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Waste Marble Dust Blended Cement

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Abstract. Marble processing activities generates a significant amount of waste in dust form. This waste, which is nowadays one of the environmental problems worldwide, presents great potential of being used as mineral addition in blended cements production. This paper shows preliminary results of an ongoing project which ultimate goal is to investigate the viability of using waste marble dust (WMD), produced by marble Portuguese industry, as cement replacement material. In order to evaluate the effects of the WMD on mechanical behaviour, different mortar blended cement mixtures were tested. These mixtures were prepared with different partial substitution level of cement with WMD. Strength results of WMD blended cements were compared to control cements with same level of incorporation of natural limestone used to produce commercial Portland-limestone cements. The results obtained show that WMD blended cements perform better than limestone blended cements for same replacement level up to 20% w/w. Therefore, WMD reveals promising attributes for blended cements production.

Introduction

Cement base materials play an important role in sustainable development because cement production demands significant amount of raw materials and energy as well as represents about 5% of current anthropogenic CO_2 global emissions [1]. The use of mineral addition blended cements contributes to reduce clinker manufacture in plants hence is an economic and feasible method to save energy and to mitigate CO_2 footprint of cement production [2]. Nowadays, European Standard EN 197-1 [3] validates the production of blended cements incorporating a significant amount of a mineral materials, namely limestone. This standard identifies limestone blended cements by the following notations: CEM II/A-L, CEM II/A-LL, CEM II/B-L, CEM II/B-LL and CEM II/A-M.

If the mineral addition employed in blended cements production is a waste from other industry – instead of a natural resource, like industrial limestone - it would also contribute: (*i*) to decrease the non-renewable materials quarrying, (*ii*) to mitigate solid waste disposal of in landfills and (*iii*) to turn a polluting waste from one industry into a product with added-value for cement industry.

Marble is one of the most popular asthetic rock used in huge quantities and is commonly available in nature. Many countries such as China, Italy, Spain, Greece, India, Portugal, etc. are making a good worldwide business out of it [4,5]. Dried marble slurry generated as a by-product during marble stones processing is a very fine powder: ninety percent of the particles are below 200 µm (d_{90}<200 µm) [4]. This waste constitutes a serious threat to the marble generating industries. Total waste generation from mining to finished product is about 50% of mined mineral [4].

Considering that dried slurry product is essentially constituted by calcium carbonate it presents a great potential of being used as mineral addition in blended cements production, as it is already been demonstrated in different studies [6,7]. Nevertheless, utilization of waste of marble in blended cement production has not yet been generally adopted.

In Portugal, in 2009, the official amount of waste marble slurry accumulates was 135 kiloton [8]. Up to now, most of the waste catalysts are disposed in landfills, the least environmentally preferred option.

Results presented is this paper are part of an ongoing project which ultimate goal is to assess the theoretical and technical viabilities of waste marble dust (WMD), produced by Portuguese industry, to be reutilized as a mineral addition in production of blended cements fostering that large-scale industrial applications can be achieved in the future. For this purpose, a series of tests were conducted aiming physical and chemical characterizing of the WMD and evaluating its effect on the physical and mechanical properties of cement type CEM I 42,5 R incorporating 0, 5, 10, 15 and 20% w/w of WMD. Cement samples incorporating same levels of natural limestone (usually used to produce commercial Portland-limestone cements) were also tested as control cements for comparison purposes. This paper presents the mechanical performance of WMD blended cements compared with commercial limestone blended cements. The results indicate that the performance of WMD blended cements is better than control cement samples.

Experimental Program

Materials. The materials used were: commercial Portland cement type CEM I 42,5R (according to European Standard EN 197-1[3]) from Cimpor Company; natural siliceous sand (according to European Standard EN 196-1(§ 5) [9]) provided by Sifucel - Sílicas, Lda; natural industrial limestone (used to produce commercial Portland-limestone cement) quarried in Alenquer (north of Lisbon, Portugal) and waste marble dust (WMD), quarryied at Évora, (south of Lisbon, Portugal) and provided by PARAPEDRA, S.A.. Although the marble processing waste was generated in slurry (semi-liquid) form it was provided already dried in dust form. It was used as-received without any previous treatment.

