CLASSIFICATION AND CHARACTERIZATION OF REFRACTORY WASTE MATERIALS USED AS AGGREGATES IN INNOVATIVE LIME-BASED MORTARS

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SUMMARY: The main objective of this research was the classification and characterization of refractory waste materials (RWM). The selected RWMs consist of waste materials of refractory bricks, porcelain and residues of bricks of aluminum factory. The recycling materials were subjected to chemical and mineralogical analysis, through EDXRF, FTIR and XRD analyses. The designed mortars contained binders of either hydrated lime with metakaolin or natural hydraulic lime (NHL) and aggregates of RWM. These materials exhibited very high mechanical properties, such as compressive and bending strength. An increase of 125% for uniaxial compression and around 60% for bending test proved the excellent mechanical properties of these composite materials. Such high-strength, lime-based mortars can be applied to floors, as strengthening agents for stone masonry foundations or can be used in constructions required high resistance to enhancing mechanical strength. Additionally, this work contributed to the management and re-utilization of refractory waste materials, as well as to the synthesis of new, cement- and additive-free materials of low energy consumption, which could be applied in modern constructions and restoration projects.

1. INTRODUCTION

Refractory materials cover a wide spectrum of applications in the industrial sector, utilized in steel manufacturing, aluminum, copper and ferro-nickel industries, as well as in some other types of industries. The production of this specific category of refractory materials requires a large range of alumino-silicate raw materials, such as chamotte, andalusites, mullites, refractory bauxites, white-fused aluminas and sintered aluminas [1]. In Greece, the availability of these materials is very limited, resulting in import of raw materials from abroad, which increases both the production cost and the energy consumption. Consequently, the effort to recycle used refractory materials from different Greek and European industry sectors is considered obligatory [2]. At the same time, in Greece, the non-hazardous industrial waste constitute 24% of all waste, part of which are refractory waste, a fact that reinforces the necessity of their management [3].

Nowadays, the use of waste materials in mortars and concrete is ordinary. Various waste materials, such as construction and demolition waste, glass, high impact polystyrene as well as plastic wastes have been added to mortars and concrete in order to enhance their properties and durability. More particularly, demolition waste have been used as partial or total replacement in lime and cement mortars, enhancing their mechanical properties [4,5]. Glass wastes of various types and sources such as glass foam extracted by glass cullet, glass beads and powder have been added to lime and cement-based mortars to alter the properties of porosity, absorption and capillarity, improving energy efficiency [6,7,8]. In case of plastic wastes, although their addition as aggregatesled to a decrease in mechanical properties so far, their use is not prohibitive and the corresponding research remains in progress [9,10]. These integrations lead to the limitation of waste landfill, combined with an effective circular economy approach.

The replacement of natural sand with refractory materials results in mortars with increased mechanical properties. Such high-strength, lime-based mortars can be applied to floors, strengthening of stone masonry foundations and any other need for mortars with increased strength, without circumventing the compatibility of materials. As a common practice, cement-based mortars are used in such applications. However, these mortars are incompatible with the porous stones and the historical mortars, thus they usually cause damage to the constructions [11]. Furthermore, cement is a material with a high energy footprint, compared to lime, therefore reducing its use contributes to energy savings.

2. MATERIALS AND METHODS

2.1. Materials

In total, 5 different types of refractory waste materials were selected as aggregates. The source of each RWM is reported in Table 1. The binders of the designed mortars are: hydrated lime (L: by CaO Hellas), natural hydraulic lime (NHL: NHL3.5z by Lafarge, Clamart, France) and metakaolin (M: Metastar 501 by Imerys, France). For comparison purposes, another 2 sets of mortars were synthesized using standard carbonaceous sand 0/4 mm as aggregates (S) and binders of ML (MLS) in the first comparison group as well as NHL in the other.

Table 2 reports the mortar mixes identification, weight ratios, percentage of L, M and aggregates weight, water/binder (W/B) ratio and the flow table consistency determined according to EN 1015-3. The mixing tools and materials were stored at a constant temperature of 23 °C for 24 hours before mixing. In order to use facile codes in the designation of mortars, the binders used were first denoted (ML and NHL) following by the letters indicating the origin of the refractory materials used as aggregates.

