The influence of biochar addition on the strength and microstructural characteristics of cement pastes

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Abstract. Nowadays, many branches of civil engineering begin to suffer from the lack of natural high-quality resources. The cement industry is one of the main consumers of such raw materials and, moreover, significantly contributes to global warming by the release of high amounts of carbon dioxide. In this sense, the incorporation of supplementary cementitious materials may help to reduce global environmental impacts of cement production. This paper is focused on the influence of the partial Portland cement replacement using a biochar. Basic material properties of both Portland cement and biochar were analysed. On hardened samples of cement pastes cured under water for 27 days, physical, mechanical and mineralogical properties were determined using several instrumental techniques. Experimental data showed the gradual decrease of bending and compressive strengths with the increasing replacement of Portland cement, however, significant lightening of produced pastes was achieved and thus the cement pastes additive with appropriate amounts of biochar may find usage in specific industrial applications.

1. Introduction

Portland cement is the most consumed binding material for the preparation of building composites used in civil engineering. The main component (up 95 wt. %) of Portland cement is clinker that is composed of calcium silicates, tricalcium aluminate, calcium aluminoferite and other phases [1]. Clinker production is a high-temperature process that takes place in rotary kilns. In the first step, the blend of limestone and clay-like materials is heated to a calcination temperature exceeding 600 ºC and subsequently sintered at temperatures reaching up to 1 500 ºC [2]. Such a procedure requires an important amount of input energy. It is estimated that for one ton of produced clinker 4 427 MJ is consumed [3] and, in addition, high amounts of greenhouse gases, represented in particular by carbon dioxide (CO₂), are released. Current estimations reported that the cement industry contributes to 8 % of global CO₂ emissions [4].

Biochar is a product originated by pyrolysis (thermal decomposition) of biomass from agricultural residues, wood residues, energy corps, activated sludge, etc. Physical and chemical properties of produced biochar are influenced by their origin and applied procedure of pyrolysis e.g. oxygen or oxygen-free atmosphere during combustion [5]. In general, biochar, as a carbonaceous solid substance
with considerable ability to cumulate liquids and gases, is used for many applications, e.g. in agriculture as a fertilizer, in the waste treatment industry and many others as reported in [6]. In the field of civil engineering, it was reported by Gupta et al. [7] that biochar may promote hydration of Portland cement and thus increase the compressive strength of composites.

With the aim to reduce the environmental impact of cement production, the potential usage of biochar as a Portland cement alternative material was tested. The used Portland cement and biochar were analysed and produced pastes were used for the determination of the physical, mechanical and mineralogical properties using a combination of various instrumental techniques.

2. Experimental

For the preparation of cement pastes mixes, Portland cement 42.5 R (Cemex, Ltd., Czech Republic) was used. The binder contained a predominant representation of following oxides, 62.89 % CaO, 18.21 % SiO₂, 5.18 % Al₂O₃, 2.98 % Fe₂O₃ and 2.40 % MgO. As a partial cement replacement, biochar (BC) provided by Biouhel, Ltd. (Czech Republic) was applied. Obtained carbon-based material originates by pyrolysis combustion of agricultural biomass at low or medium temperatures not exceeding 400 °C and in the atmosphere with limited oxygen content. Only fractions with gains size lower than 0.125 mm were introduced to partial replacement of Portland cement.

Particle size distribution was measured according to the EN 933-1 standard [8]. Samples oven-dried at 105 ± 5 °C were mechanically shaken by vibratory device Retsch AS 200 (Germany) through the set of sieves with a mesh size of 0.125, 0.90, 0.063, 0.050, 0.038, 0.020 and 0.015 mm respectively. The specific surface area was measured using the standard EN 196-6 [9]. Specific density values, with the use of the pycnometric density method described in the EN 1097-7 [10] were determined. Powder densities of Portland cement and biochar were measured accordingly to the standard EN 1097-3 [11].

