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Cold-bonded biochar-rich lightweight aggregates for net-zero concrete

Mateusz Wyrzykowski [a,*], Nikolajs Toropovs [a], Frank Winnefeld [a], Pietro Lura [a,b]

[a] Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, CH-8600, Switzerland
[b] Institute for Building Materials, ETH Zurich, Zurich, CH-8092, Switzerland

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ABSTRACT

An emerging strategy to remove CO_2 from the atmosphere and compensate for the greenhouse-gas emissions of cement and concrete is based on incorporating biochar into concrete. With this approach, concrete can be turned into a functional carbon sink (C-sink). Until now, biochar has been mainly used without modification to replace part of the cement or of the aggregates in concrete. However, this technology comes with a number of practical problems, which include the high water absorption of the biochar (due to its high specific surface) and hazards (dust, risk of combustion).

In this paper we present an alternative approach, in which biochar is first processed into lightweight aggregates in a cold-bonding process. To this end, biochar is pelletized together with water and a small amount of hydraulic binder forming round pellets that further harden with hydration. In this way, carbon-rich lightweight aggregates (C-LWA) are obtained that are easier to handle than the original biochar. The C-LWA pellets have similar porosity and strength as conventional LWA and can be used for similar applications. Yet, the CO_2 emissions from sintering traditional LWA are avoided and the C-LWA are instead an effective C-sink. We demonstrate that it is possible to incorporate in the pellets and eventually in the concrete a sufficient amount of carbon to compensate for the original emissions of concrete. The net-zero emissions concrete obtained with this approach possesses mechanical performance sufficient for typical structural applications in buildings.

1. Introduction

Cement production is responsible for about 8% of the global greenhouse-gas emissions (Andrew, 2018). Despite important technological advancements in the production of Portland cement clinker, which led to significant reductions of the emissions in the last decades, it is impossible to reduce the emissions to zero. This is because a substantial part of the emissions are geogenic, i.e. they originate from thermal decomposition of limestone which is the main constituent of the kiln feed. Further, due to the worldwide increasing demand for buildings and infrastructure, the global consumption of cement and hence the resulting emissions are bound to increase in the next years (Favier et al., 2018; de Brito and Kurda, 2021).

Hence, in parallel to the reduction of emissions, viable methods for CO_2 removal from the atmosphere need to be devised immediately.

Among different CO_2 removal strategies, pyrolysis of biomass plays a prominent role (Lehmann et al., 2021; Schmidt et al., 2021; Bolan et al., 2022; Meyer et al., 2011; EBC, 2020). The residual carbon-rich char (biochar) obtained in this way is a negative CO_2 material (Meyer et al., 2011; Tanzer and Ramírez, 2019; Woolf et al., 2021). Yet, pyrolysis of biomass results in a carbon sink (C-sink) only if the biochar can be stored for very long times (Tanzer and Ramírez, 2019). Although biochar has significantly higher permanence compared to the feedstock biomass (Woolf et al., 2021), it needs to be secured that the removed carbon does not come back to the atmosphere due to combustion or gradual decomposition. The issue of permanent storage of the biochar is challenging, considering the large quantities that may need to be accommodated if this climate action becomes global. One currently considered strategy is storing the biochar in soils, see e.g. (Woolf et al., 2021).

Integration into concrete is a promising alternative for long-term sequestration of biochar. On the one hand it could in part or in total compensate for the aforementioned high original emissions of the concrete industry. At the same time, concrete is the man-made material with the largest production worldwide, which means that the available C-sink capacity is very high. Finally, concrete could safely store types of biochar that cannot be mixed into soils: depending on the local regulations,

* Corresponding author.
E-mail addresses: mateusz.wyrzykowski@empa.ch (M. Wyrzykowski), nikolajs.toropovs@empa.ch (N. Toropovs), frank.winnefeld@empa.ch (F. Winnefeld), pietro.lura@empa.ch (P. Lura).

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usage in soil usually requires highly controlled composition, process parameters and feedstock of the biochar (EBC, 2022).

Theoretical considerations regarding the properties of biochar as a function of the feedstock and process parameters with the perspective of using it in cement and concrete have been presented in (Aman et al., 2022; Danish et al., 2021). In the last decade, several experimental studies described the use of biochar as partial cement replacement in model systems, namely cement pastes or mortars (Aman et al., 2022; Danish et al., 2021; Gupta et al., 2018; Gupta and Kua, 2018; Asadi Zeidabadi et al., 2018; Sirico et al., 2020; Maljaee et al., 2021; Restuccia and Ferro, 2016; Suarez-Riera et al., 2020; Li and Shi, 2023). The amounts of biochar in these studies did not usually exceed a couple of percent (by cement mass).

In an attempt to increase the carbon sequestration in concrete and bring the emissions toward zero, some authors studied incorporation of larger quantities of biochar in concrete. In (Chen et al., 2022) biochar was used at a biochar:cement mass ratio of up to 1:1 to produce low strength (>10 MPa) blocks. In this way, 86% of the emissions could be reduced compared to a reference concrete (with 30% mass content of OPC and strength of >15 MPa).

Yet, few studies in which biochar was added to concrete in larger amounts have been published and even fewer practical applications are known. This is not least due to the detrimental effects of large amounts of biochar on the mechanical properties and durability of concrete. Further, the fresh state properties, in particular those related to workability, are a major challenge. Due to the high porosity, high specific surface and high water absorption of biochar (Danish et al., 2021; Suliman et al., 2017), its water uptake will unavoidably reduce the workability of the concrete (Sirico et al., 2021). This must be compensated with higher dosages of superplasticizers. At the same time, the dosage of chemical additives (e.g. superplasticizers, air entrainers, shrinkage reducing agents) in the concrete may need to be increased if they are in part adsorbed on the surfaces of biochar.