Table 1: The selected typesof refractory waste materials

RWM	Source
REFAL1	Refractory bricks from anode furnace of aluminum factory
REFAL2	Refractory bricks from anode furnace of aluminum factory
REFAL3	Refractory bricks from anode furnace of aluminum factory
REFPL4	Fragments of porcelain sanitary ware
REFBL5	Refractory bricks of laterite rotary kiln of mining factory (LARKO)

Table 2: Mortar mix design

Code	BINDER			AGGREGATES						B/A	W/B	Consistency (mm)
	L	NHL	M	REFAL1	REFAL2	REFAL3	REFPL4	REFBL5	S SAND			
MLAL1	60		40	100						1	0,80	138,00
MLAL2	60		40		100					1	0,75	126,50
MLAL3	60		40			100				1	0,78	137,50
MLPL4	60		40				100			1	0,70	127,50
MLBL5	60		40					100		1	0,77	131,50
NHLAL1		100		100						1	0,58	127,50
NHLAL2		100			100					1	0,62	137,00
NHLAL3		100				100				1	0,61	133,50
NHLPL4		100					100			1	0,65	135,50
NHLBL5		100						100		1	0,68	131,00
MLS-ref	60		40						100	1	1,20	137,00
NHLS-ref		100	40						100	1	0,70	135,50

L: Hydrated lime, NHL: Natural hydraulic lime, M: Metakaolin, S Sand: Standard carbonaceous sand 0/4mm, B/A: binder to aggregates ratio, W/B: water to binder ratio

2.2. Methods

At the first stage, the RWM were characterized through various techniques. The aggregates were microscopically assessed with the aid of a USB Dino-Lite AM4515T5 Edge digital microscope. Afterwards, the distribution of the different fractions for each material was determined by granulometric analysis according to EN 933-2 European Standard. Energy dispersive X-ray fluorescence (EDXRF) and Fourier transform infrared spectroscopy (FTIR) were carried out to identify the elemental and chemical composition, respectively, of the RWM exhibiting grain size lower than 0.125 mm in diameter. The EDXRF instrumentation included 109Cd and 55Fe radioactive sources, Si(Li) semiconductor detector (resolution 150 eV at 5.9 keV), TC-244 Spectroscopy Amplifier, PCA-II Nucleus Multichannel Card, AXIL (RN) computer program analysis, whereas the IR spectra were recorded with a Thermo Scientific Nicolet^{TM} iS50 FT-IR device. Mineralogical analysis was assessed by X-ray powder diffraction analysis (XRD) on a Bruker D8 Advance Diffractometer, using Ni-filtered Cu K radiation (35 kV 35 mA) and a Bruker Lynx Eye strip silicon detector.

Subsequently, the designed mortars were moulded in prismatic and cubic moulds (4x4x16 cm and 5x5x5 cm), according to EN 196 standard, for mechanical tests, such as uniaxial compression and the three-point bending tests. After moulding, the samples were stored in a curing chamber under a 23 ± 2 °C temperature and 50 ± 5% relative humidity.

Compressive strength (Fc) and flexural strength (Fb) were measured by uniaxial compression and the three-point bending test, respectively, according to EN 1015-11:1999. The modulus of elasticity and toughness were determined by the strain–stress curve of compression test.

3. RESULTS AND DISCUSSION

3.1. Characterization of refractory waste materials

The macroscopic and microscopic inspection of the RWM, as presented in Figure 1, revealed that the coarse-grained fractions of the REFAL1, REFAL21, REFAL3 and REFBL5 are cohesive, rough with absence of porous and sharp edges. The REFPL4 coarse grained fractions are also cohesive, but the surface of the fractions is smooth.

