Review

Toward Carbon-Neutral Concrete through Biochar–Cement–Calcium Carbonate Composites: A Critical Review

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Abstract: High-density, high-permanence forms of carbon storage are in demand to save storage space on land or at sea while allowing the world to reach its climate targets. Biochar and calcium carbonate are two such forms that have been considered largely separately in the literature for carbon storage. In this paper, we consider how biochar and calcium carbonate might interact when they are used together with cement as part of a carbon storage system, ideally to form a carbon-neutral concrete. The carbon storage system stores atmospherically absorbed CO_2 within concrete, thereby reducing carbon in the atmosphere. In addition, such a system will help in reducing cement usage, thus reducing the need for clinker in cement manufacturing and directly reducing CO_2 emissions that result from limestone calcination during clinker manufacturing. Another benefit of such a composite storage system is its use in building structures, a use that has positive environmental and social impact. Thus, further research on the properties of this composite material is warranted. This paper explores the literature on the use of biochar combined with calcium carbonate and cement as carbon storage material. The use of recycled carbon aggregates (RCAs) and LC3 concrete as part of this approach is reviewed. The paper also addresses the possible compressive strength range of the biochar–cement–calcium carbonate composite material, along with other performance expectations. Obstacles to scaling the use of carbon-neutral concrete are identified and an array of research directions are presented, with the goal of improving carbon-neutral concrete and its use.

Keywords: biocement; biochar; calcium carbonate; carbon storage; carbon-neutral concrete; clinker reduction; compressive strength; UHPC

1. Introduction

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 [1]. 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 [2]. The International Biochar Initiative classifies biochar as class 1 if it has a $C_{(organic)}$ mass fraction $\geq$ 60% [3]. The energy needed to make it varies by feedstock; for example, biochar from pine requires 1.6 +/− 0.3 MJ/kg [3]. Biochar is commonly used as a soil amendment, with agronomic biochar research alone being the subject of 15,000 publications thus far [4]. However, only so much biochar can go into agricultural soils; application rates do not seem to exceed 20 tonnes/ha [5]. 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 [3]. 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 [6]. 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 [1]. 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 [7]. 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 [8].

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 [9–24]. 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 [25].

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. Methods for Producing Carbon-Neutral Concrete

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 [26]. However, there are problems with using RCA as outlined by Lippiatt et al. [27] 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 [27]. 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. [28]: 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. 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. [29] 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 considered to be 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 [12]. 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 [12]. 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 [30] 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. [31] 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 2 of this paper 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. [32] 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 with particular material properties 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 [30].

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. [33] 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 $CaCO_3$, 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.

2.3. 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 [27], 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. [34] 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 [34].

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. [35] 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 [36].

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. [37] found that biochar from mixed food waste, rice waste, and wood waste can all be used as

carbon-sequestrating 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% [38], which the biochar helps to maintain over a longer period of time.

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. [39] 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.

2.3.2. 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. [40] 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 [40], 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 [41]. A cementing material (source of aluminosilicates) and an alkaline activator (alkaline hydroxides and salts) are used in combination. Piccolo, Andreola, Barbieri, and Lancellotti [41] 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. [42] 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. [42] 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 [27] 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. [43] 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.

3. Performance Expectations for Carbon-Neutral Concrete

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 [44], 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) [45]. Kua et al. [46] 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 [39] 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 [7]. This increase, however, will also cause carbon emissions of approximately 350 gigatonnes CO_2 by 2050 [7]. 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 [2], 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 produc-

tion 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 [47]. This decomposition could be slowed by centuries to millennia if made into biochar [48], 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 [48]. 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 [49].

Separately, both biochar and calcium carbonate have seen use 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.

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 [50]. Biochar prepared from wood waste at 500 °C and used as a 5 wt% cement replacement also demonstrates the filler effect [51]—the filling in of pores that is chiefly responsible for compressive strength enhancements. Han [52] 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 [53]. 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 m^2/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 [54]. 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 pre-cast 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 [11]. 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 as a way to reduce the demand for both Portland cement and silica fume [51]. 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 [55]. This was explained by the addition of water during composite production, which increases the porosity as more biochar is added, thus decreasing compressive strength [55].

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" [56], needle-like single crystals of calcium carbonate that improve compressive, tensile, and flexural strength [57], akin to the mechanical advantages offered by trabecular bone [58,59]. 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 [60]. 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 [6].

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 deteriorate irreversibly [61].

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 [61]. 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 [62].

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.

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 Tables 1 and 2, and are described next.

Table 1. Additional performance characteristics of biochar and calcium carbonate. See text for details.

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

Table 2. Strength performance characteristics of biochar and calcium carbonate. See text for details.