Last but not least, a number of technological issues may arise from handling fine, carbon-rich dust at concrete plants or construction sites, including avoiding ignition and explosion and any health risks for the workers.

In order to overcome the aforementioned obstacles that limit the potential of a high C-sink in concrete, we developed a method for upcycling carbon-rich biochar into functional lightweight-aggregates (LWA) for concrete. We propose to produce carbon-rich LWA (C-LWA) by granulation (pelletization) followed by a cold-bonding process. Cold bonding pelletization has been previously proposed for synthetic concrete aggregates (without biochar) e.g. in (Colangelo and Cioffi, 2013; Tang et al., 2020; Jiang et al., 2020; Bijen, 1986). In this paper we propose a method of production and present a basic physical characterization of the carbon-rich LWA. The C-LWA can be used in concrete much like conventional (sintered) LWA (Zhang and GjØrv, 1991; Clarke, 1993). The CO_2 emissions of the C-LWA are estimated by accounting for the negative emissions thanks to the C-sink and the positive emissions caused by the production process.

In a following step, the C-LWA were used to replace part of the coarse aggregate (gravel) in concrete, where they made up about 20% of the total volume. The amount of the C-LWA in the concrete was calculated to compensate – via negative emissions – for the whole emissions of the concrete (originating mostly from the cement), thereby obtaining concrete with net zero emissions. C-LWA were added both in the dry state and after presaturation. In order to assess the integrity of the C-LWA during mixing and the interface with the matrix, the microstructure of concrete and the embedded C-LWA were studied with X-ray tomography. We also investigated the mechanical properties of the concretes in order to assess their suitability for structural applications.

2. Materials and methods

2.1. Production and physical properties of cold-bonded C-LWA

The biochar employed in this study was a commercially available product for use in gardening pyrolyzed at 680 °C from landscape conservation and gardening wood waste from the region of Basel, Switzerland. The biochar contained pieces of the original branches/sticks with sizes of up to about 2 cm, see Fig. 1. Before pelletization, the biochar was dried at 40 °C for a minimum of 3 d. The water content in the as-delivered biochar was relatively low (4% respect to the mass at 40 °C). In this study, pre-drying was used to enable better control of the composition of the pellets; in practical applications, the biochar could also be used wet, which could help reducing dust release (biochar is often delivered containing around 15–25 mass-% of water). The organic carbon content (in the dry state) was declared as 74 mass-%. The specific surface (BET) was >220 m^2/g and the bulk density was 221 kg/m^3.

A thick slurry of Portland cement (CEM I 42.5 R), biochar and water at mass ratios of 1.0 : 2.0 : 2.4 was prepared and pelletized in a rotating pan mixer (80 L Eirich) with a rotation speed of ca. 46 rpm at a pan inclination of 30°, see Fig. 2a. Most of the larger pieces of biochar were fractured into smaller pieces in the process. The "green" pellets were then placed on a tray in several layers and stored at high relative humidity (>90 %RH) at room temperature until hardening of the cementitious matrix (from one week up to a couple of weeks). The final product, the hardened *cured* C-LWA, is presented in Fig. 2b. The microstructure of a typical C-LWA can be seen on a cut section in Fig. 2c.

In this study we used a sieved fraction of the pellets with sizes 8–20 mm. The fraction smaller than 8 mm and larger than 20 mm each constituted 4% by mass of the batch. Other sizes could be obtained depending on the sizes of the original biochar particles and pelletization parameters.

The density and water absorption of the cured pellets was determined by exposing the pellets to drying at 80 °C or underwater storage. Each step of the procedure (wetting/drying) lasted 24 ± 1 h. The density of the pellets was determined on the saturated pellets based on Archimedes' principle. The tests were carried out on three fractions separately: 8–12 mm, 12–16 mm and 16–20 mm. For each fraction, triplicate samples were collected from a larger batch, each containing at least 50 g of cured pellets (about 60 pellets, 50 pellets or 20 pellets in a sample for each of the three size fractions, respectively).

2.2. Concrete mix composition

Ordinary Portland Cement CEM I 42.5 R was used both as the binder for producing the pellets and as the binder in concrete. The aggregate was local alluvial sand (1–4 mm) and gravel (4–16 mm) with density of

Fig. 1. Biochar used for pelletization.

