


Use of Waste Calcium Carbonate in Sustainable Cement



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Abstract The quest for a new-generation concrete, designed to be compatible with the need of mitigating the effect of greenhouse gas emissions on the climate, has prompted applied research to define a broad range of low-CO₂ cement-based materials. While minimizing CO₂ emissions is a goal of the utmost importance, research into sustainable building materials must also tackle the issue of raw material depletion (including limestone, clay and aggregate deposits, as well as water resources) in favor of secondary raw materials. One possible solution is that of minimizing the impact of quarrying by a circular economy approach that envisages the reuse of waste from stone extraction and processing. It is estimated that 200 Mt waste are produced by the stone industry worldwide each year. This includes slurries obtained from the quarrying, cutting and polishing of marble, which can be used as a source of calcium carbonate, alternative to primary limestone. This contribution illustrates the use of waste calcium carbonate, obtained from marble slurry (waste marble, WM), in sustainable cement materials alternative to Portland cement. The possibility of exploiting locally available resources is explored, and the effect of WM additions up to 50% by total mass on the macroscopic properties is investigated experimentally. It is shown that binders with adequate fresh and hardened state properties can be obtained by moderate additions of WM, which greatly enhances the environmental performance by reducing the amount of primary resources used in the mix. By reducing the amount of thermally treated clay in alkali-activated blends, the use of WM also results in a net decrease of the embodied energy.

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1 Introduction

It has become a *must*, in recent years, to begin scientific papers into cement materials with a few sentences on the effect of buildings and the construction industry on CO₂ emissivity and its aftermath. This is reasonable, of course, and the reasons are obvious and shall not be reiterated here. However, there is a second, equally important issue, associated with the building materials industry, which is resource depletion and the impact of quarrying. Mining and quarrying activities have a huge impact on societies, the environment and landscape modification [1, 2] and their role in the cement industry deserves attention. Therefore, considering the increasing demand of building materials, it will be necessary to adopt a rational approach to sourcing raw materials for cement production.

One possible approach, explored in this contribution, is that of mitigating the utilization of primary resources (limestone, clay) by implementing a circular supply chain that converts waste from the stone industry into secondary raw materials.

It is estimated that about 200 Mt of the gross 300 Mt worldwide stone production is constituted by quarrying and processing waste [3]. Limestone and marble represent over 50% of the quarried stone [3] and their production leads to the formation of dust and slurries, during quarrying, cutting and polishing, whose disposal constitutes a severe environmental issue, due to the risk of soil and water contamination [4–6].

Using waste marble and limestone for the production of cement materials is beneficial as it contributes to mitigating the consumption of primary limestone. Moreover, the reutilization of such waste materials mitigates the risk associated with disposal and reduces net production costs.

In this contribution, some possible applications of waste marble in sustainable cements are briefly illustrated.

2 Waste Marble Properties

The waste marble (WM) used is obtained in form of a slurry, from marble quarries located in the Apuan Alps (Tuscany). A white powder (Fig. 1) is obtained by oven drying at 60 °C for 24 h and grinding using an agate mortar.

This powder consists, as per XRD analysis, of 100% calcite with Mg impurities (MgO = 0.6 wt%). The particle sized distribution after micronization, obtained by laser scattering, is reported in Fig. 2.