The effect of partial cement replacement with biochar, specifically 5, 10, 15 and 20 wt. %, in mixes of cement pastes, was investigated. Due to specific behaviour of biochar given by its high specific surface area (3.7 times higher compared to used cement as reported in Table 2), the amount of added water increased with an increasing amount of added biochar. Accordingly, the same consistency with the value of spreading of 160 × 160 ± 5 mm (EN 1015-3 [12]) was kept for all manufactured batches. Mix proportion, as well as measured values of spreading of produced cement pastes, are given in Table 1.

| Mixture | Cement (g) | Biochar (g) | Water (g) | Value of spreading (mm) |
|---------|------------|-------------|-----------|------------------------|
| REF     | 1500       | 0           | 450       | 160 × 160 |
| BC 5    | 1425       | 75          | 480       | 155 × 155 |
| BC 10   | 1350       | 150         | 520       | 160 × 155 |
| BC 15   | 1275       | 225         | 560       | 160 × 160 |
| BC 20   | 1200       | 300         | 600       | 165 × 160 |

Reference and blended binder mixes were prepared using laboratory mixer E095 (Matest S.p.A., Italy). The fresh paste was cast into prismatic iron moulds with dimensions of 40 × 40 × 160 mm in two layers and each layer was compacted with 60 hits. Made sample sets were then covered by foil and placed in laboratory conditions at 20 ± 2 °C and 50 ± 5 % of relative humidity for 24 hours. After demoulding, partially hardened specimens were stored in a water bath for overall 27 days.
On hardened samples, bulk density and strength properties were measured. Bulk density values were measured according to the standard EN 1015-10 [13]. The relative expanded uncertainty of the applied method was 3 %. Bending strengths tests in three-point settings on prismatic samples having size $40 \times 40 \times 160 \text{ mm}$ were performed [14]. On broken halves of prisms, maximum compressive forces with the help of hydraulic press Servo Plus Evolution (Matest, S.p.A., Italy) with disposing loading capacity of 300/15 kN were measured. For a better understanding of biochar influence on hydration process of Portland cement, X-ray powder diffraction (XRPD) was employed. Mineralogical composition of hydrated cement pastes was analysed using a diffractometer D8 Advance (Bruker, Germany) with Bragg-Brantano geometry and equipped with LynxEye detector using CuK$_\alpha$ radiation and Ni filter. Data were recorded in the angular range from 15 to 90° ($2\theta$) with a step of 0.01° and counting time 0.4 s. Rietveld refinement method was used for quantitative phase analysis in Topas 4.2 software (Bruker). Biochar morphology was observed under a scanning electron microscope (SEM) Quanta 450 FEG (FEI). The acceleration voltage was set to be 20 KV and prior to the analysis samples were gold coated with a layer of 5 nm thickness.

3. Results and discussion
Physical properties and particle size distribution of both powders are listed in Table 2. From obtained data partially higher content of larger particles of biochar in comparison with used cement type is detectable. On the other hand, cement replacing material, with powder density slightly exceeding 300 kg·m$^{-3}$, is approximately 3 times lighter regard to powder density of 960 kg·m$^{-3}$ obtained for cement.

| Material       | Specific density (kg·m$^{-3}$) | Powder density (kg·m$^{-3}$) | Specific surface (m$^2$·kg$^{-1}$) | Loss in ignition (%) | d$_{10}$ (µm) | d$_{50}$ (µm) | d$_{90}$ (µm) |
|----------------|--------------------------------|-----------------------------|-----------------------------------|----------------------|---------------|---------------|---------------|
| Portland cement| 3 095                          | 960                         | 344                               | 4.89                 | 6.0           | 22.8          | 36.4          |
| Biochar        | 1 550                          | 318                         | 1 286                              | -                    | 10.2          | 31.9          | 68.8          |