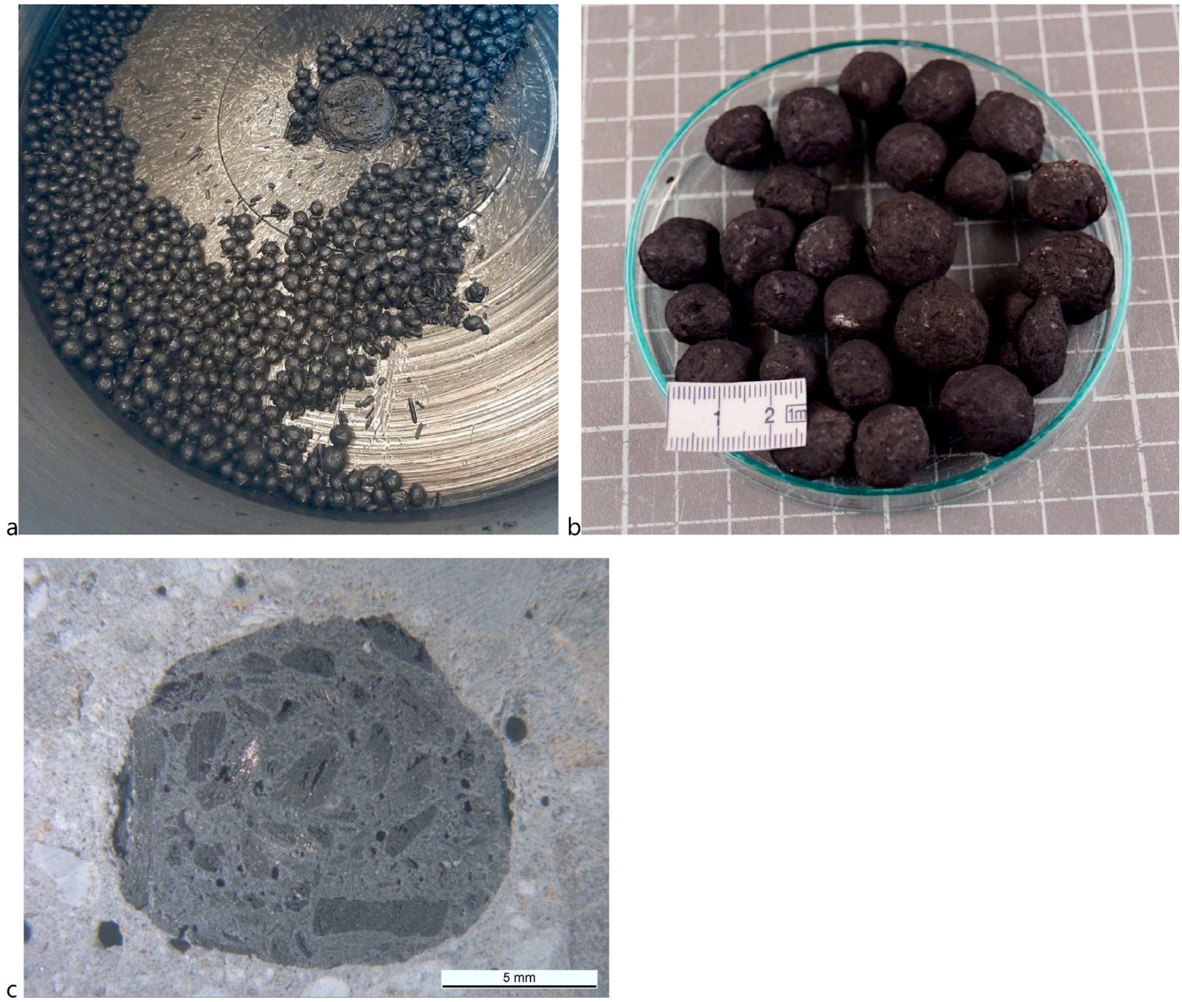

Fig. 2. a) C-LWA produced in the pelletization process in a rotating pan concrete mixer, b) C-LWA in the cured (hardened) state and c) C-LWA pellet embedded in concrete (cut section).

2670 kg/m^3 and water absorption of 0.5% by mass.

When necessary to retain workability, a superplasticizer based on polycarboxylate ether with a solid content of 40 mass-% was used. The water content of the superplasticizer was accounted for in the mixing water. The starting point for the mix design of the concretes with C-LWA was the reference concrete. The amount of the C-LWA in the mixes was calculated in a way to introduce sufficient negative emissions to compensate for the emissions of the respective concrete mix design (see the next section). The C-LWA replaced a part of the normal-weight coarse aggregate and were added in three ways (the numbers in the labels refer to the effective w/c, see Table 1):

i) *C-LWA saturated-0.53*: after presaturation with additional water for 24 h (i.e. the water that they absorb, which is on top of the mixing water),
ii) *C-LWA-saturated-0.40*: after presaturation in the mixing water for 24 h (i.e. without any extra water), and
iii) *C-LWA dry-0.40*: without presaturation, in their cured state (i.e. without any extra water).

In the latter case, the term "dry" refers to the method in which the C-LWA are added (see the list i-iii above) and does not indicate that they are absolutely dry. Using the porous aggregates along with the extra water that they will absorb or adding them without it are the two extreme strategies of mixing the LWA and accounting for their water absorption in the mix composition (Punkki, 1995). For the C-LWA saturated-0.53, the amount of water absorbed by the C-LWA was used in addition to the mixing water, hence increasing the total water content of the concrete, but not the effective w/c compared to the reference concrete (a slightly higher w/c of 0.53 compared to 0.52 of the reference concrete is due to less normal-weight aggregates in the concrete). In this

Table 1
Mix design of concretes [kg/m^3] and fresh concrete properties.

Material	REFERENCE-0.52	C-LWA saturated-0.53	C-LWA saturated-0.40	C-LWA dry-0.40
Sand 0–4 mm	769	768	782	772
Gravel 4–16 mm	1154	634	645	637
C-LWA	–	198	201	199
Cement CEM I 42.5 R	296	296	301	298
Mixing water	163	163	164	162
Superplasticizer	–	–	2.41	2.38
Additional water for C-LWA	–	38	–	–
w/c total	0.55	0.68	0.55	0.55
w/c effective [a])	0.52	0.53	0.40	0.40
Spread [cm]	36	35.5	36	37
Air content [%]	3.3	3.0	5.0	6.2
Fresh density [kg/m^3]	2370	2089	2098	2049

[a]) excluding the water absorbed by C-LWA and normal-weight aggregate.

case, the mix design, except for replacing a part of the normal-weight aggregates with the C-LWA, remained as in the reference mix. For the C-LWA saturated-0.40 and C-LWA dry-0.40, no extra water was added, hence the C-LWA reduced the effective w/c of the concrete mix by absorbing a part of the mixing water. The effective w/c thus dropped from the initial 0.55 to 0.42 due to C-LWA absorption, with further reduction down to 0.40 due to absorption by normal-weight aggregates. Even though the mix with C-LWA saturated-0.40 and C-LWA dry-0.40 was based on the same design as the reference concrete, the absorption of a part of the mixing water led to a reduction of the concrete volume from the original nominal 1 m^3. This was in part compensated by the higher air content of the C-LWA concretes. The mix compositions presented in Table 1 are corrected for the measured air contents and water absorption by the aggregates (normal-weight and C-LWA).

