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Proceeding Paper

Alkali-Activated Metashale Mortar with Waste Cementitious Aggregate: Material Characterization †

Petr Hotěk [1,*], Lukáš Fiala [1], Wei-Ting Lin [2], Yi-Hua Chang [2] and Robert Černý [1]

1 Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 2077/7, 166 29 Prague, Czech Republic
2 Department of Civil Engineering, National Ilan University, Ilan 26047, Taiwan
* Correspondence: petr.hotek@fsv.cvut.cz; Tel.: +420-2-2435-7102
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Abstract: The design of sustainable construction materials is continuously gaining increasing importance in civil engineering. Geopolymers are attractive alternatives to cementitious materials in terms of environmental impact and specific material properties, such as durability, an initial increase in mechanical properties, or chemical and thermal resistance. Such favorable properties can be advantageously utilized within various applications involving the design of materials for heavily stressed industrial floors. The research presented in the paper was focused on the design of a geopolymer composite based on metashale MEFISTO L05 and waste metashale RON D460HR binders. The 1:4 raw/waste mix of binders activated by potassium hydroxide/silicate was supplemented by 0.11 wt.% of graphite fibers to optimize electrical properties and bestow on it some new material functions, such as self-heating. The further utilization of fine waste aggregate (crushed defective concrete products, waste concrete from auto-mixers) resulted in an ~85% utilization of input waste materials. An acceptable mechanical performance of the mortar for particular civil engineering applications was observed (28d: R_f ~ 2.5 MPa, R_c ~ 15 MPa), as well as favorable thermal and DC/AC electrical properties, predicting the self-heating potential.

Keywords: alkali activation; waste metashale mortar; waste aggregate; low environmental impact

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1. Introduction

The construction industry, with its almost 30% share of the total industrial activity within the European Union (EU), is one of its largest industrial sectors. Besides the construction of new buildings, it also involves renovation, demolition, and the disposing of waste building materials. In 2020, more than 800 million tons of the produced construction and demolition waste in the EU had to be recycled or landfilled [1]. Due to the negative environmental impact of landfilled construction materials polluted by hazardous agents, the design of sustainable materials leading to a reduction in landfilling gained higher importance in recent years [1–3].

With over 25 gigatons produced per year, concrete is the most widely used building material worldwide and undoubtedly also a major component of construction waste [4]. Therefore, its reuse in the construction industry, e.g., as a recycled waste aggregate for new composites, is beneficial for the reduction in landfilled material as well as the protection of natural resources [5,6]. It should be noted that the use of recycled concrete aggregate has its limits and rules. Nováková and Mikulica [6] emphasized that in the case of landfilled concrete, special attention needs to be paid to the removal of impurities coming from other materials, such as asphalts, bricks or plastics. They also noted that the European standard EN 12 620+A1 requirements for the use of aggregate in concretes slightly differs from country to country [7].

The degree of the environmental impact of the construction composite production significantly depends on the used binder and filler. Although alternative binders can positively influence the total environmental impact of the composite, the choice of aggregate plays the decisive role since it is present in a significantly higher amount than the binder. Alkali-activated composites (geopolymers) based on aluminosilicate waste/industrial product precursors (slag, brick dust, fly ash, metakaolin, metashale, etc.) offer a good environmental performance as far as the binder is concerned [8,9]. Despite the use of alkali activators (potassium/sodium hydroxides and water glasses), which are characterized by a higher negative environmental impact, the amount necessary for activation is low in comparison with the amount of binder and filler [10,11]. Geopolymers have a huge potential in civil engineering due to their various beneficial properties, e.g., high initial mechanical properties and chemical and fire resistance, ensuring durability and a low environmental impact, which can be further improved by replacing natural products with recycled aggregate [12–14].

