Influence of Graphite Oxide Addition on the Properties of Magnesium Oxychloride Cement Composites

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Abstract. Magnesium oxychloride cement (MOC) is as an eco-friendly construction material used in industrial as well as in residential applications thanks to its better performance in comparison with Portland cement (PC) considered. Magnesium oxychloride cement composites formed during the reaction between light-burned magnesium oxide powder and magnesium chloride solution, belong to non-hydraulic materials and offer the advantage of high early strength and low porosity. These performances could, however, be further improved by incorporating of selected nanomaterials. This paper therefore presents an experimental investigation of magnesium oxychloride cement paste with graphite oxide admixture. The chemical composition of raw light-burned magnesium oxide powder was analysed by X-Ray Fluorescence (XRF) and the morphology of graphite oxide was characterised using High Resolution Transmission Electron Microscopy (HR-TEM). Graphite oxide (GO) was added into the mixture in a concentration of 0.5 wt. %. Subsequently, the influence of GO on the properties of hardened MOC paste was analysed in terms of its bulk density, specific density, open porosity and compressive and flexural strength measurement. The characterisation of studied pastes using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis was done as well. It was found that the presence of GO significantly enhanced the flexural strength, decreased the open porosity and slightly improved the compressive strength compared to the plain MOC paste. The obtained results suggest that with the addition of graphite oxide to magnesium oxychloride cement, MOC-based nanocomposites intended for civil engineering can be developed. These are characterised by high strength and low porosity, which is particularly important for reduction of moisture related damage.

1. Introduction

Nowadays, Portland cement is the most consumed building material worldwide. It is well know that manufacturing of Portland cement products is to large amount of carbon dioxide (CO₂) emissions linked. In order to reduce the negative environmental impact of CO₂, the construction industry is currently looking for alternative building materials [1]. Magnesium oxychloride cement (MOC), also called Sorel cement, is among environmentally friendly non-hydraulic binders ranked. It is characterized by fast setting and hardening, high early compressive and flexural strengths, and possess high fire and abrasion resistance [2]. The strength of MOC is derived from the MgO-MgCl₂-H₂O ternary composite crystal salt with the main crystalline phases of 3MgO-MgCl₂·8H₂O (phase 3) and
It was reported that MOC-based materials are able to offset the CO$_2$ emissions during the carbonation, and the final net emitted CO$_2$ associated with the life cycle of this materials is therefore of 40%-50% lower than that in the case of Portland cement manufacturing. Moreover, the carbonation also contributes to strength improvement of MOC-based materials [4]. Thanks to its excellent properties, the most common applications of MOC in construction industry are industrial floors, decoration purposes (stucco, ornamental applications) and different types of panels used for fire protection and for thermal and sound isolation. However, poor water resistance limited the wider use of this material [5].

Generally, many types of admixtures are investigated to modify selected properties of building materials. In recent years, a plenty of carbon-based nanofillers were studied to reinforce cementitious matrices, to get superior composite performance particularly in terms of physical properties and strength parameters. These carbon-based materials can be used in form of nanoplatelets, nanotubes and hybrid systems of graphene oxide/carbon nanotubes [6, 7]. To date, no study dealing with the incorporation of carbon-based nanomaterials into MOC binder was found.

In the presented research, the effect of graphite oxide admixture on the structural and mechanical properties of magnesium oxychloride cement composites was investigated. In addition, the characterization of the developed pastes by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) was done. The main aim was to prepare environmentally friendly material with enhanced mechanical and structural properties intended for use in construction industry.

2. Experimental

The raw materials used for preparation of MOC composites were light burned magnesium oxide powder, magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O), graphite oxide (GO), and tap water. The light burned magnesium oxide was obtained from Styromagnesit Steirische Magnesitindustrie Ltd. Its chemical composition determined by X-Ray Fluorescence analysis (EDXRF Spectrometer, ARL QUANT’X, Thermo Scientific) is given in Table 1.

| Table 1. The chemical composition of light burned magnesium oxide powder. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| MgO             | SiO$_2$         | CaO             | Al$_2$O$_3$     | Fe$_2$O$_3$     | SO$_3$          |
| 80.7            | 4.1             | 5.0             | 5.8             | 3.9             | 0.2             |