In the design of the concrete mix, the water absorption of the C-LWA respect to the cured mass, i.e. 0.19 g water/g LWA, was used (see Table 2).

Concretes were mixed for about 15 min in an 80 L rotating pan mixer (Eirich). In the case of the concrete with the saturated C-LWA (both with extra water or just with the mixing water), the latter were added after first mixing of all other components. For the C-LWA added in their cured state (C-LWA dry-0.40), they were first mixed with all dry components and next water and superplasticizer were added to the mix.

The spread, air content and fresh density were measured according to EN 12350-5. The determination of air content and density and further mechanical tests were carried out on samples compacted with a needle vibrator.

2.3. Mechanical tests

Different specimens were cast in plastic molds directly after mixing and stored at >90 %RH and 20 ± 0.3 °C until the age of testing. The compressive strength was tested at different ages on triplicate cube specimens (150 × 150 × 150 mm^3) according to EN 12390-3. The Young's modulus was tested on triplicate prismatic specimens (120 × 120 × 360 mm^3) according to EN 12390-13.

2.4. X-ray tomography

For X-ray tomography (X-ray CT), cylindrical specimens with diameter of 50 mm and height of about 60 mm were cast in plastic molds and cured sealed at 20 ± 0.3 °C until the time of testing (2.5 months after casting).

We performed X-ray tomography with a tomograph manufactured by RX Solutions (Chavanod, France), model EasyTomo XL-Ultra, available at Empa's Center for X-ray Analytics. Each tomography measurement consisted in acquiring and storing 3600 radiographs, while each specimen was rotated over 360° around its symmetry axis. The specimen was illuminated with an X-ray beam produced with an acceleration voltage of 110 kV and a source current of 130 μA. The source-to-detector distance, d_{SD}, was 550.6 mm, and the source-to-specimen distance, d_{Ss}, was 127.7 mm. Such a configuration led to a geometric magnification factor, $M = \frac{d_{SD}}{d_{Ss}}$, due to the X-ray beam's cone geometry, of about 4.3. The voxel size of the tomograms was thus $\widetilde{p} = \frac{p}{M} \cong 29.4$ μm. We reconstructed the tomograms by RX Solutions' XAct software (version 1.1), which relies upon an implementation of a version of the Feldkamp-David-Kreiss cone-beam filtered back-projection algorithm (Feldkamp et al., 1984) optimized for GPU processing.

3. Results

3.1. C-LWA properties

The results of the physical characterization of the C-LWA pellets are presented in Table 2. No statistically significant differences were found between the three size fractions (8–12, 12–16 and 16–20 mm), hence the results presented in Table 2 were averaged.

The microstructure of the C-LWA embedded in concretes studied with X-ray tomography is presented in Figs. 3 and 4. Larger pieces of the original biochar, with their characteristic layered structure (see also (Sirico et al., 2021)) can be identified within the pellets. The lower grayscale intensity of the pellets compared to the surrounding cement paste and aggregates is due to their high porosity (stemming from the original high content of water) and fine biochar particles that are below the resolution, whereas the high grayscale intensity regions correspond to higher density. When the C-LWA are embedded in the concrete, no particular interfacial features are evident at the given resolution between the pellets and the surrounding concrete.

3.2. C-LWA C-sink potential

The C-sink potential of the C-LWA can be estimated based on the following equation, similarly as for the C-sink potential in soils (Woolf et al., 2021). It must be remarked that the calculation presented below only serves as a general indication, since in lack of directly measured emissions the values of certain variables were assumed based on the literature.

$$E_{C-LWA} = E_{biochar} + E_{cement} + E_{C-LWA-production} \quad (1)$$

The emissions of dry biochar are calculated as:

$$E_{biochar} = -\frac{M_{CO_2}}{M_C} \cdot \frac{m_{biochar}}{(m_{biochar} + m_{cement} + m_{water})} \cdot (F_{c-stored} - F_{c-released}) \quad (2)$$

where, m indicates the masses of different components (biochar, cement and water) that make up the C-LWA pellets. In our case, $m_{biochar} : m_{cement} = 2 : 1$ (see section 2.1). $\frac{M_{CO_2}}{M_C} \approx \frac{44}{12}$ is the ratio of molar masses of CO_2 and C (conversion factor from C to CO_2) and the minus sign accounts for the actual sink. The water included in the calculation, m_{water}, refers to the water contained in the pellets in their dried state (as a reference state we assumed 24 h at 80 °C). As water stored in the pores of the pellets should be lost in this condition, we assumed that only water bound by the hydrated cement remains in the pellets. This is mostly chemically bound water, approximately 0.23 g/g of the reacted cement (Brouwers, 2004).

The term $F_{C-stored}$ is the organic carbon content of the biochar and corresponds to the carbon removed from the atmosphere by the plants and later separated in the pyrolysis process; for the particular batch used here, $F_{C-stored} = 0.74$. This is close to the mean value of 0.81 ± 0.07 for wood biomass pyrolyzed at high temperatures (>600 °C) reported in (Woolf et al., 2021). A similar range (0.7–0.85) was also reported in (He et al., 2021).

Table 2
Physical properties of the C-LWA, fraction 8–20 mm (average ± standard deviation).