This paper is focused on the design of a geopolymer mortar based on the mix of the newly produced and waste metashale binder, potassium hydroxide/silicate activator and recycled concrete aggregate filler. The composite was supplemented with a small amount of carbon fibers to examine their influence on electrical properties, which would be crucial for the new functional properties, such as self-sensing, self-heating or energy harvesting. The composite was characterized in terms of the basic physical, thermal and electrical properties.

2. Experimental Stage

2.1. Materials

The designed composite was based on the mix of two aluminosilicate precursors, Mefisto L05 and RON D460 HR (Figure 1). Mefisto L05 is a very fine metashale powder (d_{50} = 3 µm, d_{90} = 10 µm) originating from the thermal and granulometric treatment of clays and float kaolins. RON D460 HR is an industrial waste from the production of Mefisto L05, consisting of some unburnt particles that are of slightly higher size than in Mefisto L05 (d_{50} = 4.5 µm and d_{90} = 23 µm). The chemical composition and particle size distributions of the precursors are summarized in Table 1 and Figure 2.

(a) (b)

Figure 1. (**a**) Mefisto L05, (**b**) RON D460 HR.

Table 1. XRF analysis of Mefisto L05 and RON D460 HR precursors (%).

Precursor	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O
Mefisto L05	49.58	41.04	2.76	2.39	1.08	0.9	1.03
RON D460 HR	49.1	47.3	0.9	1.6	0.1	0.2	0.5

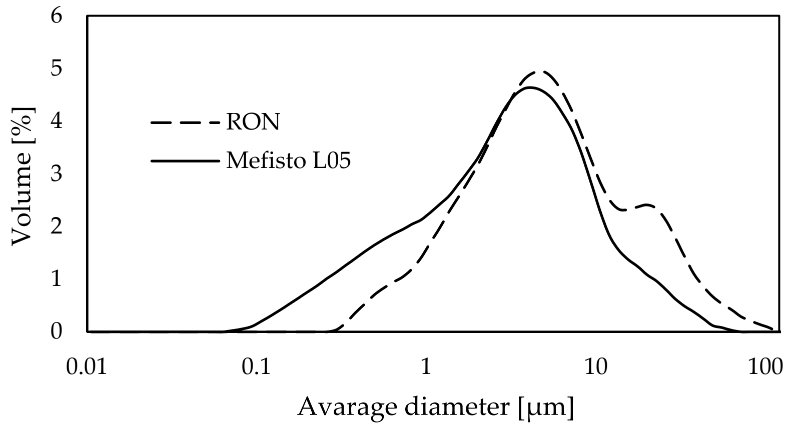

Figure 2. Particle size distribution of Mefisto L05 and RON D460 HR.

Metashale precursors were activated by a mix of potassium alkalis: potassium water glass with a K_2O/SiO_2 ratio = 1.7 and potassium hydroxide to avoid efflorescence, which occurs upon activation by sodium water glass/hydroxide [15]. The filler—a recycled cementitious aggregate—was of a grain size within the range of 0.063 to 2 mm, prepared by crushing damaged structural formworks. The H-shaped structural formwork (Figure 3a) was first crushed into smaller pieces using an EDB 400 mechanical press. Subsequently, smaller pieces were crushed using a crusher with 2.2 mm maximum jaw distance. The resulting aggregate was sieved and sorted into individual fractions of 0.063–0.5 mm, 0.5–1 mm and 1–2 mm, following the pattern of standardized quartz sand fractions (Figure 3b). The fresh mixture was supplemented with a small amount of carbon fibers to examine their influence on the electrical properties of the designed composite.

(**a**) (**b**)

Figure 3. (**a**) H-shape structural formwork, (**b**) fractions of waste aggregates.

