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Assessing the Recovery Opportunities of Different Types of Wastes by their Embedment in Inorganic Binders

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Abstract. The use of wastes in the architecture of new binders for construction domain is the key for the success of the progress regarding environmental, technical and economical issues. For instance, bricks wastes have huge recycling value but are often discarded for worthless junk. The wastes glasses which are difficult to be recovered are regularly disposed in landfills although they successfully could replace the fine and coarse aggregates in concrete. More than that the glass aggregates can be used for decoration of concrete structure floors, patio, entrances etc. Paper slag ash has a similar chemical composition to that of cement, but the mineral phase composition significantly differs and is no reactive with water. Therefore she can be used in the production of concrete, a beneficial idea regarding exhaustible resources and intelligent recycling within circular economy and durable development context. Although the large paper producers fight with this challenge, until now the construction industry didn't find the courage to tackle these opportunities, continuing to adopt classical methods for designing construction materials. In this context the paper presents reuse potential of different types of wastes as supplementary addition for cement based materials obtaining. In order to demonstrate their functionality the new mortars specimens were mechanically tested. The obtained results highlighted of many times similar properties with that of the classical compositions, sustaining thus the idea of sustainable development within civil industry domain.

1. Introduction

Nowadays the production of environmental friendly materials becomes a new challenge and a sustainable opportunity to obtain appropriate performances comparable with those of the traditional construction materials. The cement production represents an energy-intensive and highly polluting process, which contributes up to 8% to the worldwide CO₂ emissions, having a great impact on climate changes [1,2]. It is very well known that within the cement production process, CO₂ emissions, derived from both of fuel and raw material burning are released into the atmosphere. Thus, the use of alternative materials (solid waste or industrial by-products with chemical composition similar to cement) is a handy and sustainable approach for reducing the environmental and energy impacts of concrete industry [3]. Furthermore, the recycling method minimizes the incineration step from the waste circuit and saves a lot of landfill space. Amongst various types of industrial by-products, (silica



fume, fly ash, slags etc.) [4-6], the use of alternatives materials such as bricks waste, paper slag ash or glass waste in the design of new binders for construction materials field [7-12] is the key for the success of the progress regarding environmental, technical and economic issues. But even so, to obtain a reliable certified material, ready to be put in work, there is a stringent need to perform intensive and complex preliminary researches in order to establish the optimum compositions (based on chemical compatibility between solid waste and cement, and quality assessment in terms of mechanical performances) which must be further evaluated in terms of durability features (figure 1).