Density dry skeleton (24 h at 80 °C), [g/cm^3]	Particle density - dry pellet, [g/cm^3]	Particle density - cured pellet, [g/cm^3]	Particle density - saturated pellet, [g/cm^3]	Water absorption (24 h) respect to dry mass, [g/g]	Water absorption (24 h) respect to cured mass, [g/g]	Water content in cured state respect to dry mass [g/g]	Porosity [-]
1.37 ± 0.03	0.75 ± 0.02	1.01 ± 0.02	1.20 ± 0.02	0.60 ± 0.03	0.19 ± 0.02	0.26 ± 0.02	0.45 ± 0.01

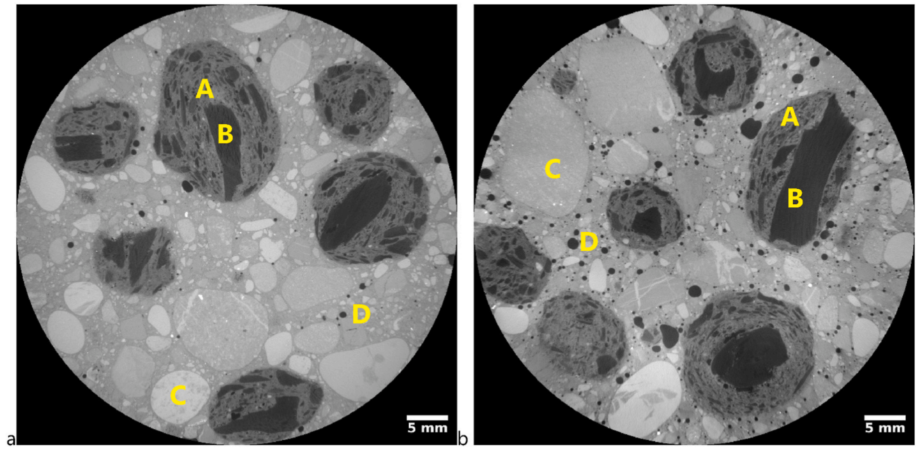

Fig. 3. X-ray tomography results: horizontal slices through the tomogram of the cylindrical concrete samples: a) C-LWA saturated-0.53 and b) C-LWA dry-0.40. The labels refer to: A: C-LWA pellet, B: piece of original biochar enclosed in the pellet, C: normal-weight aggregate, D: air voids entrapped in cement paste.

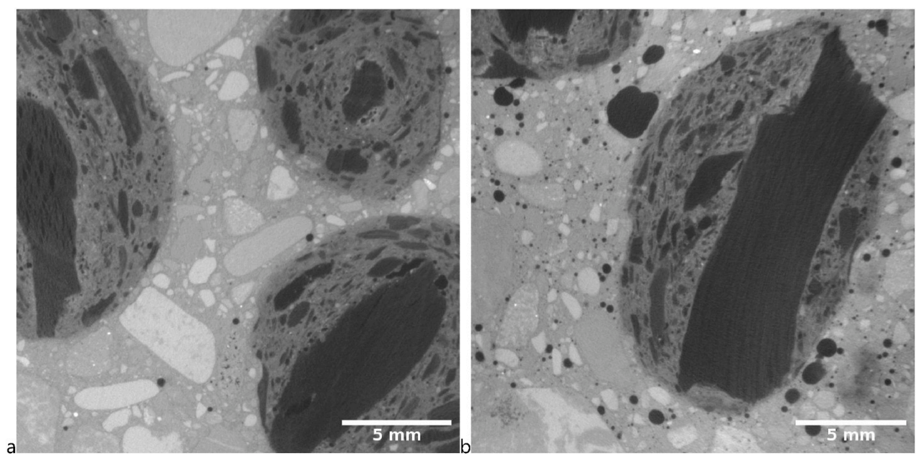

Fig. 4. X-ray tomography results (see caption of Fig. 3): magnified images showing the microstructure of the C-LWA pellets and the interfaces between the pellets and the concrete.

The term $F_{c-released}$ is the C-sink loss due to the CO_2 expenditure from provision and handling of the biomass and from the pyrolysis process itself. As the biomass consisted of wood from landscape conservation and gardening, it can be considered carbon neutral according to (EBC, 2020). Further, as waste biomass was used, no emissions from cultivation of the biomass (e.g. due to fertilizers) need to be accounted for. Only the emissions due to the use of fossil fuels during collection and processing of the biomass were included, corresponding to a carbon expenditure of 0.7% of the mass of biochar according to the example presented in (EBC, 2020). Emissions resulting from the pyrolysis process originate mainly from preheating of the reactors with fossil fuels, emissions of methane and electricity to operate the plant; they were assumed after (EBC, 2020) as corresponding to a carbon content loss of 2.4% by mass of biochar. A further 10% of the safety margin was accounted for due to the so-called indirect emissions that fall outside those estimated as provision of biochar and pyrolysis (EBC, 2020), finally yielding $F_{c-released} = 1.1 \cdot (0.007 + 0.024) = 0.034$.

The calculation with equation (2) yields $E_{biochar} = -1.603$ kg CO_2/kg.

At the same time, the C-LWA contain cement as a binder, so the related emissions need to be accounted for as follows:

$$E_{cement} = \frac{m_{cement}}{(m_{biochar} + m_{cement} + m_{water})} \cdot \left(E^*_{cement} - E_{carb}\right) \quad (3)$$

where the E^*_{cement} are the specific emissions of the cement. It should be mentioned that this parameter can vary depending on the type of binder (mainly with the ratio of clinker replacement with low-CO_2 components) and production processes (in particular, different ratios of primary and bio fuels used in cement kilns). We used CEM I as the cement with the highest emissions, with $E^*_{cement} = 0.641$ *kg CO_2/kg* (production in Switzerland) (cemsuisse, 2022). Composite cements, e.g. of type CEM II, have lower emissions. At the same time, the absorption of CO_2 due to the carbonation of the cement in the pellets should be considered, E_{carb}. This is relevant because, due to the small size of the pellets and their high porosity, this process can take place relatively fast during initial conditioning/curing of the pellets. From this point of view, the pellets are similar to recycled concrete aggregates that experience an accelerated carbonation within months after they were crushed from the original concrete elements. According to a recent study (Leemann et al., 2023), carbonation in such conditions may bind between 6 and 22% of the initial emissions of cement. Assuming 15% of absorption of the original emissions, $E_{carb} = 0.096$ kg CO_2/kg. The calculation with equation (3) yields $E_{cement} = 0.169$ kg CO_2/kg.

