MOC Cement-Based Composites with Silica Filler and Wood Chips Ash Admixture

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Abstract. As Portland cement and cement-based materials are the most widespread materials in construction industry, there is a concern to develop and search cement alternative materials with similar or better functional properties and a lower negative environmental impact. Magnesium oxychloride cement (MOC) is considered as low-energy and low-carbon binder possessing some advantageous properties superior to Portland cement. Therefore, lightweight MOC-based composites were designed and tested in the presented study. As filler, silica sand was used in composition of control composite mix. Later, it was partially replaced with wood chips ash coming from bioenergy production from biomass. The chemical composition and morphology of wood chips ash were characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analyses. For the hardened composites, bulk density, specific density, and total open porosity were measured. Among mechanical parameters, flexural and mechanical strengths were tested. The thermal performance of composites was studied using a transient hot disk method and the assessed parameters were thermal conductivity and volumetric heat capacity. The use of fly ash led to the great decrease in porosity compared to the control materials with silica sand as only filler. The mechanical strength of all developed materials was high. Both the compressive strength and flexural strength decreased the dosage of wood chips ash in composite mix. However, the decrease in mechanical resistance was lower than the send replacement ratio. It clearly proved assumption of filler function of fly ash, whereas its assumed reactivity with MOC cement components was not proven. The heat transport was partially mitigated by wood chips use, similarly as heat storage. Based on the obtained data, the developed composites were considered as alternative low-carbon materials possessing interesting functional properties for construction practice. Moreover, the reuse of by-product from biomass bioenergy treatment can be considered as an environmentally friendly solution for production of sustainable advanced building materials.

1. Introduction

Highest greenhouse gas (GHG) emissions are recorded in industry sector mainly from the production of metallic products and non-metallic minerals such as Portland cement (PC). Billions of metric tons of Portland cement are produced over the Earth annually which represents serious environmental burden due to the release of huge amount of CO₂ within the decomposition of limestone and burning of coal in cement production plants. Also transportation of Portland clinker and cement as the final...
product contributes to the total carbon dioxide volume emitted within the cement manufacturing [1]. Production of PC is above 4 billion tons every year with estimated increase in following years and increased environmental burden due to GHG emissions. [2]. One possible way how to reduce GHG emissions is to reduce production of PC and use of alternative binders such as magnesia based cements. Magnesium oxychloride cement (MOC), also known as Sorel cement, is magnesia based non-hydraulic binder founded in 19th century which is formed by reaction of light burned MgO with MgCl$_2$ water solution [3]. In comparison with PC, MgO produce less CO$_2$ emissions due to the lower calcination temperature (700-1000 °C) and is considered as alternative to PC with a lower environmental impact [3]. Moreover, rapid carbonation of MOC-based materials allows accommodate CO$_2$ from the environment, whereas the MOC structure is well stabilized by the progress of carbonation rate. The maximum theoretical CO$_2$ uptake capacity of MOC Phase 5 is about 33 %. It is more than two times higher compared to CO$_2$ uptake capacity of PC (12.3 %) calculated during accelerated carbonation test [4].

MOC possesses high compressive strength [5], fire resistance [6], and ability to embody large volume of traditional mineral, organic, and waste fillers such as plastic waste [7] or hemp residues [8]. Incorporation of solid waste into construction material is beneficial method of waste disposal. Waste or industrial by-products used as substitutes to raw materials in construction composites reduce the volume of used raw minerals and waste disposed on landfills. Thus their reuse has positive impact on human health and environment. Also financial benefit is indispensable in this manner [9].

In building industry, fly ash coming from coal combustion in thermal power plants as substitute to cement [10] is commonly used. As alternative to fly ash use in cement-based materials, effect of the partial substitution of silica sand by biomass ash in magnesia based composites was studied in this paper.