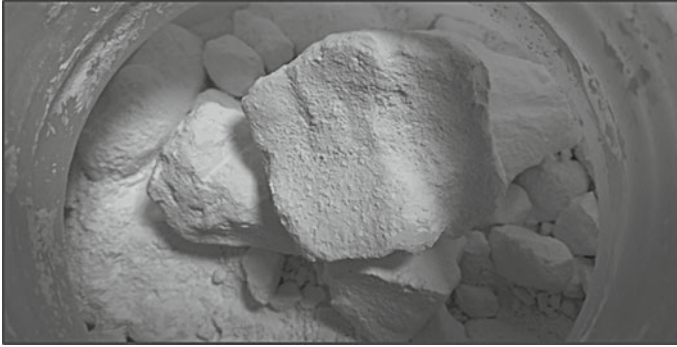


Fig. 1 Aspect of the waste marble powder used in the study

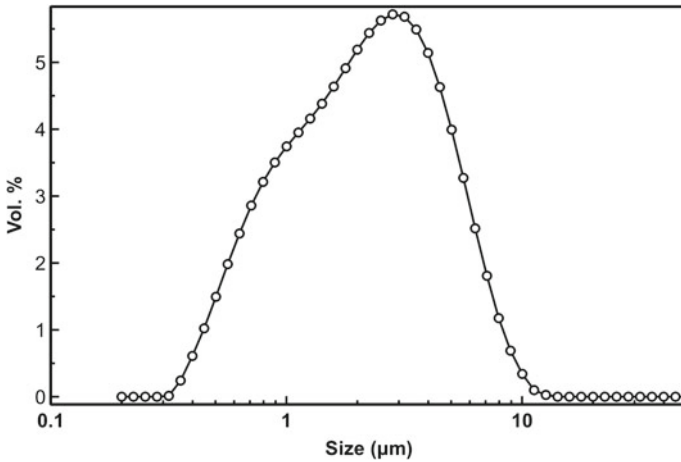


Fig. 2 Particle size distribution of the used waste marble powder

3 Blended Cements

Ternary blends of OPC, calcined clays and limestone are emerging as a possible, less impacting cement binder [7]. The environmental performance of such alternative binders can be further enhanced if waste calcium carbonate is used in the mix [8].

Several studies have investigated the hardened properties of these blended cements, but the fresh state properties have not been explored as accurately so far [9].

Here, we present the results of preliminary rheological investigations performed on a blended cement consisting of 50% OPC clinker, 30% calcined clay, 15% WM and 5% gypsum. The clay, consisting of kaolinite and minor phases that include

Table 1 XRF composition (wt%) of the Kenyan clay

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
73.48	0.56	22.80	1.97	0.11	0.14	0.22	0.17	0.47	0.08

Table 2 Summary of the blended cements measured by rheometry

	% clinker	% calcined clay	% waste marble	% gypsum
95Clink_5G	95	–	–	5
50Clink_30Clay_15WM_5G	50	30	15	5
50Clink_45WM_5G	50	–	45	5
50Clink_45Clay_5G	50	45	–	5

quartz, feldspars and oxides, was sampled in Kenya (XRF composition reported in Table 1). Clay calcination was performed at 850 °C for 3 h.

The rheological properties of the ternary blend were compared with that of the mixes reported in Table 2, each having a water/solid ratio of 0.5. The measurements have been performed by a stress-controlled rheometer equipped with a plate-plate system and a gap of 2 mm. The actual measurements have been preceded by a pre-shear at high oscillation amplitude of 10% and frequency of 10 Hz for 1 min. A recovery of the structure has been performed at low oscillation amplitude of 5.10⁻³% and frequency of 1 Hz for 2 min. Then, a triangular procedure and logarithmic ramps of shear rate of 10⁻² s⁻¹ to 10 s⁻¹ allowing 5 s measuring time per point have been used for the measurements. The flow curves and viscosity curves displayed in Fig. 3 represent the analyses of the down-ramp measurements.

It can be observed that the yield stress was significantly increased in the binary and ternary systems when waste marble was added, whereas the addition of calcined clay alone did not alter the viscosity behavior of the pastes. When added together, WM and calcined clay apparently display a synergic effect in increasing the paste viscosity.

4 Alkali-Activated GGBFS

Clinker can be reduced in a significative amount when using ground granulated blast-furnace slag (GGBFS) to manufacture slag cements (CEM III) or composite cements (CEM V). However, in the current industrial practice these cements are limited to specific applications where their low hydration heat or their high resistance to aggressive environments is needed, because of their slow hardening kinetics.