2.2. Sample Preparation

First, Mefisto L05 and Ron D460 HR precursors were mixed with three waste aggregate fractions. Pellets of carbon fibers were dispersed in water with non-ionic surfactant Triton X-100 and siloxane-based air-detraining agent Lukosan S to reduce the surface tension of the carbonaceous admixture and defoam the suspension. The vessel with the suspension was then treated in an ultrasonic bath for 10 min to effectively crumble the pellets and disperse individual fibers. The well-prepared suspension was poured into a dry mixture of precursors, aggregate, and alkali activator and mixed for 10 min. Fresh mortar was finally placed into molds (Figure 4): 160 × 40 × 40 mm^3—mechanical properties, 100 × 100 × 100 mm^3—electrical properties, 70 × 70 × 70 mm^3—thermal properties. The 100 × 100 × 100 mm^3 samples were additionally embedded with copper-grid electrodes using a 3D-printed plastic board for precise positioning. After 24 h of curing in laboratory conditions (22 °C, 50% RH), samples were unmolded and left in equal conditions for a further 28 days. The composition of the studied geopolymer is summarized in Table 2.

Figure 4. RMCF1 mortar samples.

Table 2. Composition of RMCF1 mortar.

Component	RMCF1
Mefisto L05 [g]	272
RON D460 HR [g]	1088
Carbon fibers [g]	1.5
Potassium water glass [g]	474
Potassium hydroxide [g]	51
Aggregate 0.063–0.5 mm [g]	1700
Aggregate 0.5–1 mm [g]	850
Aggregate 1–2 mm [g]	1020
Water [g]	500

2.3. Methods

The bulk density ρ_v [kg·m^{-3}] was determined on the 40 × 40 × 160 mm^3 samples using the gravimetric method (Equation (1)). The matrix density ρ_{mat} [kg·m^{-3}] was evaluated by helium pycnometry (Pycnomatic ATC EVO). The total open porosity ψ [%] was then calculated using Equation (2).

$$\rho_v = \frac{m}{V} \tag{1}$$

$$\psi = \left(1 - \frac{\rho_v}{\rho_{mat}}\right) \cdot 100 \tag{2}$$

The dynamic modulus of elasticity E_{dyn} [MPa] was determined on the 40 × 40 × 160 mm^3 samples via a non-destructive method using the Pundit ultrasonic device according to Equation (3).

$$E_{dyn} = \rho_v \cdot v^2 \tag{3}$$

where ρ_v [kg·m^{-3}] is the bulk density of the material, and v [m·s^{-1}] is the speed of ultrasonic wave propagation through the sample.

Mechanical properties represented by the flexural and compressive strength were determined according to the ČSN EN 196-1 [16] using FP 100 and ED60 presses on the 40 × 40 × 160 mm^3 samples after 7 and 28 days.

The thermal properties, the thermal conductivity λ [W·m^{-1}·K^{-1}] and the specific heat capacity c_p [J·kg^{-1}·K^{-1}] were determined on the 70 × 70 × 70 mm^3 samples via non-stationary measurements using the ISOMET 2114 device equipped with a flat surface probe.

The DC electrical conductivity was determined on the 100 × 100 × 100 mm^3 electrode-embedded samples using a GW Instek GPR-11H30D power source and two Fluke 8846A multimeters for the voltage and current measurements. The electrical conductivity σ [$S \cdot m^{-1}$] was determined for three different input voltage levels according to Equation (4).

$$\sigma = \frac{I}{U} \cdot \frac{l}{S} = \frac{1}{R} \cdot \frac{l}{S} \quad (4)$$

where I [A] is the electric current, U [V] is the voltage, S = 0.0072 [m^2] is the area of electrodes, l = 0.07 [m] is the distance between electrodes and R [Ω] is the resistance of the material.

AC electrical properties represented by the magnitude of the impedance Z [Ω] and the phase shift θ [°] were determined in the range of 10 Hz–10 MHz on the 100 × 100 × 100 mm^3 samples using a GW Instek 8210 LCR bridge.