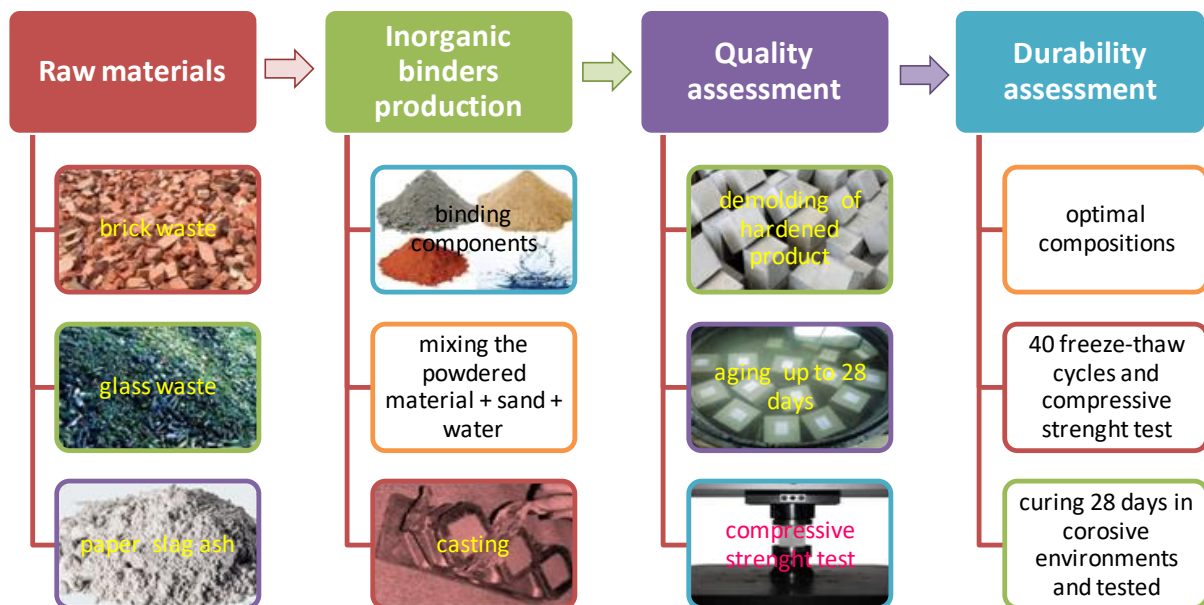


Figure 1. The overall concept to obtain new environmental friendly cement based materials.

In this context, the main objective of this work is to highlight the opportunity to obtain environmental friendly cement based materials considering three types of wastes (brick powder waste and paper slag ash as cement replacement, as well as cathode ray tubes glass as partial replacement of fine aggregates in mortars). In this regard mechanical properties were determined after 28 of hardening and the micro structure particularities were investigated by using electron microscopy analyses.

2. Materials and methods

In order to assess the recovery opportunities of different types of wastes, mortar specimens with 20% content of wastes were obtained, used as cement substitute or fine aggregates, cured up to 28 days in normal conditions ($T = 20^{\circ}\text{C}$ and $\text{R.H.} = 95\%$) and afterwards mechanically tested. The materials used in experiments were ordinary Portland cement, CEM I 42.5, and three types of wastes: bricks wastes (BW), cathode ray tube glass waste (CRGW) and paper slag ash wastes (PAW). The chemical composition determined by x-ray fluorescence (XRF) analyses, performed with a Rigaku Supermini fluorescence spectrometer, and the fineness properties of the used materials are presented in Table 1. Cubic mortars specimens with 25mm side dimensions were obtained using a binder / sand ratio = $\frac{1}{2}$ and a water / binder ratio of 0.45. The mortar specimens' compositions are presented in Table 2. After 1, 2, 7 and 28 days of hardening, the cubic specimens were subjected to compression tests, by using a compression and flexural testing machine from MATEST. The mechanical resistance was calculated as percent of the etalon binders, expressed by the equation (1).

$$M_r = \frac{C_{S_{specimen}}}{C_{S_{etalon}}} \times 100 \quad (1)$$

Where, M_r is the mechanical resistance (%), $C_{S_{specimen}}$ – the compressive strength of the specimens with waste addition (MPa), $C_{S_{etalon}}$ – the compressive strength of the reference binders (MPa).

Table 1. Chemical composition of used materials for inorganic binders obtaining.

Oxide composition (%)	OPC (%)	BW (%)	PAW (%)	CRGW (%)
SiO ₂	16.94	64.46	23.2	58.59
Al ₂ O ₃	4.75	16.94	17.10	2.74
Fe ₂ O ₃	2.46	6,13	0.8	0.26
CaO	60.75	3.23	54.4	1.08
MgO	2.23	2.59	2.28	1.37
SO ₃	2.93	0.13	0.42	-
Na ₂ O	0.3	2.16	-	9.46
K ₂ O	0.72	1.89	-	5.98
TiO ₂	-	1,47	-	-
SrO	-	-	-	5.1
ZrO	-	-	-	1.04
BaO	-	-	-	6.71
PbO	-	-	-	7.06
Minor components	-	0,91	1.68	0.61
P.C.	8.58	-	26.42	-
Ssp (cm ² /g)	3793	3476	2713	-

In order to analyse the inorganic binders microstructure, scanning electron microscopy (SEM) analyses were performed on binder pastes samples cured for 7 days in closed vials, using the Hitachi SU-70 FE-SEM microscope. The analyzed specimens were preliminary washed with ethanol and dried at 55°C for 2 hours (to stop hydration processes and remove the water film from the sample surface) and subsequently coated with an Au/Pd conductive layer.