MgCl$_2$·6H$_2$O from Lach-Ner Ltd. of p.a. purity was dissolved in tap water to prepare the magnesium chloride solution of concentration expressed as 26 °Bé. The graphite oxide was supplied by ACS Material, LLC. The High Resolution Transmission Electron Microscopy (HR-TEM) images of GO, obtained using an EFTEM Jeol 2200 FS microscope (Jeol, Japan), is shown in Figure 1. Wrinkled layered structure typical for GO was obtained, the particle size of GO was about 1 μm. GO was added in the amount of 0.5 % by weight of binder material (light burned magnesium oxide and MgCl$_2$·6H$_2$O). The mix proportions of developed MOC composites were to get similar consistency of both investigated pastes adjusted and are summarized in Table 2. Before mixing, GO was sonicated for 15 min in a part of MgCl$_2$ solution to produce graphite oxide suspension.

| Table 2. The mix proportions of MOC-based pastes. |
|-----------------|-----------------|-----------------|-----------------|
| Mixture         | MgO             | MgCl$_2$ solution | Graphite oxide  |
| MOC-R           | 959.0           | 707.2           | -               |
| MOC-GO          | 959.0           | 870.2           | 6.919           |
The casted prismatic samples of dimension 40 mm × 40 mm × 160 mm were demoulded after 24 h and air cured for next 6 days at laboratory conditions until testing. The fabricated samples were referred to as MOC-R (reference sample without GO) and MOC-GO (sample with a GO addition).

Figure 1. HR-TEM images of graphite oxide

The basic structural, mechanical and chemical properties as well as morphology of 7 days air cured MOC composites were characterized using selected experimental techniques described below. Then, GO reinforced MOC paste was with a reference sample compared.

The flexural strength was determined on 40 mm × 40 mm × 160 mm samples following the standard EN 12390-5 [8]. For compressive strength measurement according to the standard EN 12390-3 [9], the fragments from the flexural strength testing were used. The loading area was 40 mm × 40 mm. The relative expanded uncertainties of the flexural and compressive strength tests were 1.4 %.

The samples for specific and matrix density measurement were before testing in a vacuum drier at 60 °C dried. The specific density was using the automatic helium pycnometer Pycnomatic ATC (Thermo Scientific) assessed. The evaluation of dry bulk density was on the gravimetric principle by determination of sample weight and dimensions performed. Based on the bulk and specific density measurement, the open porosity was calculated. The relative expanded uncertainty of the applied measuring method was 5 %.

The morphology of MOC composites was on a fractured composite surface using SEM with a FEG electron source (Tescan Lyra dual beam microscope) investigated. To conduct the measurements, the samples were on a carbon conductive tape placed.

X-ray powder diffraction data were collected at room temperature on Bruker D8 Phaser (Bruker, Germany) powder diffractometer with parafocusing Bragg–Brentano geometry using CuKα radiation (λ = 0.15418 nm, U = 30 kV, I = 10 mA). The data was over the angular range 5–80° (2θ) with a step size of 0.019° (2θ) scanned. The evaluation of the measured data was in the software HighScore Plus conducted.
3. Results and discussions
In Table 3, the basic structural parameters of MOC composites are given. As can be seen, both the bulk and specific densities increased with a GO addition. Conversely, MOC-GO exhibited very low open porosity, which decreased to 51.5 % of the reference sample value. This is a highly promising finding as low porosity of MOC-GO can contribute to the improvement of its resistance and durability against disruptive moisture action.

**Table 3. Basic structural parameters of MOC-based pastes.**

| Mixture  | Bulk density (kg·m⁻³) | Specific density (kg·m⁻³) | Open porosity (%) |
|----------|-----------------------|---------------------------|-------------------|
| MOC-R    | 1912                  | 1976                      | 3.3               |
| MOC-GO   | 1991                  | 2025                      | 1.7               |

Looking at the results summarized in Table 4, there was higher mechanical resistance of composites with the GO reinforcement observed. The noticeable improvement was significant mainly for flexural strength; its value for MOC-GO sample increased by 41.9 % compared to the reference sample. In the case of compressive strength, the increase with the GO addition was only small.