The emissions stemming from the production of the pellets, $E_{C-LWA-production}$, can be estimated as similar to those in the production of concrete, because similar processes of wet mixing, curing, etc. are involved. Assuming 17.5 kg CO_2/m^3(for wet pellets) after (Miller et al., 2016), this yields emissions of $E_{C-LWA-production} = 0.023$ kg CO_2/kg of dry pellets.

Finally, the CO_2 sink potential of the pellets estimated according to equation (1) yields $E_{C-LWA} = -1.411$ kg CO_2/kg of dried pellets. This further corresponds based on the difference in densities (see Table 2) to E_{C-LWA}=−1.050 kg CO_2/kg of cured pellets. With this number, it is possible to calculate the effect of the C-LWA pellets on the overall emissions of the concrete (see Tables 1 and 4).

A simple sensitivity analysis with the most feasible range of parameters responsible for the cement-related part of the calculation in eqs. (1)–(3) shows that the C-sink potential E_{C-LWA} can be in the range from −0.9 to −1.1 kg CO_2/kg of C-LWA pellets in their cured state, which shows that the binder has a rather minor effect on the total C-sink. On the contrary, the C-sink can be significantly altered by varying the amount of biochar incorporated in the pellets. The proportions used in our study stem from an iterative process in which the easiness of pelletization and the apparent strength of the pellets were optimized – a further optimization remains possible though.

Finally, the C-sink potential will most heavily rely upon the organic carbon content of the used biochar, $F_{C-stored}$ (here equal to 0.74). The mean value of 0.76 ± 0.06 (mean value for wood biochar pyrolyzed at different temperatures, from low to high) reported in (Woolf et al., 2021) would correspond to a C-sink with E_{C-LWA}=−1.08 ± 0.10 kg CO_2/kg of C-LWA pellets in their cured state. While wood pyrolyzed at high temperatures yields relatively high carbon content, other feedstocks will often have lower carbon content. For a hypothetical case of biochar obtained from manure, with relatively low organic carbon content of $F_{C-stored}$= 0.39 (Woolf et al., 2021), the C-sink would correspond to E_{C-LWA}=−0.46 kg CO_2/kg of cured pellets.

3.3. Concretes with C-LWA

During mixing of the concretes with the C-LWA no segregation was evident despite the low density of the pellets. This could be also confirmed by inspecting the cut surfaces of concrete cubes – no accumulation of the lighter C-LWA at the upper surfaces of concrete cubes was found, see Fig. 5. Also, the pellets appeared all as rounded particles and no fracturing of the single pellets could be observed, as also evidenced in the X-ray CT (see section 3.2).

The concrete with the saturated C-LWA and extra water (C-LWA saturated-0.53) had similar workability as the reference concrete (both without superplasticizer), which confirms that the amount of pre-absorbed water calculated based on the absorption of 0.19 g/g was correct. For the concretes with C-LWA added dry or C-LWA presaturated in the mixing water, the absorption of part of the mixing water by the C-LWA led to a significant loss of workability. In these cases, superplasticizer was necessary to reach the desired spread of the concrete (see Table 1).

The concretes with C-LWA had lower density in the hardened state of about 12% for the C-LWA presaturated (both with extra water and without it) and of about 14% for the C-LWA dry, compared to the reference concrete (Table 3). The concretes with the C-LWA contained about 20% vol-% of the LWA with their water-accessible porosity of 45% (see Table 2), hence the porosity of concretes should nominally increase by about 9%. In addition to this extra porosity, a further reduction of concrete density was due to the fact that the solid part of the pellets is less dense than the normal-weight aggregates that are replaced. These effects can be accounted for in the mix design based on the known densities of the components. Finally, additional porosity is due to entrapped air bubbles in the concrete. Part of these entrapped air bubbles originate from the LWA when they absorb water while in the concrete, as was the case for the C-LWA dry-0.40 mix. Some of the entrapped air may also originate from the reduced workability of the mix - this was the case both for the C-LWA saturated-0.40 and C-LWA dry-0.40 concretes. Considering the small difference in the air contents of C-LWA saturated-0.40 and C-LWA dry-0.40 concretes (5.0% and 6.2%, respectively), we can estimate that the majority of the air escaping from the pellets could be evacuated from the concrete during casting and vibration.

Table 3
Young's modulus and density at 28 d (average ± standard deviation).

Concrete	Young's modulus [GPa]	Density [kg/m^3]
REFERENCE-0.52	35.6 ± 0.6	2406 ± 4
C-LWA saturated-0.53	22.6 ± 1.1	2118 ± 10
C-LWA saturated-0.40	24.6 ± 0.8	2117 ± 3
C-LWA dry-0.40	23.1 ± 0.9	2074 ± 5

Table 4
Estimation of the CO_2 emissions of concretes with C-LWA [kgCO_2/m^3 concrete].

Source of emissions	REFERENCE-0.52	C-LWA saturated-0.53	C-LWA saturated-0.40	C-LWA dry-0.40
Cement	0.641•296 = 189.7	0.641•296 = 189.7	0.641•301 = 192.9	0.641•298 = 191.0
Other components/ production of concrete	17.5	17.5	17.5	17.5
C-LWA	–	−1.05•198 = −207.9	−1.05•201 = −211.1	−1.05•199 = −209.0
Sum	207	−1	−1	−1

The results of the compressive strength tests are presented in Fig. 6. The incorporation of porous pellets led to a reduction of strength by about 6%, 9% and 23% for the C-LWA saturated-0.40, C-LWA dry-0.40 and C-LWA saturated-0.53, respectively.