The chemical analysis of the cement, WMD and limestone were performed by X-ray fluorescence spectrometry using a *PANalytical* model *Axios* equipment (Table 1). Based on this analysis it was observed that WMD used consists of basically CaO (53,90%), SiO_2 (1,19%) and MgO (0,54%).

Table 1 – Chemical composition of the cement, WMD, and L (% w/w).

Compound	Cement	WMD	L
SiO_2	19,41	1,19	1,67
Al_2O_3	5,45	0,31	0,42
Fe_2O_3	3,23	0,05	0,45
CaO	62,57	53,90	53,59
MgO	1,91	0,54	0,45
SO_3	2,89	1,19	0,07
K_2O	1,10	0,03	0,03
Ti_2O_3	0,27	0,02	0,03
P_2O_5	0,10	0,00	0,00
Mn_2O	0,05	0,54	0,01
SrO	0,07	0,01	0,00

The particle size distributions (PSD) of the cement, waste marble dust and limestone were obtained by laser diffraction using a *PANalytical* X'Pert PRO diffractometer (Fig. 1). From PSD it was observed that 50% particles of WMD had a diameter lower than 21,05 μm (d_{50}(WMD)) and 90% had a diameter lower than 51,40 μm (d_{90}(WMD).

Since the fineness of the WMD particles is similar to those of cement particles (d_{50}(CEMI) = 21,5 μm), production of waste marble blended cement do not need extra energy neither to dry nor to grind the waste material. Moreover, WMD particles filling ability is not expected to be significant.

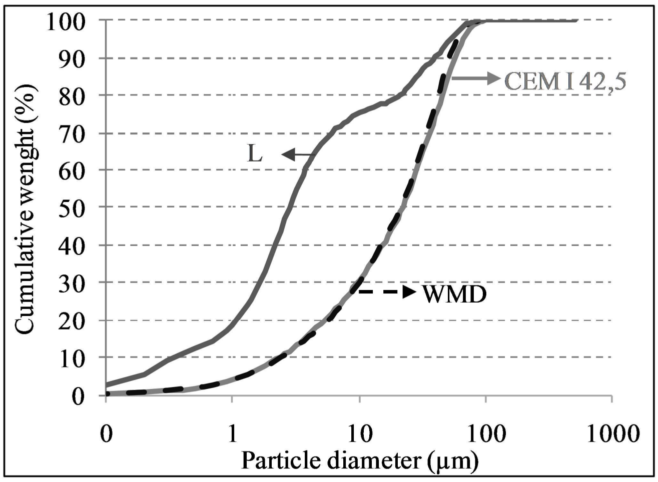

Fig. 1 - Cumulative particle size distribution of cement, WMD and L.

Mortars Preparation. Mortar mixtures were prepared using deionised water, sand and binder, in a weight ratio (w/s/b) of 0.5/3/1, respectively. Three kinds of binders were used: (*i*) commercial cement, (*ii*) cement partially replaced with WMD, and (*iii*) cement partially replaced with limestone. Mortar mixture proportions are summarised in Table 2. The mortar mixing procedure was performed in accordance with European Standard EN 196-1 § 6.2 [9].

Mortar mixtures were placed in 40x40x160 mm-prismatic steel moulds. After casting, mortar specimens were left covered with an acrylic sheet. After removal from moulds, at 24 h of age, specimens were immersed in water at 20 ºC until the age of testing. Compression tests were conducted at 2, 7 and 28 days of age. (in accordance with European Standard EN 196-1 § 9.2) [9]. The strength results are the average of at least six compression tests.

Table 2 – Binder mixtures proportions (% w/w).

Mixes notation	Cement	WMD	L
CEM 42,5 R	100	-	-
WMD 5	95	5	-
WMD 10	90	10	-
WMD 15	85	15	-
WMD 20	80	20	-
L 15	85	-	15
L 20	80	-	20

Results and Discussion

Fig. 2 shows the compressive strength of the mortars with 0, 5, 10, 15 and 20% w/w of cement replacement with WMD for different curing ages.