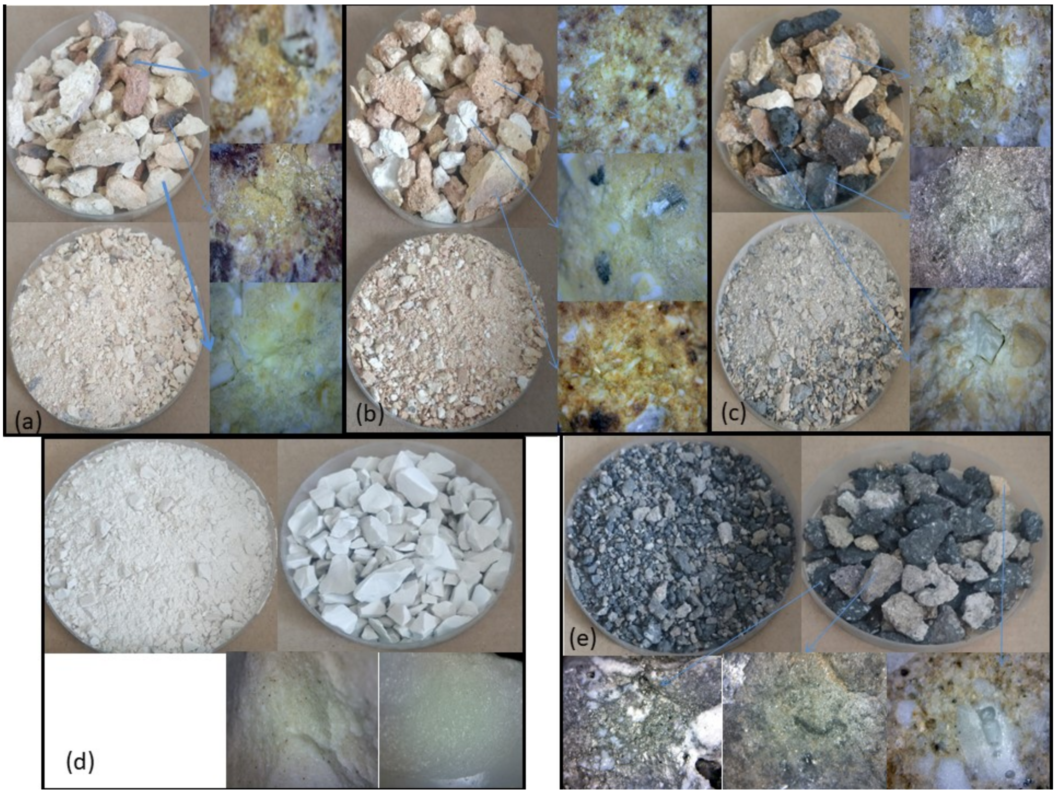


Figure 1: Macroscopic and microscopic inspection of (a)REFAL1, (b) REFAL2, (c) REFAL3, (d) REFPL4 and (e) REFBL5

The grain size distribution of the 5 fine-grained samples shown in Figure 2 are with respect to the standard sand's distribution. All samples are coarser than standard sand in all sieve sizes from 0.063 mm to 4 mm. The samples also contained a large quantity of silt.

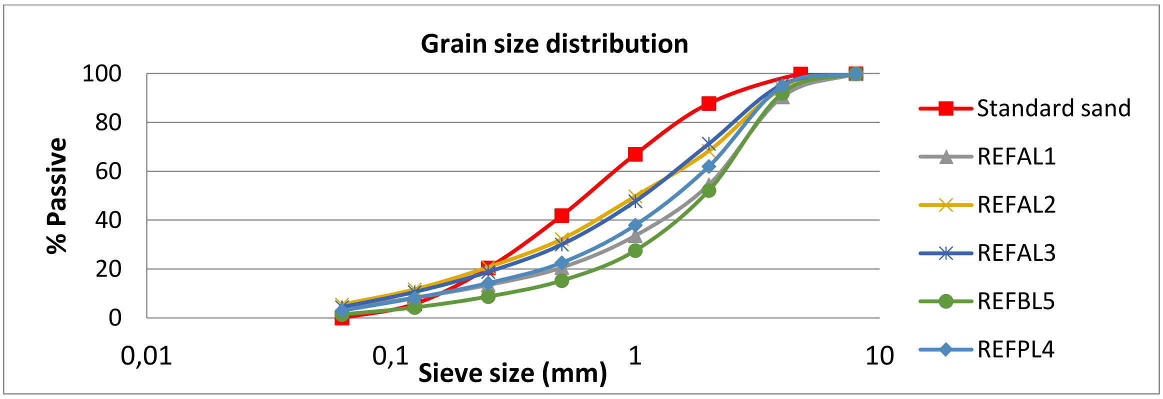


Figure 2: Grain size distribution of RWM

The elemental XRF analysis was performed on the finest fractions of the samples with diameter lower than 0.125 mm. The main elements identified were common in all RWMs, with some variations in concentrations. More particularly:

- The main element of the REFAL1 sample was aluminum (Al) and thereafter silicon (Si). In addition, in smaller concentrations iron (Fe) and titanium (Ti) were identified and in even smaller concentrations potassium (K), calcium (Ca) and sodium (Na) were observed.
- Respectively, in the REFAL2 sample the main element was aluminum (Al) and thereafter silicon (Si). In small concentrations iron (Fe) and titanium (Ti) were identified, together with potassium (K) and calcium (Ca) in even smaller concentrations.
- Almost identical, in the REFAL3 sample the main element was aluminum (Al) and

thereafter silicon (Si). In addition, small concentrations of iron (Fe) and titanium (Ti), together with potassium (K), calcium (Ca) and sodium (Na) in even smaller concentrations.