Alkaline activation of GGBFS is needed to formulate binders of more general use, able to replace ordinary Portland cement in everyday applications. A “one part” solid alkaline activation results in a binder that sets and hardens upon mixing with water, like Portland cement, and is thus easy and safe to use.

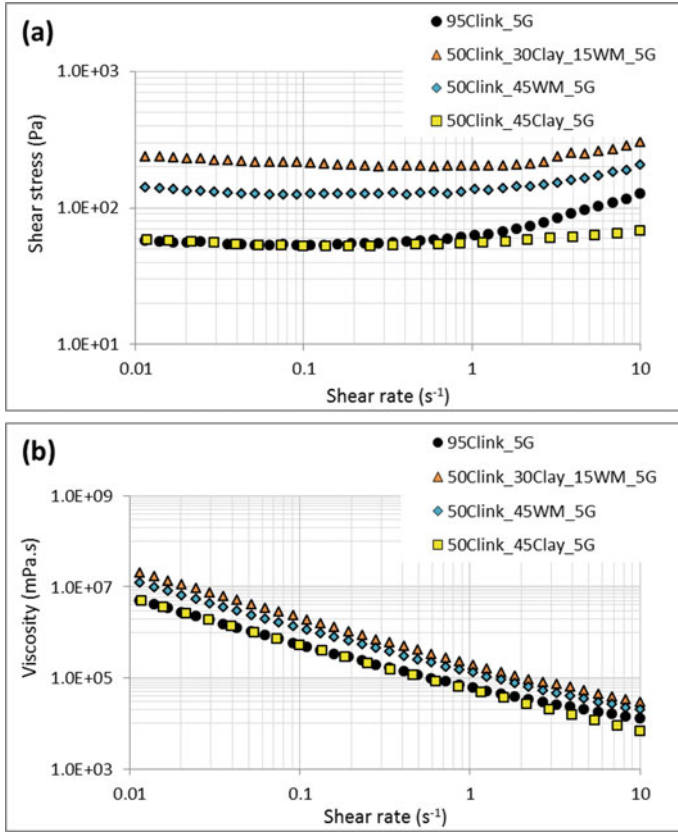


Fig. 3 Flow curves (a) and viscosity curves (b) of the studied blended cements

Activation by sodium carbonate or sodium sulfate can be used, but neither is enough by itself to provide sufficient reactivity. Sodium carbonate activation is widely practiced, with setting and hardening occurring when the carbonate ions in solution are exhausted [10]. Different approaches have been adopted to accelerate the depletion of carbonate ions in solution, the most straightforward being adding Ca²⁺ ions in solution to precipitate calcium carbonate [11]. Hydrated lime or Portland cement clinker can be used as a source of Ca²⁺ ions.

Here, as an alternative, micronized WM was used as a source of Ca²⁺ ions in solution, in combination with GGBFS (XRF composition reported in Table 3). A one-part alkali-activated binder was formulated by blending 47.5% GGBFS, 47.5% WM

Table 3 XRF composition (wt%) of the GGBFS

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
37.12	0.70	10.96	0.74	0.28	7.59	41.92	0.23	0.46	0.01

and 5% Na_2CO_3 . This binder presented good workability, even at low water/binder ratios, and a compressive strength of 26 MPa at 2 days and 49 MPa at 28 days.

5 Alkali-Activated Calcined Clays

The production of alkali-activated binders using low-grade calcined clays as precursors may represent a sustainable alternative to OPC, especially in emerging countries at subequatorial latitudes, where soils are enriched in clay minerals and the supply of Portland clinker or limestone may have to rely on import from foreign markets. Blending of calcined clays with waste calcium carbonate can reduce the environmental footprint to a further extent.