3. Results and Discussion

The summary of the material properties of the geopolymer mortar is given in Table 3. The total open porosity of ~17%, corresponding to the bulk and matrix density of 1954 $kg \cdot m^{-3}$ and 2362 $kg \cdot m^{-3}$, was mainly affected by the amount of mixing water (water/binder = ~0.37) due to the use of waste aggregates and carbon fibers [17]. The thermal conductivity and specific heat capacity were of 1.18 $W \cdot m^{-1} \cdot K^{-1}$ and 884 $J \cdot kg^{-1} \cdot K^{-1}$ which are typical values for such composites. Thermal conductivity was reasonably high for an effective spreading of the heat, which is an important presumption for self-heating ability.

Table 3. Basic physical, thermal and electrical properties of RMCF1 mortar.

Material Property [Unit]	RMCF1
Bulk Density [$kg \cdot m^{-3}$]	1954
Matrix Density [$kg \cdot m^{-3}$]	2362
Total Open Porosity [%]	17.3
Dynamic Modulus of Elasticity (28 days) [MPa]	7.5
Thermal Conductivity [$W \cdot m^{-1} \cdot K^{-1}$]	1.18
Specific Heat Capacity [$J \cdot kg^{-1} \cdot K^{-1}$]	884
Electrical Conductivity [$S \cdot m^{-1}$]	$3.95 \cdot 10^{-2}$

The flexural and compressive strengths at 7 d and 28 d are summarized in Figure 5. An increase in flexural strength from 2 MPa to 2.5 MPa and 12.5 MPa to 15 MPa in compressive strength was observed. The relatively low strength values were mainly due to the use of a significant amount of waste metashale binder, as well as fine waste aggregate (input waste materials ~85 wt.%). The decrease in the strength of cementitious and geopolymer composites due to the substitution of natural aggregate with waste counterparts is well known and mentioned in the literature, e.g., Nuaklong et al. [18], who investigated fly ash geopolymers with limestone and recycled aggregate, observing that the recycled aggregate led to a reduction in strength from 40 MPa to 30.6 MPa. Zaid et al. [19] studied natural aggregate replacement with recycled aggregate in steel-fiber-reinforced concrete and concluded that with an increasing amount of the recycled aggregate, the strength of the composites decreased. It was justified by a higher porosity of the recycled aggregate, resulting in an increase in material drying shrinkage and the formation of microcracks.

AC electrical properties represented by the frequency-dependent magnitude of the impedance and phase shift are presented in Figure 6. The magnitude of the impedance, involving both the resistive and capacitive component (resistance, capacitance), decreased from the initial ~175 Ω (10 Hz) to ~100 Ω (10 MHz), which due to the low values, revealed the potential for new functional properties, such as self-heating. The phase shift was from −3° to −10° in the tested frequency range and a noticeable decrease was observed at higher frequencies of 1–10 MHz. The phase shift close to 0° confirmed the resistive nature of the mortar and its potential for the self-heating function in an AC electric field. Since the DC electrical conductivity of the mortar (σ = 3.9·10^{-2} S·m^{-1}) was reasonably high, the self-heating potential was confirmed also in a DC electric field.