**Table 4. Mechanical parameters of MOC-based pastes.**

| Mixture  | Compressive strength (MPa) | Flexural strength (MPa) |
|----------|----------------------------|------------------------|
| MOC-R    | 64.3                       | 15.5                   |
| MOC-GO   | 65.2                       | 22.0                   |

![Figure 2. XRD patterns of MOC-based pastes: MOC-R (A) and MOC-GO (B)](image-url)
XRD analysis (Figure 2) indicated for both MOC-R and MOC-GO samples typical products of mixing light burned MgO with aqueous solution of MgCl₂ such as 5MgO·MgCl₂·8H₂O (phase 5) and unreacted MgO. No new material formation related with the presence of GO was identified. It was due to the low content of GO in paste composition. Phase 3 and MgCl₂ were in the patterns not found which means that MgCl₂ was during the reaction fully consumed.

The morphology investigated by SEM is in Figure 3 shown. The needle-like structure, which is typical for phase 5 was in the MOC-R sample observed. It is apparent from the SEM images that microstructure of MOC-GO sample is more compact as GO particles filled the gaps between phase 5 crystals. This clearly demonstrated the GO efficiency, and was consistent with the achieved mechanical and basic structural properties of MOC composites.

![Figure 3. SEM images of MOC-based pastes](image)

4. Conclusions
This paper focused on the influence of graphite oxide admixture on the basic structural, mechanical, chemical and microstructural parameters of MOC composites. It was observed that GO in a low concentration of 0.5 % by weight enhanced both the flexural and compressive strengths and decreased the open porosity. The obtained results indicate that MOC, as an environmentally friendly construction material, particularly as regards the CO₂ emissions associated with its life cycle, can be by the addition of carbon-based nanomaterials further improved.

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References
[1] M. Sinka, P. Van den Heede, N. De Belle, D. Bajare and G. Sahmenko, “Comparative life cycle assessment of magnesium binders as and alternative for hemp concrete,” Resour., Conserv. Recycl., vol. 133, pp. 288–299, 2018.
[2] Z. Zhou, H. Chen, Z. Li and H. Li, “Simulation of the properties of MgO-MgCl₂·H₂O system by thermodynamic method,” Cem. Concr. Res., vol. 68, pp. 105–111, 2015.
[3] T. Huang, Q. Yuan and D. Deng, “The role of phosphoric acid in improving the strength of magnesium oxychloride cement pastes with large molar ratios of $\text{H}_2\text{O}/\text{MgCl}_2$,” *Cem. Concr. Compos.*, vol. 97, pp. 379-386, 2019.

[4] S. Tang, Y. Hu, W. Ren, P. Yu, Q. Huang, X. Qi, Y. Li and E. Chen, “Modeling on the hydration and leaching of eco-friendly magnesium oxychloride cement paste at the micro-scale,” *Constr. Build. Mater.*, vol. 204, pp. 684-690, 2019.

[5] M. Záleská, M. Pavlíková, O. Jankovský, M. Lojka, F. Antončík, A. Pivák and Z. Pavlík, “Influence of waste plastics aggregate and water-repellent additive on the properties of lightweight magnesium oxychloride cement composites,” *Appl. Šči.*, vol. 9, pp. 1-15, 2019.

[6] M. Birenboim, R. Nadv, A. Alatawna, M. Buzaglo, G. Schahar, J. Lee, G. Kim, A. Peled and O. Regev, “Reinforcement and workability aspects of graphene-oxide-reinforced cement nanocomposites,” *Compos. Part B*, vol. 161, pp. 68-76, 2019.

[7] T. S. Qureshi, D. K. Panesar, B. Sidhureddy, A. Chen and P. C. Wood, “Nano-cement composite with graphene oxide produced from epigenetic graphite deposit,” *Compos. Part B*, vol. 159, pp. 248-258, 2019.

[8] EN 12390-5 Testing hardened concrete – Part 5: Flexural strength of test specimens, CEN, 2009.

[9] EN 12390-3 Testing hardened concrete – Part 3: Compressive strength of test specimens, CEN, 2009.