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]				

Wood waste biochar findings: Gupta, Kua, and Pang [63] 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. [9] 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 more superplasticizer than recommended. Suarez-Riera, Restuccia and Ferro [20] 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 [64] 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 [65] 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 [66] 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 by 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 similar 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 [67] 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. [68], the percentage of biochar in 3D-printable cement mortars was 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 [39] 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 [13] 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.

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 [69]. Another is the use of calcium carbonate to stabilize biochar for longer residence times in soil [70]. 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 [71]. 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 [11]. The lowest point belongs to a carbon-negative standard concrete with a high rate of aggregate substitution (30 wt%) from biochar [8]. All four points denote 28-day strength, and the four points appear to have a linear relationship as shown in Figure 1.
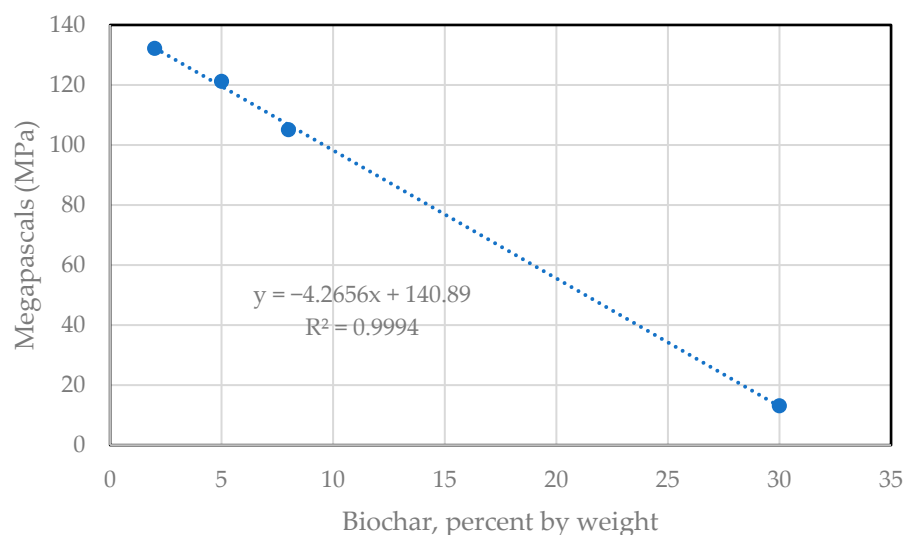

$$y = -4.2656x + 140.89$$
$$R^2 = 0.9994$$

Figure 1. Data from two studies [8,11], 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 [8]. 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.

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. [72] 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 $10\times$ higher than in situ methods such as CO_2 injection and sequestration into subsurface reservoirs [72]. Given that geologic storage for CO_2 is neither available everywhere 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. [73] 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.

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 [74]. 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. [75] 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. [76] 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 with regard to 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 [76] 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.

4.2. Uncertainties and Delays Create Resistance to Change

Habert et al. [77] 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. As long as 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.

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 [78]. 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.

4.4. Cost

The use of carbon-neutral concrete has to make strong economic sense before it is able to 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 [79] 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 [45] describe how the primary costs of biochar production are feedstock collection and pyrolysis. Transport and biochar application 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 [45].

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. [16] 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.

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. [80], 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 [44]. In China alone, where most of the Earth's concrete is manufactured, Yang et al. [81] 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. [45] 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 [44] 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.

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. [82], 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 source. 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 [38] 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. [83] 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 [13] 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.

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. [84] 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. [85] 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 [85]. It would be ideal to apply this or other models to the data in Table 1 of [86] 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. [87] 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 that is a balance of shrinkage induced by dissolution and expansion induced by crystallization.

Pyrolysis Temperature, Volatile Matter, and Carbon Storage: Mensah et al. [16] demonstrate that higher pyrolysis temperatures were found to decrease the amount of volatile matter in the pores, leaving behind the carbon. Figure 1 of [16] 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. [22] 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: Tahanpour Javadabadi and Hajmohammadian Baghban [88] 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 [89] found strong positive correlations (R^2 = 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 fairly 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 [84] 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 [65] 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 [13] 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 [44] examine how pyrolysis temperatures affects 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 [90] 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 [91] 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 [91] 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 [91] 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 [90] 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 of these 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 [65]. 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 [34] 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 [12] 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.

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 [21] 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 [92] 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. [93] 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. [94] 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%. The enhanced durability must also be factored in since this will lengthen the service life of the concrete, ultimately lowering costs over that service life.

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. [95] 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 [74] 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. [96], 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. [97] 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.

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 [78]: (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 [78].

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 [86], 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 H_2O molecules for the CO_2 adsorbing sites [86].

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 [91] 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, N_2 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 [91]. 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.

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 [77] 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/m^3/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 [74]: (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 [40] 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.

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.

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