- In the REFPL4 sample, the main element was silicon (Si) and thereafter aluminum (Al). Additionally, small concentrations of sodium (Na) and calcium (Ca) and even smaller concentrations of potassium (K), zirconium (Zr), iron (Fe), titanium (Ti) and magnesium (Mg) were identified.
- In the REFBL5 sample, the main element was silicon (Si), followed by aluminum (Al). In addition, small concentrations of iron (Fe), titanium (Ti) and even smaller concentrations of calcium (Ca), sodium (Na), potassium (K), magnesium (Mg) and zirconium (Zr) were observed.

The main elements found by XRF analysis are presented in Figure 3 (a).

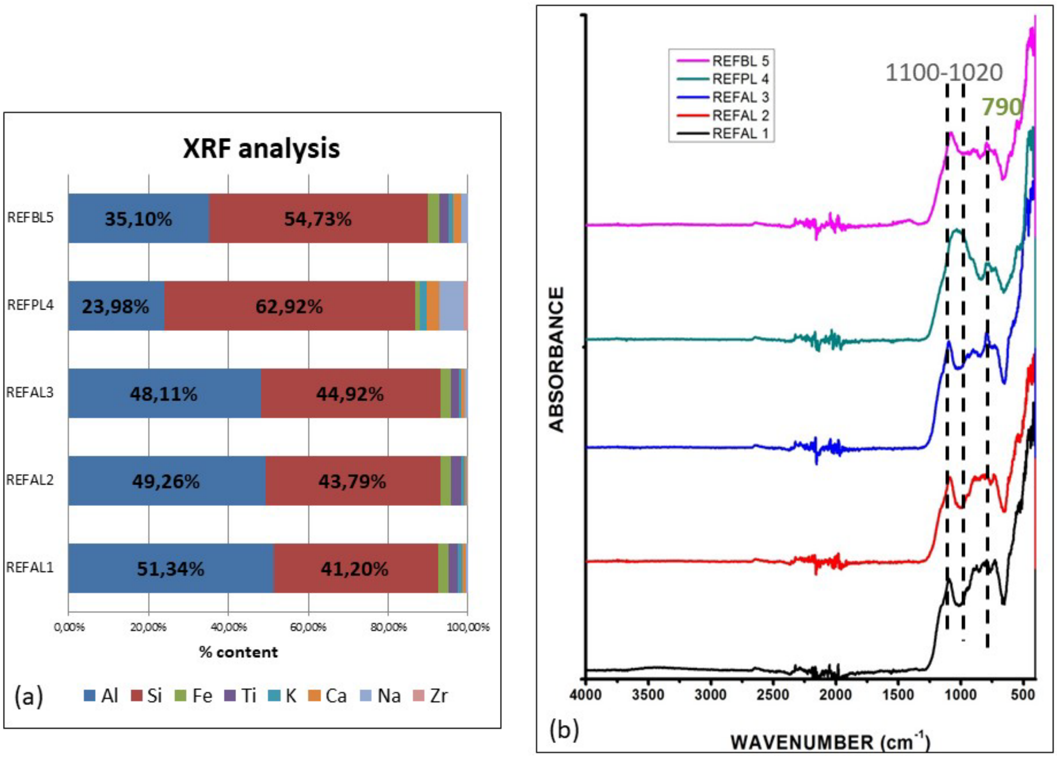
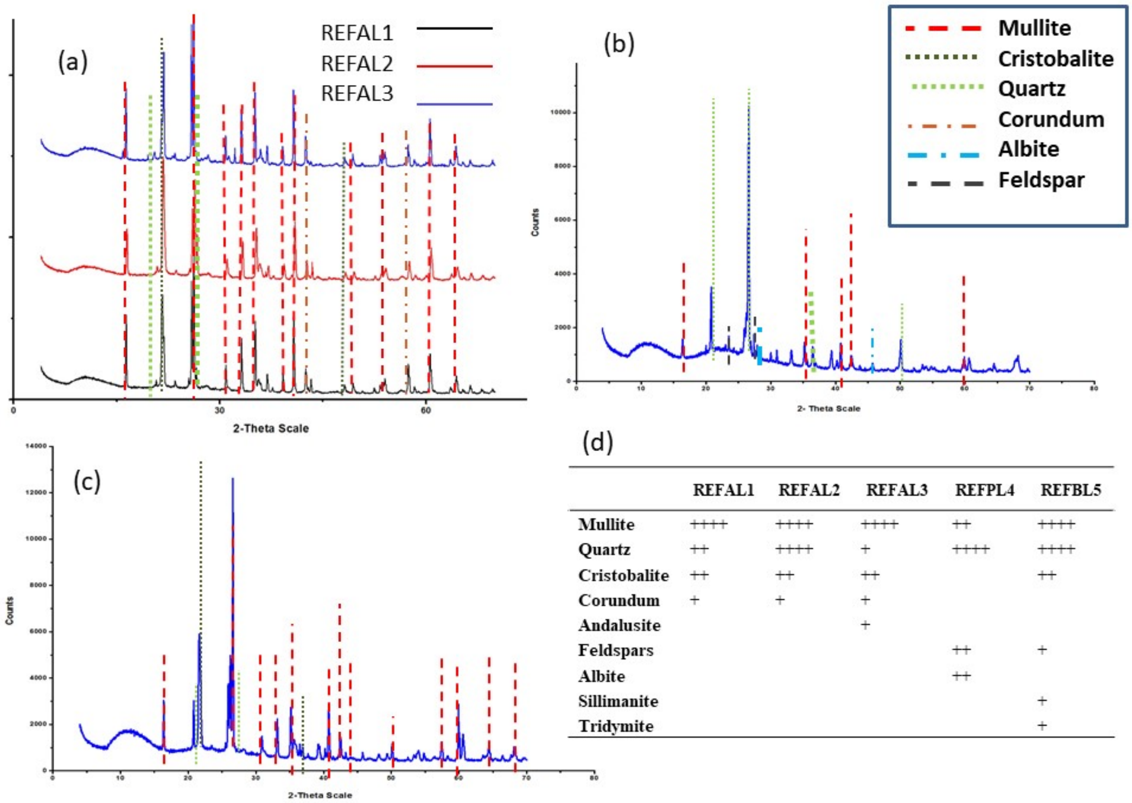