Bulk density and mechanical properties determined on hardened blended cement pastes and reference material (REF) composed of only cement are presented in Table 3. The Portland cement substitution with 3 times lighter carbon-based pyrolysis product resulted in the important decrease in bulk density. In this context, the unit weight of material BC 20 was reduced by about 32.7 % regard to reference samples. Such behaviour could be ascribed to lightweight biochar particles. The decrease of bulk densities is accompanied by decreasing of bending and compressive strengths. Nevertheless, the mechanical properties of samples with the 5 wt. % of replacement were detected to be only slightly lower. The average values of compressive and bending strengths were reduced for 5.7 and 1.5 MPa, respectively. However, it should be noted that for the compressive strength of REF value was measured with higher standard deviation (Table 3) and if the lowest value of compressive strength for REF sample is considered, the difference with BC 5 samples is only 2.1 MPa. Aforementioned observation may be attributed to the arrangement and distribution of biochar particles, as is depicted in Figure 1. Wide range of particles morphology with sizes from nanoscale diameters, 1 – 5 µm (represented in considerable amount) and up to grains overcoming 10 µm in diameter are clearly visible. Nano and micro particles can act as nucleation sites and thus in some extent may promote hydration rate of Portland cement [7]. Furthermore, biochar particles tend to adsorb on their surface and in their porous structure free water. Thereby, it was reported that increase water demands resulted in the change of the capillary system and total open porosity of hardened composites [15].

Mineralogical composition of cement pastes with 5 and 20 % content of biochar and REF sample were analysed with XRPD and obtained results from quantitative phase analysis are summarized in Table 4. From the point of examined materials, basic minerals occurring in cement clinker, calcium-silicates (namely alite and belite) and brownmillerite were detected. Other found mineral phases such
as portlandite, calcite, vaterite and ettringite are related to the hydration of Portland cement. Increasing cement substitution with non-reactive carbon-rich biochar brought the decrease in the content of clinker minerals. The highest content of formed portlandite and calcite was recorded for paste with 5% of biochar.

**Table 3.** Physical and mechanical properties of produced blend cement pastes

| Paste | Bulk density (kg·m⁻³) | Compressive strength (MPa) | Bending strength (MPa) |
|-------|------------------------|-----------------------------|------------------------|
| REF   | 1 789                  | 80.8 ± 3.6                  | 13.3 ± 0.7             |
| BC 5  | 1 545                  | 75.1 ± 0.8                  | 11.8 ± 0.6             |
| BC 10 | 1 397                  | 59.8 ± 0.5                  | 9.4 ± 0.5              |
| BC 15 | 1 303                  | 48.2 ± 0.5                  | 7.2 ± 0.4              |
| BC 20 | 1 204                  | 39.8 ± 0.3                  | 5.7 ± 0.2              |

**Figure 1.** SEM image of biochar particles

**Table 4.** Mineralogical composition of selected blend cement pastes

| Mineral      | REF (wt. %) | BC 5 (wt. %) | BC 20 (wt. %) |
|--------------|-------------|--------------|---------------|
| Alite        | 8.8         | 8.3          | 2.6           |
| Belite       | 6.3         | 4.7          | 2.3           |
| Brownmillerite | 3.2       | 3.1          | 1.7           |
| Calcite      | 11.8        | 12.4         | 10.1          |
| Ettringite   | 2.4         | 3.6          | 4.9           |
| Portlandite  | 8.9         | 10.3         | 5.8           |
| Quartz       | 0.4         | 0.4          | 0.4           |
| Vaterite     | 4.4         | 5.4          | 8.6           |
| Amorphous content | 53.9 | 58.0         | 63.8          |
The growing occurrence of metastable calcium carbonate polymorph, vaterite, tied with increased biochar content was recorded. The BC 20 samples consist of the highest amount of ettringite, calcium carbonate phases (calcite and vaterite) and amorphous phase and the lowest content of portlandite in the comparison with analysed samples. Revealed changes in vaterite content may be connected with capturing of gaseous CO2 from the air into a porous structure of biochar grains [16]. This observation confirms the role of biochar particles as real nucleation sites. It could be noted that partial replacement of Portland cement with biochar influenced the hydration process and brought important lightening of manufactured pastes with increasing biochar content.