The Young's modulus and density results are presented in Table 3. The effect of porous C-LWA on the Young's modulus was more prominent than in the case of compressive strength. This phenomenon is well known for concretes with porous aggregates that have lower stiffness than conventional quartz-based aggregates, in particular LWA (Nilsen et al., 1995) or recycled concrete aggregates (Hoffmann et al., 2012). Based on these results, one can estimate the elastic modulus of the aggregates using a composite model, e.g. the Mori-Tanaka method, similarly as in (Nilsen et al., 1995). This yields an estimated elastic modulus of the C-LWA of about 8.5 GPa.

4. Discussion

4.1. Negative emissions of C-LWA

The emissions from the reference concrete can be estimated as those resulting from the used cement (296 kg/m^3 of concrete), with specific emissions of 0.641 kg CO_2/kg (in Switzerland) (cemsuisse, 2022). As already mentioned in Section 3.1, the specific emissions of the cement vary strongly depending on the type of cement and production processes. In this study we used CEM I as an extreme case with higher emissions than when using composite cements to demonstrate the high compensation potential of the C-LWA.

Additionally, emissions from other components and concrete production are assumed for Europe as 17.5 kg CO_2/m^3 of concrete (Miller et al., 2016). The overall emissions from the reference concrete are thus estimated as 207 kg CO_2/m^3 of concrete, see Table 4. A similar level of positive CO_2 emissions applies to the concretes containing C-LWA. However, by capitalizing on the C-sink potential of the C-LWA, these high emissions can be compensated. In fact, the concretes with C-LWA produced in this study had net-zero emissions thanks to the incorporation of about 20 %-volume of C-LWA, see Table 4. If the concrete mixture in this study had contained composite cements, with a similar amount of C-LWA the overall emissions of the concrete would become substantially negative.

The C-LWA, despite using a primary binder (Portland cement) still display a significant C-sink potential. Our estimate based on the nominal parameters yields E_{C-LWA}=−1.05 kg CO_2/kg of C-LWA pellets in their cured state (see Section 3.1). The overall sustainability of C-LWA could

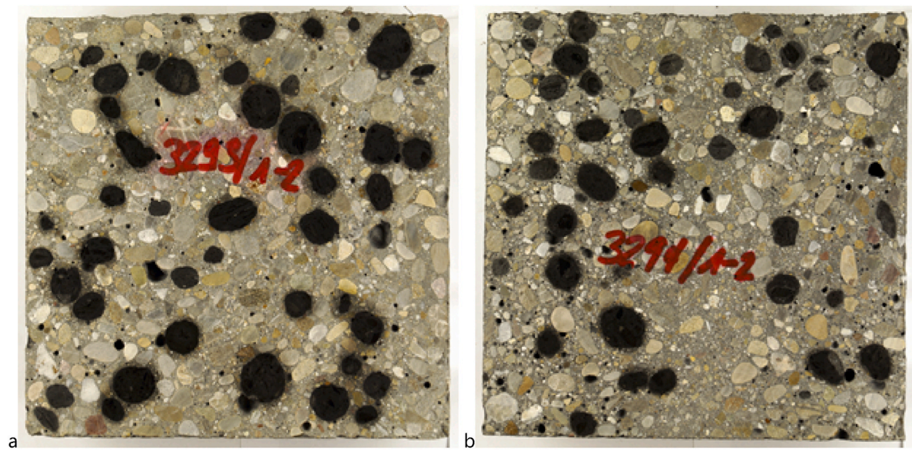

Fig. 5. Cut surfaces of concrete cubes (150 mm) of concrete with a) C-LWA saturated-0.53 and b) C-LWA dry-0.40.

Fig. 6. Compressive strength results (average ± standard deviation). The numbers in the labels of concretes refer to the effective w/c (see Table 1).

be further improved by using secondary, possibly waste-derived binders with lower emissions (e.g. natural or industrial-waste pozzolana). However, it should be stressed that the emission balance would not be necessarily improved even if low-emission binders were used for pelletizing the LWA. The main effect on the total (negative) emissions of the C-LWA is thanks to their high carbon content. By switching to a binder with lower emissions, but at the same time with likely lower mechanical properties (lower strength and stiffness), the mechanical properties of the pellets would most likely decrease. Hence, with a weaker skeleton of the pellets, less biochar could be integrated in the pellets in order to maintain their desired mechanical performance. This would likely result in overall lower C-sink potential. For example, by cutting the emissions of the binder in the pellets by half, the C-sink would increase by about 6% only. In comparison, a similar effect would be obtained (or, conversely, lost) if the biochar content would be increased by only 12% (or, conversely, reduced by it).

The negative emissions of the C-LWA are especially promising considering the high emissions and energy consumption of the traditionally-produced LWA. The latter are usually hardened by sintering at temperatures of 900–1200 °C (Bijen, 1986; Nadesan and Dinakar, 2017). The production process of the sintered LWA causes emissions of about 0.05–0.06 kg CO_2/kg (Barbieri et al., 2021; Jung and Yang, 2022). Hence, replacement of the C-LWA with sintered LWA would actually increase the emissions of concrete by about 10–12 kg CO_2/m^3, i.e. by about 5% (for the particular mix composition as presented in Table 1). The emissions balance of the C-LWA vs sintered LWA would become even more extreme for an actual lightweight concrete (the concretes produced in this study contained a relatively small amount of LWA and were classified as normal weight concretes). For an exemplary case of a concrete with 1800 kg/m^3 density and ca. 45% volume occupied by lightweight aggregates (with density of 1000 kg/m^3), the emissions of the concrete with sintered LWA would reach about 230 kg CO_2/m^3, whereas the use of C-LWA would lead to negative emissions of about −290 kg CO_2/m^3. This shows the very high potential of the C-LWA as a carbon-removal technology, in particular in lightweight concrete.