Figure 3: (a) main elements of RWMs in XRF analysis, (b) FTIR spectra of the tested RWMs

The IR spectra shown in Figure 3 (b) exhibited predominant peaks in the region of 950-1250 cm^{-1}, as well as large absorption bands before 650 cm^{-1}, whereas a peak at 790 cm^{-1} was mainly observed in the spectra of REFAL3, REPL4 and REFBL5. The absorption bands around 1000 cm^{-1} together with the band at 790 cm^{-1} were attributted to the stretching and bending vibrations of the four coordinated Si-O bonds, respectively, while the bands in the region of 400-500 cm^{-1} belong to the Si-O and Al-O bending vibrations [12,13]. It is worth mentioning that there is a shift of the Si-O band at 1100 cm^{-1}, which can be explained by the incorporation of Al^{3+} in Si-O-Si bonds [14]. Therefore, it should be noted that the REFPL4 sample which has the highest percentages of silicon, as determined by XRF analysis, exhibits the largest absorption in the area around 1000 cm^{-1}.

The mineralogical analysis through XRD is presented in Figure 4 (a-c). The aluminum waste (REFAL 1,2 and 3 samples) have similar minerals identified, among which the predominant mineral is mullite ($Al_6Si_2O_{13}$), following quartz (SiO_2) and cristobalite (SiO_2). The main mineral of REFPL4 sample is quartz, whereas feldspars, as well as albite ($NaAlSi_3O_8$) are identified, a fact that could explain the increased percentage of sodium in the XRF analysis.