Table 2. The compositional matrix of cement based materials specimens.

Specimen	Binder			Aggregate	
	OPC (%)	BW	PAW	Sand (%)	CRGW (%)
E	100	-	-	100	-
MS1	80	20	-	100	-
MS2	80	-	20	100	-
MS3	100	-	-	80	20

3. Results and discussions

3.1. Mechanical resistance

The mechanical resistance of all mortar specimens was calculated for samples cured up to 28 days, the results being presented in figures 2 - 4. The MS1 specimens with 20% of BW (figure 2) recorded good mechanical strengths which increase in time. After one day of hydration MS1 sample tackled 80% of the etalon resistance, reaching 90% after 28 days. This behaviour can be explained on one hand due to the dilution effect of the OPC and on the other hand the small BW particles could have slowed down the hydration process of the cement grains.

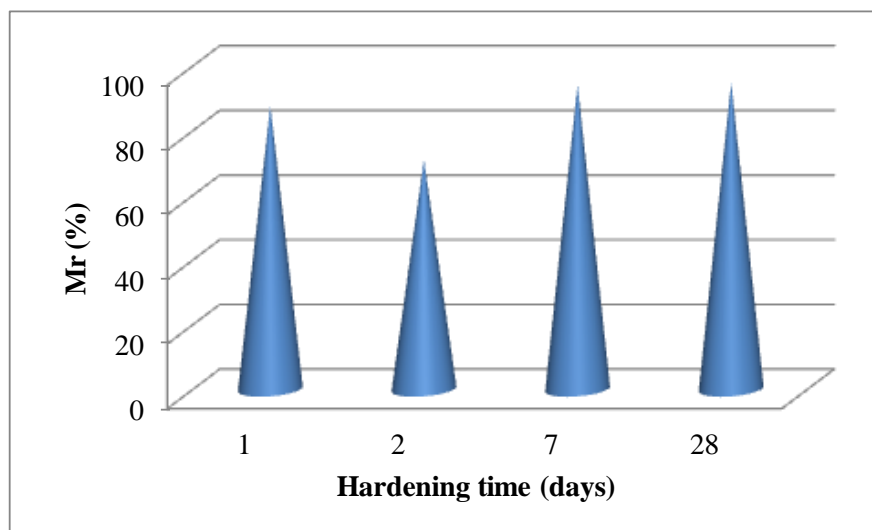


Figure 2. Mechanical resistance of cement based materials with 20% BW content, hardened up to 28 days.

The compressive strengths of MS2 mortar specimens (figure 3) are lower than that of the etalon for all hardening times, but for the entire curing period their tendency is progressive. However, after 1 day of hardening, the mechanical resistance values decrease since the OPC is reduced with 20%. After 28 days of curing, the mechanical resistance of MS2 increases up to 91% of the etalon value. Despite the higher substitution degrees of OPC in MS2 inorganic binders, the calcium silicates hydrates (CSH) resulted by $\text{Ca}(\text{OH})_2$ bonding in pozzolanic reaction definitely contributed to the increase of mechanical resistances after 7 and especially after 28 days of hardening.