4.2. Feasibility of using C-LWA as aggregate in concrete

Our results show that the C-LWA produced by pelletization and cold-bonding can be used in a similar way as conventional LWA. Although the concrete with the C-LWA exhibits lower mechanical properties compared to concrete with normal-weight aggregates, this effect is to be expected considering the introduced porosity and is well known for concretes with regular LWA (Zhang and GjØrv, 1991; Bentur et al., 2001; Domagała, 2015). The reduction of strength caused by the introduction of the C-LWA (with estimated increase in porosity by 9% of porosity) can be analyzed from the point of view of the reduced density of concrete. In Zhang and GjØrv (1991), the reduction of density by 1% corresponded to about 3% reduction in compressive strength. These results were however obtained for high strength lightweight concrete; they are thus not necessarily relevant for the normal-weight concrete studied here. For the C-LWA saturated-0.53 concrete (where the effective w/c was close to that of the reference concrete), the reduction of density by 1% corresponds to about 2% loss in strength.

At the same time, the lower density and higher porosity can be beneficial in certain applications as a lightweight concrete. The concretes produced here had density >2000 kg/m^3 and could be hence classified as normal density concretes with ordinary strength. However, the amount of the C-LWA could be increased to reach even lower density and better thermal-insulating properties, further capitalizing on the high C-sink potential (see previous section).

In many studies, LWA were combined with high strength cement paste to produce lightweight high performance concretes, e.g. (Zhang and GjØrv, 1991; Punkki, 1995; Weber and Reinhardt, 1997). In such case, the high strength and stiffness of the cement matrix allows to partially compensate for the low mechanical properties of the LWA (Lura et al., 2014). Further, the water contained in the LWA could deliver internal curing to the concretes with low w/c (Bentur et al., 2001; Weber and Reinhardt, 1997; Cusson and Hoogeveen, 2008). Although we see a potential of the C-LWA also for such applications, this study is dedicated to ordinary-strength concrete (C20/25 – C30/37) because it makes up the largest amount of the market and could be a large carbon sink.The concretes with C-LWA either presaturated in the mixing water or added dry had lower effective w/c than the reference concrete and the strength drop was thus limited. In fact, these concretes could be still classified as belonging to the same strength class as the reference concrete, i.e. C30/37 according to Eurocode 2. The water absorbed by the C-LWA (either in a presaturation step or during mixing) decreased the workability of the mixes. A small amount of superplasticizer was added to recover the workability. For the concrete with the presaturated C-LWA and extra water, the strength reduction was more pronounced, but it could be still classified as belonging to strength class C25/30. The reduced Young's moduli should be accounted for in the design, similarly as for the concrete with recycled concrete aggregates or other non-standard aggregates.

The concrete with the C-LWA added dry had higher air content. The air voids were well distributed in the bulk of the concrete rather than accumulated at the aggregate surfaces. If the air escaped from the LWA had accumulated at their interface with the mortar, it could have had detrimental effects on the bond between the LWA and the matrix and further on the mechanical properties, as suggested in (Punkki, 1995; Lura et al., 2007) and reported in (Helland and Maage, 1993). No such accumulation was evident in the X-ray tomography results, see Fig. 3b and 4b. In fact, no particular interfacial features that would affect the bond between the C-LWA and the concrete could be identified. The rather uniform distribution of air voids was likely thanks to the long mixing time (ca. 10 min) and subsequent vibration of the samples.

Integration of biochar into the C-LWA before using them in concrete has important advantages compared to the direct addition of biochar into concrete. Contrary to biochar as-delivered, the use of LWA is a well-grounded practice by many concrete producers and contractors. The use of C-LWA in concrete mixing eliminates the risk associated with high dusting, ignition, excessive use of superplasticizers, etc. Finally, replacement of the virgin normal-weight aggregates with the synthetic aggregates may further contribute to the improved sustainability of concrete, in particular in regions where the aggregate sources are scarce (de Brito and Kurda, 2021).

5. Conclusions

In this study we present a novel method for incorporating biochar into concrete. Instead of the simple addition of biochar to concrete as partial cement or aggregate replacement, we first processed the biochar into carbon-rich lightweight aggregates (C-LWA). This allows to alleviate some of the issues related to the use of as-delivered biochar (dust, incompatibility with chemical additives, etc.). The C-LWA pellets are obtained by wet pelletization with cement and water and cold-bonding hardening. In this way, a stable, lightweight material with grain sizes 8–20 mm is obtained. The C-LWA produced in this study have a very high C-sink potential, about −1.05 kg CO_2/kg of C-LWA.

The C-LWA can be incorporated in concrete similarly to conventional (sintered) LWA. In the examples presented here, the C-LWA replaced about 27% of volume of normal-weight aggregates and constituted about 20% of the volume of concrete. Even though the replacement of normal-weight aggregates with porous C-LWA leads to a reduction of strength and even more so of elastic Young's modulus, concrete mixtures with compressive strengths at 28 d exceeding 30 MPa can be obtained in this way (strength classes C20/25 and C30/37 according to Eurocode 2). Ongoing studies focus on the long-term performance, in particular with regard to shrinkage, creep and durability.

Our estimations show that the incorporation of the C-LWA allows to compensate for the high CO_2 emissions of concrete – in fact, the concretes with the C-LWA had net-zero emissions. The novel technology presented in this paper could thus represent a potential solution towards effective atmospheric CO_2 removal and long-term safe storage of the carbon.

CRediT authorship contribution statement

Mateusz Wyrzykowski: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Funding acquisition, Supervision. **Nikolajs Toropovs:** Conceptualization, Methodology, Investigation, Writing – review & editing. **Frank Winnefeld:** Conceptualization, Writing – review & editing. **Pietro Lura:** Conceptualization, Methodology, Writing – original draft, Funding acquisition, Supervision.

Declaration of competing interest

The authors delare that financial support was provided by BASF Schweiz AG.

Data availability

Data will be made available on request.

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