2. Experimental
Magnesium oxychloride cement (MOC) used in this work was composed of light burned MgO (Styromagnesit Steirische Magnesitindustrie GmbH, Oberdorf, Austria) and 55% aqueous solution of MgCl$_2$·6H$_2$O (Lach-Ner, s.r.o, Neratovice, Czech Republic). The silica sand with fraction 0-2 mm (Filtrační písky s.r.o, Chlum u Doks, Czech Republic) was used as main filler in control composite mixture. Sand was partially replaced with wood chips-based biomass ash (BA) obtained in a heating plant Žlutice, Czech Republic. The filler replacement ratio was 5, 10, and 15 wt. %. Mortar samples were prepared according to the standard EN 14016-2 [11]. The composition of researched mortars is introduced in Table 1. Samples were casted in cubic (70 mm × 70 mm × 70 mm) and prismatic (40 mm × 40 × 160 mm) moulds, and after demoulding air-cured for 28 days in a laboratory environment with temperature of (23 ± 2) °C and relative humidity of (30 ± 5) %.

| Mortar mix | Magnesium oxide | Magnesium chloride | Water | Silica sand | Wood chips ash |
|------------|-----------------|--------------------|-------|-------------|----------------|
| REF        | 990             | 439                | 364   | 3 × 723     | -              |
| BA-5       | 990             | 439                | 364   | 3 × 686     | 44             |
| BA-10      | 990             | 439                | 364   | 3 × 650     | 88             |
| BA-15      | 990             | 439                | 364   | 3 × 614     | 132            |

Mineral and chemical composition, morphology, and particle size of BA were measured. X-ray powder diffraction (XRD) data were collected at room temperature on a Bruker D8 Discoverer powder diffractometer with parafocusing Bragg–Brentano geometry using Cu Kα radiation. Data evaluation was performed in the software package HighScorePlus. Morphology of BA was examined using
scanning electron microscopy (SEM) with a FEG electron source (Tescan Lyra dual beam microscope). Elemental composition and mapping were performed using energy dispersive spectroscopy (EDS) analyser (X-MaxN) with a 20 mm² SDD detector (Oxford instruments) and AZtecEnergy software.

Hardened cubic and prismatic samples of the examined composites were used to measure structural material parameters, mechanical resistance, and thermal transport and storage properties. Specimens were air-cured for 28 days, and then dried in a vacuum drier at 60 °C until their steady-state mass was reached.

For the basic characterization of the developed composites, bulk density, matrix density, and total open porosity were measured on casted cubic samples. The bulk density was calculated from sample dimensions and dry mass according to the standard EN 1015-10 [12]. The expanded combined uncertainty of the bulk density test was 2.4 %. The matrix density was measured by an automatic helium pycnometer Pyromatic ATS (Thermo Scientific). The total open porosity was calculated on the basis of bulk and matrix density values with the expanded combined uncertainty of 3.5 %.

Among mechanical parameters of the hardened MOC-based mortars, flexural strength and compressive strength were measured. The flexural strength was measured in three point bending test arrangement for 3 prismatic samples with the dimensions of 40 mm × 40 mm × 160 mm. The fragments from the flexural strength testing were used to measure the compressive strength. The loading area was 40 mm × 40 mm. The testing of mechanical properties was carried out according to the standard EN 1015-11 [13]. The expanded combined uncertainty of the both strength tests was 1.4 %.

Heat transport and storage parameters (thermal conductivity and volumetric heat capacity) were measured by a transient plane source technique using a hot-disk TPS 1500 apparatus (Hot Disk AB) equipped with a Kapton circular sensor with 6.4 mm radius. The measurement was at room temperature of (23 ± 2) °C performed. For each composite mix, 5 cubic specimens with the dimensions of 70 mm × 70 mm × 70 mm were tested.

3. Results and discussion

The X-ray diffraction pattern of wooden biomass ash is shown in Figure 1. Main phases of biomass ash were calcite (CaCO₃) and quartz (SiO₂) which corresponded with the data provided by the EDS analysis (see Table 2).

![XRD pattern of BA](image)

**Figure 1.** XRD pattern of BA

The elemental EDS analysis showed (Table 2) that the main components of biomass ash were carbon (C), oxygen (O), calcium (Ca), potassium (K), and silica (Si).
Table 2. Chemical composition of wood chips ash.

| Element (wt. %) | C  | O  | Ca | K  | Si | Mg | P  | Al | S  |
|----------------|----|----|----|----|----|----|----|----|----|
|                | 38.9 | 24.0 | 21.0 | 9.2 | 2.4 | 1.6 | 1.5 | 0.9 | 0.4 |

The morphology of wood chips ash analysed using SEM is apparent from Figure 2. BA particles exhibited inconsistent shapes with diameter range from few to 20 microns.