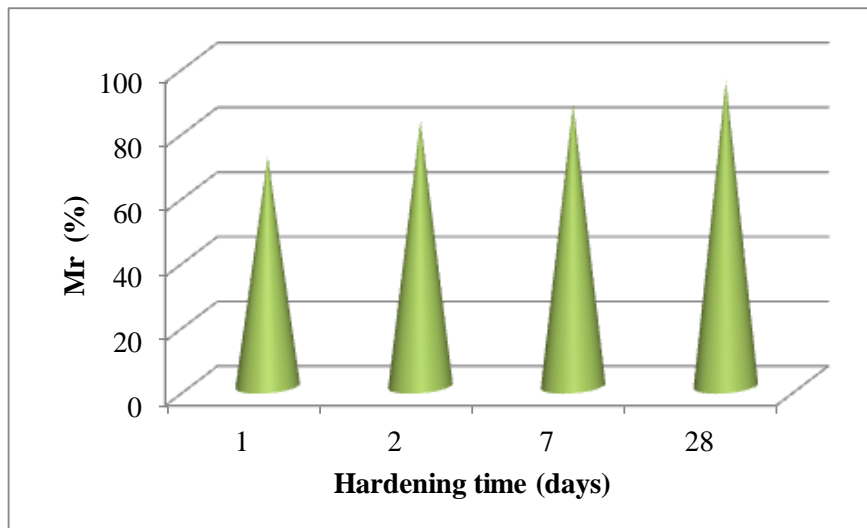


Figure 3. Mechanical resistance of cement based materials with 20% PAW content, hardened up to 28 days.

When the CRGW replaces 20% from the aggregate the loss of resistance becomes more evident (figure 4). Thus, the MS3 mortar specimens, designed with CRGW as fine aggregate, highlight substantial decreases of mechanical resistances up to 28 days (around 50% of the etalon one). Considering that the CRT glass contains heavy metals the cement hydration can be modified by them due to the formation of three-dimensional structures, up to 100–300 nm thick, containing in their network heavy metals which form a coating film around the cement grains [13].

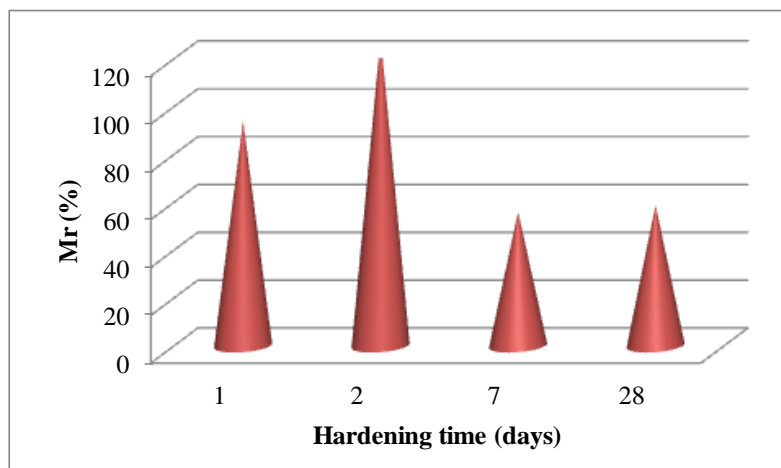


Figure 4. Mechanical resistance of cement based materials with 20% CRGW content, hardened up to 28 days.

3.2. Microstructure particularities

In order to explain the mechanical behaviour, SEM analyses were performed on binder specimens after 7 days of hardening, the results being presented in figures 5 and 6.

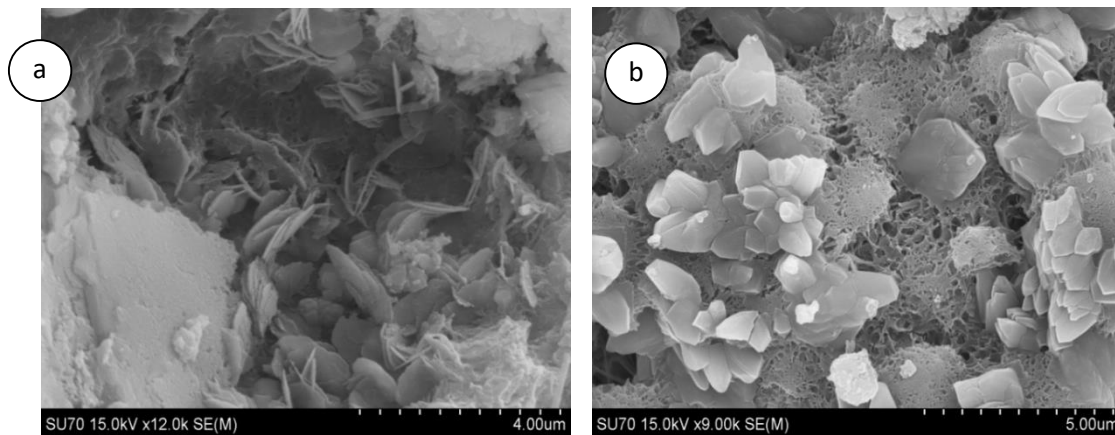


Figure 5. SEM images of mortar specimens hydrated for 7 days: a) - E and b) - MS1.