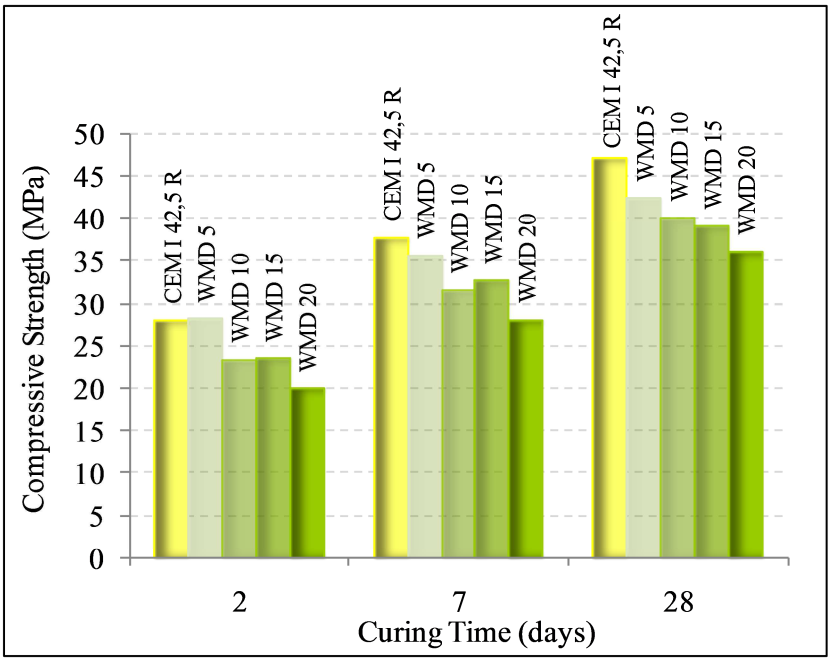

Fig. 2 - Compressive strength of mortars with 0, 5, 10, 15 and 20% w/w of cement replacement with WMD.

The Strength Activity Index (SAI) of a certain percentage of cement replacement by an addition, corresponds to comparing strength of mortar produced with that percentage replacement with the strength of equivalent mortar with no cement replacement, at the same age, produced in exactly the same conditions. Table 3 presents SAI values for mortars produced with cement replacement with WMD for different curing ages.

Results presented in Fig. 2 and Table 3 it can be noticed that: (*i*) WMD blended cement mortars develop lower strength than mortars produced with no cement replacement at ages up to 28 days, (*ii*) incorporation of higher percentage of waste as cement replacement material cause higher strength decrease, and (*iii*) typically, this loss of strength, for 28 curing days, is comparable to the percentage of cement replacement with WMD.

Table 3- Strength Activity Index values for mortars produced with 0, 5, 10, 15 and 20 % (w/w) WMD incorporation, at 2, 7 and 28 days of age.

Mixes notation	SAI		
	2 days	7 days	28 days
CEM 42,5 R	1	1	1
WMD 5	1.00	0.94	0,90
WMD 10	0.84	0.84	0,85
WMD 15	0.84	0.87	0,83
WMD 20	0.71	0.74	0,77

Fig. 3 shows a comparation among compressive strength for mortars prepared without cement replacement and mortars with cement replacement with 15 and 20% of WMD as well as same cement substitution level with limestone, for different curing ages.