Figure 2. SEM and EDS analysis of wood chips ash

Basic structural and mechanical properties of the hardened MOC composites with silica filler and biomass ash substitute are shown in Table 3. Ash substitute to silica filler resulted in the significant reduction of the total open porosity and increase in the bulk density. Both the tested strengths of control MOC-based mortar were high. In spite of the great drop in porosity, the flexural and compressive strength decreased with the silica sand replacement ratio. On the other hand, the decrease in the compressive strength was for composites labelled BA-5 and BA-10 lower than the silica sand substitution. This clearly pointed out to the filler effect of BA that not reacted with MOC but filled the gaps between sand particles and precipitated MOC phases, and thus contributed to the total compressive strength of BA containing composites. The compressive strength/flexural strength ratio was in the range 3.0-3.7 which gave information that MOC-based composites can withstand high bending load. Taking into consideration the high strength of composite BA-15, it is possible to incorporate more waste into MOC-based materials with lower strength requirements. If required, this can enable lightening of the composite structure and thus improvement of its thermal insulation performance.
Table 3. Basic structural and mechanical properties of MOC composites.

| Mortar mix | Bulk density (kg·m⁻³) | Matrix density (kg·m⁻³) | Total open porosity (%) | Flexural strength (MPa) | Compressive strength (MPa) |
|------------|-----------------------|-------------------------|-------------------------|------------------------|---------------------------|
| REF        | 2125                  | 2430                    | 12.6                    | 25.9                   | 77.7                      |
| BA-5       | 2163                  | 2260                    | 4.3                     | 20.0                   | 74.4                      |
| BA-10      | 2162                  | 2270                    | 4.8                     | 20.9                   | 73.1                      |
| BA-15      | 2141                  | 2297                    | 6.8                     | 21.1                   | 66.3                      |

The use of biomass ash as silica sand substitute resulted despite of the lower total open porosity in a slight reduction in the thermal conductivity and increase in the volumetric heat capacity as shown in Table 4. The more silica filler was substituted, the higher was reduction in the thermal conductivity. The reduction of the thermal conductivity was assigned to the higher volume of BA in composite mix compared to silica sand as well as to its lower thermal conductivity. On the other hand, the filling of the voids between silica sand particles and formed MOC phases increased partially volumetric heat capacity.

Table 4. Thermal properties of MOC composites.

| Mortar mix | Thermal conductivity (W·m⁻¹·K⁻¹) | Volumetric heat capacity (MJ·m⁻³·K⁻¹) |
|------------|----------------------------------|--------------------------------------|
| REF        | 3.079                            | 1.809                                |
| BA-5       | 2.973                            | 2.006                                |
| BA-10      | 2.878                            | 2.095                                |
| BA-15      | 2.754                            | 2.014                                |

4. Conclusions
The effect of wooden biomass ash on composites formed from magnesia-based cement was studied in this paper. Application of biomass ash as filler substitute led to the partial filling of the pores in composite matrix and changed their diameter. This had the effect on the reduced total open porosity and increased specific heat capacity. The mechanical strength decreased with the replacement ratio of silica sand with BA. This was due to the lower mechanical resistance of BA particles themselves compared to that of silica sand. Moreover, the BA particles acted as filler only, whereas they did not interact with the components of MOC. Nevertheless, all composites with partial substitution of silica sand with BA exhibited the compressive strength values higher than 60 MPa. This pointed to the possibility to apply higher volume of biomass ash in composition of MOC-based materials which will bring both environmental and economic benefits.

It can be concluded, the use of MOC binder with incorporated biomass ash as construction material can reduce GHG emissions coming from building industry sector and volume of waste disposed on landfills. It this respect, the investigated MOC-BA-based composites can be considered as eco-friendly materials.

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