2014-V1.1.pdf

133. Yu R, Spiesz P, Brouwers HJH. Mix design and properties assessment of Ultra-High Performance Fibre Reinforced Concrete (UHPFRC). Cement and Concrete Research. 2014 Feb;56:29–39.

134. Sanjuán MÁ, Andrade C. Reactive powder concrete: durability and applications. Appl Sci. 2021 Jun 18;11(12):5629.

135. Smith-Gillis R, Lopez-Anido R, Rushing TS, Landis EN. Development of Thermoplastic Composite Reinforced Ultra-High-Performance Concrete Panels for Impact Resistance. Materials (Basel). 2021 May 12;14(10).

136. Kusumawardaningsih Y, Fehling E, Ismail M. UHPC compressive strength test specimens: cylinder or cube? Procedia Engineering. 2015;125:1076–80.

137. Tafraoui A, Escadeillas G, Lebaili S, Vidal T. Metakaolin in the formulation of UHPC. Constr Build Mater. 2009 Feb;23(2):669–74.

138. Harle SM. Durability and long-term performance of fiber reinforced polymer (FRP) composites: A review. Structures. 2024 Feb;60:105881.

139. Liu H, Yu Y, Liu Y, Zhang M, Li L, Ma L, et al. A review on basalt fiber composites and their applications in clean energy sector and power grids. Polymers (Basel). 2022 Jun 12;14(12).

140. Orca is Climeworks' new large-scale carbon dioxide removal plant [Internet]. [cited 2024 Oct 28]. Available from: https://climeworks.com/plant-orca

141. Iqbal Khan M, Abbas YM. Significance of fiber characteristics on the mechanical properties of steel fiber-reinforced high-strength concrete at different water-cement ratios. Constr Build Mater. 2023 Dec;408:133742.

142. Batuecas E, Liendo F, Tommasi T, Bensaid S, Deorsola FA, Fino D. Recycling CO2 from flue gas for CaCO3 nanoparticles production as cement filler: A Life Cycle Assessment. Journal of CO2 Utilization. 2021 Mar;45:101446.

143. Selim Ustun T, editor. Reducing carbon footprint in different sectors for sustainability. IntechOpen; 2024.

144. El-Sheikh SM, El-Sherbiny S, Barhoum A, Deng Y. Effects of cationic surfactant during the precipitation of calcium carbonate nano-particles on their size, morphology, and other characteristics. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2013 Apr;422:44–9.

145. Chang R, Choi D, Kim MH, Park Y. Tuning crystal polymorphisms and structural investigation of precipitated calcium carbonates for co_2 mineralization. ACS Sustain Chem Eng. 2017 Feb 6;5(2):1659–67.

146. Aldea S, Snåre M, Eränen K, Grenman H, Rautio A-R, Kordás K, et al. Crystallization of Nano-Calcium Carbonate: The Influence of Process Parameters. Chemie Ingenieur Technik. 2016 Nov;88(11):1609–16.

147. Boyjoo Y, Pareek VK, Liu J. Synthesis of micro and nano-sized calcium carbonate particles and their applications. J Mater Chem A. 2014;2(35):14270–88.

148. Liu X, Chen L, Liu A, Wang X. Effect of Nano-CaCO3 on Properties of Cement Paste. Energy Procedia. 2012;16:991–6.

149. Farrag M, Brill F, Dung NV, Sairam N, Schröter K, Kreibich H, et al. On the role of floodplain storage and hydrodynamic interactions in flood risk estimation. Hydrological Sciences Journal.

2022 Mar 12;67(4):508–34.

150. d’Amora M, Liendo F, Deorsola FA, Bensaid S, Giordani S. Toxicological profile of calcium carbonate nanoparticles for industrial applications. Colloids Surf B Biointerfaces. 2020 Jun;190:110947.

151. McDonald L, Glasser FP, Imbabi MS. A New, Carbon-Negative Precipitated Calcium Carbonate Admixture (PCC-A) for Low Carbon Portland Cements. Materials (Basel). 2019 Feb 13;12(4).

152. Han JS, Jung SY, Kang DS, Seo YB. Development of flexible calcium carbonate for papermaking filler. ACS Sustain Chem Eng. 2020 Jun 22;8(24):8994–9001.

153. Tunstall LE. The Feasibility of Biochar as a Cement Replacement to Reduce Concrete’s Carbon Footprint. USBI; 2024 [cited 2024 Oct 25]. Available from: https://biochar-us.org/sites/default/files/presentations/USBI-NABC24-Lori-Tunstall-Biochar-Cement.pdf

154. Hylton J, Hugen A, Rowland SM, Griffin M, Tunstall LE. Relevant biochar characteristics influencing compressive strength of biochar-cement mortars. Biochar. 2024 Oct 15;6(1):87.

155. Hills TP, Sceats M, Rennie D, Fennell P. LEILAC: low cost CO2 capture for the cement and lime industries. Energy Procedia. 2017 Jul;114:6166–70.

156. Plaza MG, Martínez S, Rubiera F. CO2 capture, use, and storage in the cement industry: state of the art and expectations. Energies. 2020 Oct 30;13(21):5692.

157. Ravikumar D, Zhang D, Keoleian G, Miller S, Sick V, Li V. Carbon dioxide utilization in concrete curing or mixing might not produce a net climate benefit. Nat Commun. 2021 Feb 8;12(1):855.

158. Podder J, Patra BR, Pattnaik F, Nanda S, Dalai AK. A review of carbon capture and valorization technologies. Energies. 2023 Mar 9;16(6):2589.

159. NOAA. Sea Level Rise Viewer [Internet]. 2024 [cited 2024 Oct 27]. Available from:

https://coast.noaa.gov/slr/

160. Diab A, Elmoaty A, Aly A. Long term study of mechanical properties, durability and environmental impact of limestone cement concrete. Alexandria Engineering Journal [Internet]. 2017 Dec 4 [cited 2024 Oct 28]; Available from: https://www.scipedia.com/public/Diab_et_al_2016a