As it can be observed the etalon sample (figure 5a) evidences the presence of $\text{Ca}(\text{OH})_2$ crystals with shapes like plates often overlapped, CSH flakes poorly crystallised on the surface of cement grains, ettringite crystals shaped like thin rods, as well as unreacted cement grains. The MSI microstructure (figure 5b) highlights a more porous structure in which well defined hexagonal portlandite crystals are developed and the CSH crystals form a continuous woven network between $\text{Ca}(\text{OH})_2$ crystals and BW granules.

The MS2 microstructure (figure 6a) reveals abundant CSH crystals, ettringite rods and OPC grains. At the opposite side the MS3 microstructure (the binder specimen with 20% CRGW and the smallest mechanical resistances, presented in Figure 6b) evidences a heterogeneous structure with partially reacted OPC and embedded CRT glass grains, hexagonal $\text{Ca}(\text{OH})_2$ crystals and gel like CSH crystals.

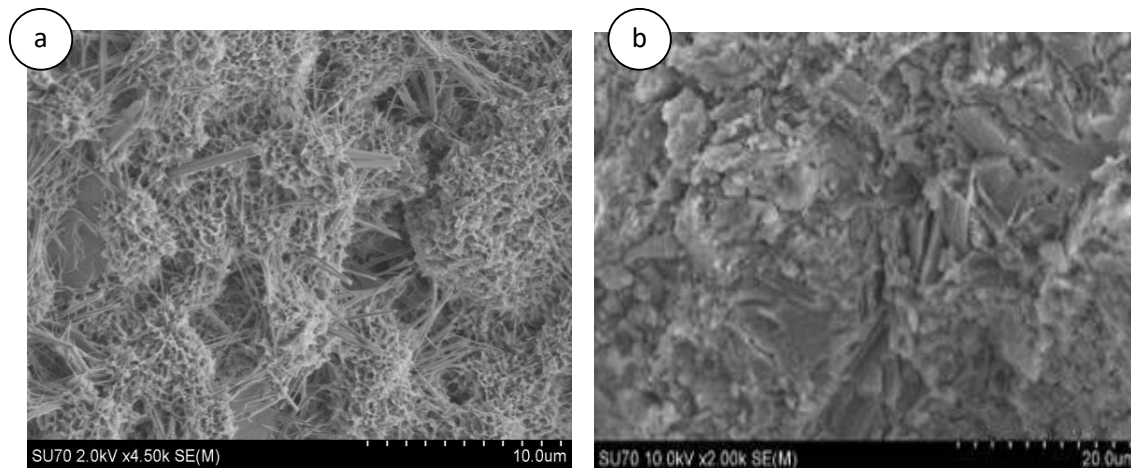


Figure 6. SEM images of mortar specimens hydrated for 7 days: a) – MS2 and b) – MS3.

4. Conclusions

The present work aimed to highlight the possibilities of obtaining ecological materials, with good mechanical properties, which could be suitable for non-structural construction works. For this purpose three types of cement based materials were prepared with different types of wastes, cured up to 28 days and mechanically tested, highlighting for MS1 and MS2 specimens small decreases of compressive strengths. For the MS3 specimen the compressive strength resistance presented the smallest values due to the heavy metals content in CRT glass. The microstructure of all mortar specimens highlighted the presence of main mineralogical compounds formed by cement hydration, in higher or smaller

quantities according to compositional diversity. The MS3 microstructure was heterogeneous with large unreacted quantities of OPC, being in good correlation with the mechanical resistances results.

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