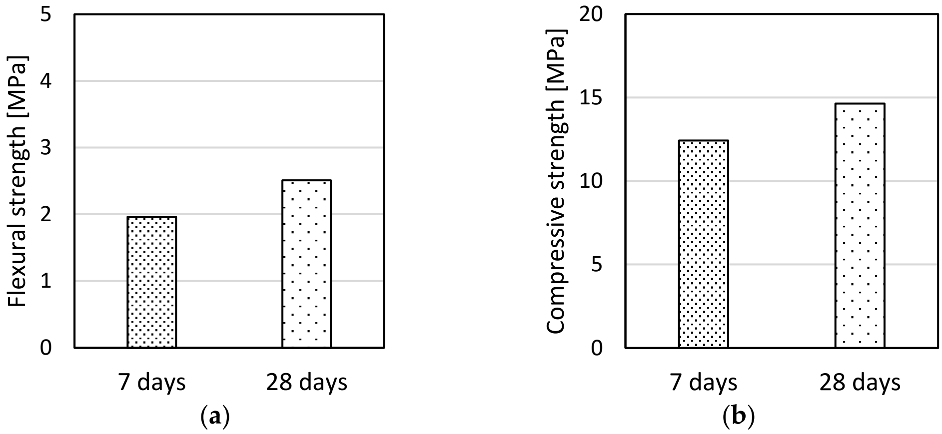

Figure 5. (**a**) Flexural strength, (**b**) Compressive strength of RMCF1 mortar.

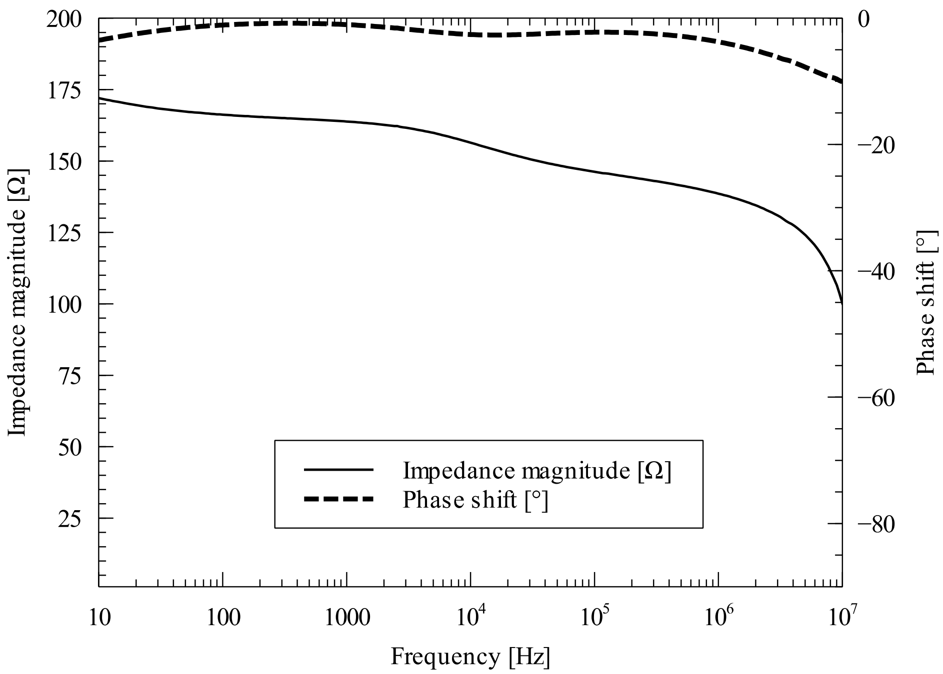

Figure 6. AC characteristics of RMCF1 mortar.

4. Conclusions

The study was focused on the design and basic material characterization of a geopolymer mortar with a special emphasis on the utilization of a significant amount of waste input materials. The waste metashale binder and waste cementitious aggregate originating from crushed defective cementitious products and cement mix used within the design of the geopolymer composite ensured an ~85 wt.% waste origin of input materials.

The mechanical properties of the mortar (28 d: R_f ~ 2.5 MPa, R_c ~ 15 MPa) are acceptable for some civil engineering applications. Nevertheless, it is important to target further efforts on the optimization of the geopolymer mortar composition, ensuring better mechanical performance. The thermal and electrical properties were favorable for the self-heating function in a DC and AC electric field, even with a low amount of carbon fibers. Nevertheless, it should be noted that the samples were characterized in a partially water-saturated state (curing in laboratory conditions, successive measurements without the preceding drying). Since the porous system in a heterogeneous geopolymer matrix is partially filled with water/salt solutions, which is beneficial in view of the thermal and electrical conductivity increase, the evaluated self-heating potential is slightly higher than in the case of dry material.

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