	REFAL1	REFAL2	REFAL3	REFPL4	REFBL5
Mullite	++++	++++	++++	++	++++
Quartz	++	++++	+	++++	++++
Cristobalite	++	++	++		++
Corundum	+	+	+		
Andalusite			+		
Feldspars				++	+
Albite				++	
Sillimanite					+
Tridymite					+

Figure 4: (a) XRD spectra of aluminum samples REFAL1,2 and 3, (b) XRD spectrum of REFPL4, (c) XRD spectrum of REFBL5, (d) approximate concentrations of minerals

3.2. Characterization of lime-based mortars containing RWM as aggregates

Table 3: Mechanical results of designed mortars

Code	Fc (MPa)		E (GPa)		max e (%)		Fb (MPa)		% Increase of Fc	
MLAL1	17.29	± 0.187	0.81	± 0.062	3.36	± 0.378%			15.1%	
MLAL2	18.28	± 1.117	0.76	± 0.026	3.73	± 0.638%			21.6%	
MLAL3	16.27	± 0.859	0.77	± 0.067	3.53	± 0.113%			8.3%	
MLPL	14.67	± 0.203	0.59	± 0.061	3.91	± 0.480%			-2.4%	
MLBL	19.78	± 0.150	0.84	± 0.005	2.68	± 0.024%			31.6%	% Change of Fb
MLS-ref	15.03	± 0.362	0.67	±0. 160	2.59	± 0.298%				
NHLAL1	11.85	± 1.008	0.77	± 0.144	3.27	± 0.523%	2.88	± 0.162	126.4%	64.57%
NHLAL2	10.54	± 1.281	0.62	± 0.163	4.05	± 0.643%	2.72	± 0.276	101.4%	55.43%
NHLAL3	6.34	± 0.385	0.54	± 0.059	3.06	± 0.297%	1.34	± 0.099	21.1%	-23.43%
NHLPL	6.97	± 0.463	0.61	± 0.050	3.08	± 0.147%	1.23	± 0.122	33.2%	-29.71%
NHLBL	8.21	± 0.830	0.59	± 0.120	3.68	± 0.457%	1.54	± 0.122	56.9%	-12.00%
NHLS-ref	5.23	± 0.107	0.15	± 0.120	3.24	± 1.200%	1.75	± 0.100		

Fc: compression strength, E: modulus of elasticity, max e: maximum deformation, Fb: bending strength, % increase is compared to MLS and NHLS mortars respectively

The results of the compression and 3 points bending tests are reported in Table 3. The mortars containing lime, metakaolin and RWMs were assessed through uniaxial compression test and compared to the corresponding MLS mortars with sand as aggregates. For all RWMs, except for

REFPL4 used as aggregate in MLPL mortar, the compression strength was significantly increased comparing to the reference MLS sample, whereas modulus of elasticity and maximum deformation had minor differences. Concerning the NHL syntheses, the increase of compression strength was even more remarkable for all RWMs, though bending strength was increased only in REFAL 1 and 2 replacements. However, the bending strength of lime-based mortars is expected to be low. Moreover, the designed mortars provided larger modulus of elasticity, displaying approximately the same maximum deformations. Comparing, the RWMs, it should me mentioned that the REFAL1 material had the most significant performance for both LM and NHL composites, whereas REFPL4 had the lowest contribution. This observation could be possibly related to their mineralogical composition according to XRD analysis, where most of RWMs had mullite as the predominant mineral, while on the contrary quartz was the most abundant mineral for the REFPL4 material [15].

4. CONCLUSIONS

Five different refractories from industrial waste were analyzed, namely REFAL1, REFAL2, REFAL3, REFPL 4 and REFBL 5. The chemical and mineralogical analyses revealed that the waste materials consist mainly of silicon and aluminum, as well as the corresponding aluminosilicate minerals such as mullite, quartz and christoballite. Furthermore, no toxic and dangerous contaminants were found. The REFAL1 and REFAL2 materials had the same composition, whereas REFAL3 had a few different mineral proportions, which may explain the partial macroscopic differentiation. The porcelain wastes (REFPL4) had the highest percentage of silicon and REFBL5 material contained the majority of impurities, as shown in mineralogical analysis.

The replacement of natural sand with the RWM fine aggregates in Lime-Metakaolin and Natural Hydraulic Lime mortars was beneficial for the majority of the investigated materials. The REFAL1 was the most effective material for both lime-metakaolin and NHL syntheses, whereas REFPL4 decreased the compression strength for lime-metakaolin mortars. The bending strength of the novel synthesis was higher only in the cases of REFAL1 and REFAL2.

Overall, it can be stated that this work contributed to the management and re-utilization of refractory waste materials, as well as to the synthesis of new materials of low energy consumption, which could be applied in modern constructions and restoration projects.

5. ACKNOWLEDGEMENTS

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