Here, we report a preliminary assessment of selected properties of binders produced by alkaline activation of blends of calcined clays of diverse compositions and waste marble powder. The materials used include three clay soils of kaolinitic composition, sampled in Cameroon (K1), Croatia (K2) and Ghana (K3), and two clays sampled in Italy, of smectitic (S1) and illitic (I1) composition. XRF compositions are reported in Table 4. The amount of clay minerals in these soils, as obtained by XRD and Rietveld refinement, varies from 28% (illitic clay) to 66% (smectitic clay), with the three kaolinitic clays having a kaolinite content in the range 40–60%. Minor mineralogical phases include quartz, feldspars, carbonates, apatite, Fe and Ti oxides. All clays were calcined in a laboratory muffle at a temperature of 800 °C, except for the smectitic clay, which was calcined at 750 °C.

The calcined clays were blended with up to 50% WM and subsequently mixed with sodium silicate activating solutions. The ratio of total water to total mass of the binders varied between 0.24 and 0.31. After mixing, the alkali-activated paste samples were placed in teflon molds and cured at ambient temperature and 95% RH. After three days, the samples were demolded and cured in air at ambient conditions.

Figure 4 reports a compilation of compressive strengths for the studied samples, plotted as a function of $\text{Na}_2\text{O}_{\text{eq}}$ %, which is used as a qualitative indicator of the environmental impact, given that the major contributor to the ecological footprint of alkali-activated materials is represented by the alkaline activators. From this perspective, in addition to reducing: (1) the consumption of primary limestone and (2) the energy associated with clay calcination, the addition of waste marble also results in

Table 4 XRF composition (wt%) of the calcined clays used for alkaline activation

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
K1	47.49	1.88	34.50	15.55	0.05	0.10	0.12	0.00	0.15	0.16
K2	58.73	1.33	25.96	9.86	0.15	1.05	0.69	0.47	1.60	0.15
K3	69.11	0.11	27.47	1.10	0.00	0.01	0.13	1.36	0.70	0.00
I1	60.49	0.85	16.52	5.03	0.10	4.98	7.19	1.45	3.14	0.26
S1	54.15	3.63	17.10	9.59	0.13	5.57	7.38	0.13	0.91	1.42

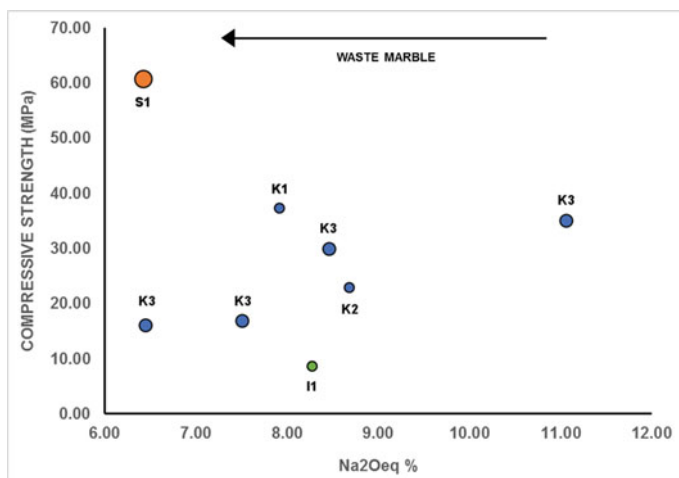


Fig. 4 Compressive strengths measured for the alkali-activated calcined clays blended with WM, as a function of equivalent $\text{Na}_2\text{O}\%$. Blue: kaolinitic clays; green: illitic clay; orange: smectitic clay. The symbols' size is proportional to the time at which the compressive strength tests were performed (small circles: 1 week; medium circles: 2 weeks; large circle: 3 weeks)

a significant net decrease in the environmental impact by reducing the amount of activator needed.