4. Conclusions

This paper was focused on the usage of biochar for partial cement substitution. The produced blended cement pastes, as well as its constituents, were analysed with different instrumental techniques to obtain the information about their physical, mechanical and mineralogical properties. Due to 3 times lower powder density of biochar in comparison with Portland cement, an important decrease of bulk densities of hardened pastes with blended binder was observed. In this sense, samples with 20 wt. % of biochar were lighter of about 32.7 % regard to the reference sample. For composites with a high amount of cement replacement with biochar, an important decrease of compressive and bending strengths was observed. However, with biochar incorporation in the amount of 5 wt. %, compressive and bending strength were reduced only slightly in the comparison with the reference sample. Lower cement substitutions seemed to be more suitable for applications whereas higher content of biochar particles influence the hydration reaction of cement and the highest contents of calcium carbonate and ettringite together with the lowest content of portlandite were detected. The obtained data implied the potential of biochar for the CO2 capturing and thus may play an important role in carbon sequestration. The results showed the possible application of biochar in civil engineering as the cement replacement material, nonetheless, more extensive research is needed to tune the properties of final cement composites.

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References

[1] K. L. Scrivener, V. M. John, and E. M. Gartner, “Eco-efficient cements: Potential economically viable solutions for a low-CO2 cement-based materials industry,” Cem. Concr. Res., vol. 114, pp. 2-26, 2018.
[2] F. A. C. Oliveira, J. C. Fernandes, J. Galindo, J. Rodriguez, I. Canadas, V. Vermelho, A. Nunes, and L. G. Rosa, “Portland cement clinker production using concentrated solar energy – A proof-of-concept approach,” Sol. Energy, vol. 183, pp. 677-688, 2019.
[3] M. E. Boesch, A. Koehler and S. Hellweg, “Model for cradle-to-gate life cycle assessment of clinker production,” Environ. Sci. Technol., vol. 43, pp. 7578-7583, 2009.
[4] H. Mikulčić, J. J. Klemes, M. Vujanović, K. Urbanieca, and N. Dučić, “Reducing greenhouse gases emissions by foresting the deployment of alternative raw materials and energy sources in the cleaner cement manufacturing process,” J. Cleaner Prod., vol. 136, pp. 119-132, 2016.
[5] G. Pilon, and J. M. Lavoire, “Biomass char production at low severity conditions under CO2 nad N2 environments,” WIT Trans. Ecol. Environ., vol. 143, 2011.
[6] S. K. Mohanty, R. Valenca, A. W. Berger, I. K. M. Yu, X. Xiong, T. M. Saunders, and D. C. V. Tsang, “Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment,” Sci. Total. Environ., vol. 625, pp. 1644-1658, 2018.
[7] S. Gupta, H. W. Kau, and H. J. Koh, “Application of biochar from food and wood waste as
green admixture for cement mortar” Sci. Total. Environ., vol. 619-620, pp. 419-435, 2018.
[8] EN 933-1, Test of geometrical properties of aggregate – Part 1: Determination of particle size distribution – Sieving method, CEN, Brussels, 2012.
[9] EN 196-6, Methods of testing cement – Part 6: Determination of fineness, CEN, Brussels, 2010.
[10] EN 1097-7, Test of mechanical and physical properties of aggregate – Part 7: Determination of particle density of filler – Pyknometer method, CEN, Brussels, 2008.
[11] EN 1097-3, Test of mechanical and physical properties of aggregate – Part 3: Determination of loose bulk density and voids, CEN, Brussels, 1999.
[12] EN 1015-3, Methods of test for mortar for masonry – Part 3: Determination of consistence of fresh mortar, CEN, Brussels, 2000.
[13] EN 1015-10, Methods of test for mortar for masonry - Part 10: Determination of dry bulk density of hardened mortar, CEN, Brussels, 1999.
[14] M. Keppert, M. Urbanová, J. Brus, M. Čáchová, J. Fořt, A. Trník, L. Scheinherrová, M. Záleská and R. Černý, “Rational design of cement composites containing pozzolanic additions,” Constr. Build. Mater., vol. 148, pp. 411-418, 2017.
[15] A. N. Ofori-Boadu, R. Kelly, F. Aryeetey, E. Fini and P. Akangah, “The influence of swine-waste biochar on the early-age characteristics of cement paste,” Int. J. Eng. Res. Appl., vol. 7, pp. 1-7, 2017.
[16] S. Gupta, H. W. Kau, and C. Y. Low, “Use of biochar as carbon sequestering additive in cement mortar,” Cem. Concr. Compos., vol. 87, pp. 110-129, 2018.