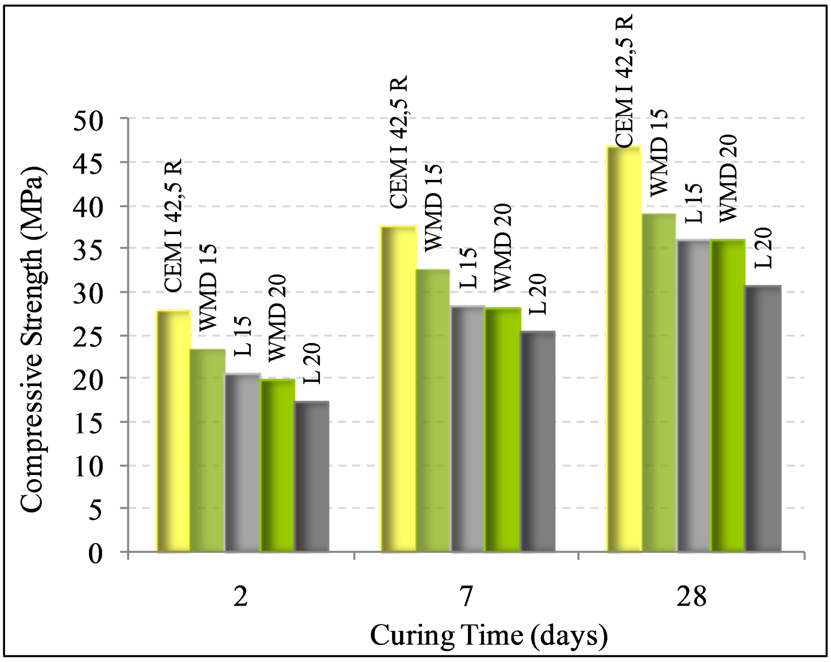

Fig. 3 - Compressive strength of mortars with 0, 15 and 20% (w/w) of cement replacement with WMD and L.

Results from Fig. 3 and Table 4 show that for same cement substitution level (15 and 20 % w/w) compressive strengths of WDM blended cement mortars are higher than those of mortars with incorporating limestone, at all ages.

Table 4 - Strength Activity Index values for mortar with 0, 15 and 20 % (w/w) L incorporation, at 2, 7 and 28 days of age.

Mixes notation	SAI		
	2 days	7 days	28 days
CEM 42,5 R	1	1	1
L 15	0.73	0.75	0.76
L 20	0.62	0.67	0.65

Strength development and therefore, SAI values, are affected by the physico-chemical properties of additions that contribute to strength development. Cyr et al. [10] reported that the contribution for mortars strength of a chemically inert material can be discriminated into two parts: dilution and physical effects. The dilution effect is a consequence of the partial replacement of cement by the same quantity of an inert material leading to an increase in the water/cement ratio as well as less cement which implies less hydrated cement and lower compressive strength compared to a reference without inert addition. Physical effects are often decoupled in two terms: filler effect and heterogeneous nucleation. Filler effect is due to the deposition of the addition particles in the intergranular voids between cement particles, allowing a denser packing of the cement paste microstructure and therefore contributing to mechanical properties improvement. This effect occurs when addition particles are finer than cement particles. Heterogeneous nucleation is related to the nucleation of and growth of cement hydration products on foreign inert particles that leads to an increase in compressive strength namely early strength [10, 11]. This effect consists in an indirect influence on the chemical structure of the cement paste.

SAI values for mortars with cement replacement with WMD (Table 3) are higher than those for the same level of cement replacement with L (Table 4). In these circumstances, the amount of cement is the same and, consequently, the difference in the values of strength cannot be explained by the dilution effect. On the other hand, as the WMD is of similar fineness to the cement (Fig. 1), the filler effect should not occur in the mortars with WMD particles incorporation, meaning that it cannot also explain the increase on compressive strength in the presence of this addition. Hence, the higher strength of WMD blended cement mortars compared with limestone blended cement mortars should be due to the different in heterogeneous nucleation ability of both additions i.e, the nucleus forming effect of addition particles to produce cement hydration products, $Ca(OH)_2$ and CSH. Moreover, despite limestone and marble are usually assumed to be inert materials, $CaCO_3$ particles may not be totally inert [12-14], since they may react with aluminates cement compounds, C_3A and C_4AF, to form carboaluminates [13-16]. The occurrence of these chemical reactions depends of mineral powder affinity with cement, which is related to the nature of the addition. More work is in progress, to clarify the reason for strength values difference associated to both additions under study, namely using scanning electronic microscopy and X-ray diffraction analysis.

Conclusion

The conclusions derived from presented results can be summarized as follows: (*i*) incorporation of WMD as cement replacement material lower mortars compressive strength compared to reference mortars without inert addition, (*ii*) incorporation of higher percentage of waste causes mortars higher strength decrease, and (*iii*) cements with WMD incorporation up to 20% (w/w) perform better than limestone blended cements with same level of incorporation.

Major findings in this investigation revealed that the use of WMD as a mineral addition is feasible, strengthening the belief that this waste may represent a steady supply for cement industry making a significant contribution for more sustainable construction materials.

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