The samples prepared with the kaolinitic clay from Ghana (K3) showed an overall positive trend in the plot, meaning that both compressive strength and $\text{Na}_2\text{O}_{\text{eq}}\%$ decreased as the amount of calcined clay is progressively diluted by WM addition. However, in general, the compressive strength does not simply depend on the amount of WM, but also on the quality of the specific clay used. For instance, clay K1 (Cameroon) has an excellent mechanical performance (37.35 MPa after 7 days) with an addition of 30% WM (7.91 $\text{Na}_2\text{O}_{\text{eq}}\%$). Sample S1 gave a compressive strength of 60.70 MPa after 3 weeks, with an addition of 25% WM (6.42 $\text{Na}_2\text{O}_{\text{eq}}\%$).

The addition of WM also enhanced the workability of the fresh pastes, as measured by mini-slump tests (Fig. 5). A more quantitative study of the effect of WM additions on the fresh state properties will be performed in a follow-up work, by means of systematic rheological measurements.

6 Conclusions

We reported a short preliminary account on the potential of waste calcium carbonate from the stone industry as an SCM in sustainable binders, including blended and alkali-activated cements. Retrieving accurate numbers on the world availability (which can vary locally) of calcium carbonate waste is not easy. However, considering that calcareous stones represent more than 50% of the total stone production

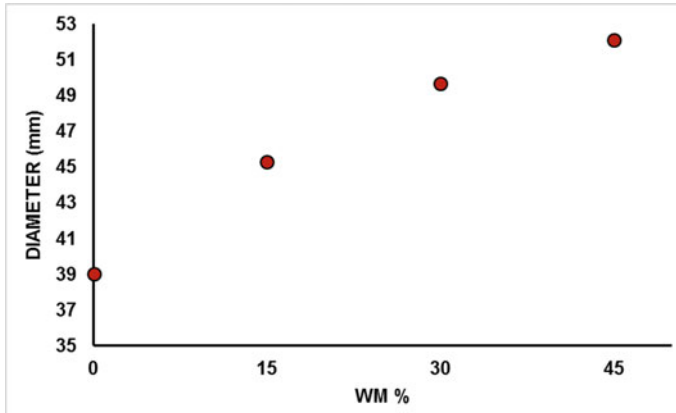


Fig. 5 Measured diameter (mini-slump test) as a function of waste marble addition, for sample K2

and that about two thirds of the global stone production is represented by waste [3], a rough estimate of 100 Mt per year of waste calcium carbonate can be inferred. It is also worth underlying the potential for local production of sustainable binders, using raw materials that are locally available in areas of emerging economic growth, such as Sub-Saharan Africa. Specifically, in this study, tests have been performed on the effect of waste marble on alternative cements formulated with clays from Kenya (ternary OPC-calcined clay-waste marble blend), Cameroon and Ghana (sodium-silicate-activated blends of calcined clays and waste marble). The waste marble used in these blends was of EU provenance, however, based on recent reports, the amount of waste from the stone industry in Africa amounts to about 7 Mt per year [3]. Specifically, marble and limestone waste have previously been used as a secondary raw material in the African continent [12, 13]. For alkali-activated calcined clays, the supply of sodium silicate solutions in the African continent may remain an issue in terms of overall cost and environmental footprint, however the possible use of carbonates as alkaline activators, even in combination with sustainable sources of soluble silica, such as rice husk ash, may potentially alleviate the economic and environmental burden, given the broad availability of alkaline carbonates of geological origin across the continent [14].

The results of this study show that moderate additions of WM are not detrimental to mechanical strength development. Excellent values of the compressive strength could be obtained for a sodium-carbonate-activated GGBFS formulated with 47.5% WM and alkali-activated smectitic and kaolinitic clays, with WM additions of 25% and 30% respectively.

The effect on the fresh properties needs to be further elucidated by systematic rheological measurements. However, it has been observed by preliminary tests that the addition of WM improves the workability of alkali-activated calcined clays. Moreover, the combined use of WM and calcined clays apparently exert a synergic effect in controlling the viscosity of ternary blends.

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