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Research Article

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Utilization of Limestone Quarry Waste as a Part of the LC³ Cement

Matea Flegar[1], Gaspard Houdayer[1], Kiran Ram[1], Marijana Serdar[1*] and Karen Scrivener[2]

[1]Department of Materials, Faculty of Civil Engineering, University of Zagreb, Zagreb, Croatia

[2]University or Laboratory of Construction Materials, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

[*]Correspondence to:
Marijana Serdar
Department of Materials,
Faculty of Civil Engineering,
University of Zagreb, Zagreb, Croatia.
E-mail: marijana.serdar@grad.unizg.hr

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Abstract

The use of supplementary cementitious materials (SCMs) offers the cement industry a rapid transition to minimise CO_2 emissions associated with clinker production. It is already known that cements containing calcined clays in combination with limestone (LC³) are a good alternative to reduce the clinker factor without compromising mechanical properties or durability. This study analyses the possibility of limestone quarry waste utilisation as limestone addition in the LC³ system. The differences in limestone particles, defined by particle size distribution, are investigated, and compared with commercially available limestone filler (LF). The limestone quarry waste (LQW) was adopted in the study in two ways, as received (AR) and processed by grinding in a disc mill (DM). The LC³ mixes were developed with a 45% of cement replacement which contains 30% calcined clay and 15% limestone. They were tested to address the reactivity and the compressive strength of mortars. The results indicate a higher reactivity of the finer limestone powder from industrial production, although the difference is not very large. This could open the path for a more sustainable use of quarry waste and lover the CO_2 emissions regarding cement production.

Keywords

LC³, Limestone, Quarry waste, Cement, Reactivity

Introduction

As urban populations continue to grow, so does the demand for building materials. The Organization for Economic Cooperation and Development has projected rapid growth in this sector from 35 Gt of material produced in 2011 to 82 GT in 2060 [1]. Concrete, as the most commonly used material in construction, takes a large share of these figures. The weak point of this otherwise durable, accessible, and uncomplicated material is the environmental impact of its production, more specifically cement production. Industry has recognized that SCMs are the key option to reduce the environmental impact [2]. These types of binders have already been used in cement production, but with the decreasing availability of most common SCMs (slag and fly ash), the question of new, achievable, and cost-effective environmental SCMs arises [3].

LC³ has potential for large-scale implementation because of their worldwide availability [4]. The ternary blend which contains 30% of calcined "low grade" kaolinite clay, 15% of limestone and clinker has shown to give good mechanical properties [5] without compromising or even increasing the durability and service life of concrete [6-8]. Limestone in cement mainly serves as filler or has a dilution effect. In the LC³ system it additional acts as a source of calcium carbonate which reacts with the aluminate component from clay and forms space filling carbo

aluminate hydrates. These effects are influenced by particle size, dosage, mineralogical composition, and dissolution rate of the limestone powder [9].

The cement factories usually use crushed limestone that is either milled separately or (more often) intergrind with the clinker. The crushed limestone is mostly supplied by the aggregate industry. Depending on the type of quarry, process method and geological characteristics, the production of aggregates results in production of quarry dust and waste [10]. On the one hand, this causes an environmental concern to the aggregate industry, while on the other offers a less energy demanding option for cement industry. LF that is used in the production of Portland cement with limestone addition, has to follow specifications according to the national standards, to ensure the quality of cement. Meanwhile, the characteristics of limestone powder for the production of the LC³ system have not yet been defined.

This study questions the possibility of LQW utilization in LC³ cement and compares the results with the commercially available LF. The LQW was used as received and additionally milled in a DM to evaluate if additional energy for milling is indeed required for satisfying the basic cement requirements such as 7- and 28-day strength [11].

Materials and Method

Materials

This study compares the influence of two different types of limestone as a part of the LC³ system, LQW and commercially available LF as shown in figure 1. The LQW powder was used AR and milled in a DM for 60 s. Table 1 shows the chemical composition of the two limestone samples. The LQW sample shows lower amount of CaO and higher values of SiO_2, Fe_2O_3, and Al_2O_3 than the mostly pure LF. The impurities could be associated with the possible inclusion of clay or dolomite in the quarry [12], although there is almost no difference in the MgO content. The higher iron content could influence the reddish color. The clay used for the LC³ system is obtained from a quarry in the southeast Europe region, containing around 40% kaolinite. The clay was first dried for 24 h at 60 °C, after that milled in a DM for 30 s and then calcined at 800 °C for 1 h. The materials are of nanoscale.

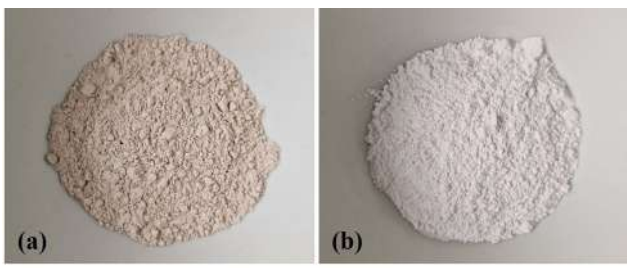


Figure 1: (a) LQW and **(b)** commercial LF.

Methods

To distinguish the differences in the particle size, the samples were tested with a wet laser diffraction method using the SALD-3101 (Shimadzu) apparatus according to recommendations [13]. Approximately 2 g of sample was dispersed in 150 ml of solvent (water) and treated with an ultrasonic horn (200 W, 25 kHz) for 5 min. Samples were then stirred with an ultrasonic magnet stirrer until reaching room temperature. The apparatus was cleaned 3 times before each test, the 4th time dispersed sample was added using a pipette until the set obscuration was met (13.2%). Fraunhofer diffraction theory was used to calculate the particle size based on the diffraction angle. Each sample was measured 3 to 7 times from which an average value is show in the results.

The reactivity of each sample was observed through the measurement of the heat of hydration using isothermal calorimeter TAM Air (TA Instruments) for 7 days at 20 °C. Cement pastes were prepared with a 0.4 w/b ratio, using 70 g of solid material. The samples were mixed in an automated mixer with a rotation of 1600 rpm for 2 min. One sample containing only CEM I 42.5 N was mixed as a reference (OPC). The LC³ binders were composed of 30% calcined clay, 15% limestone, and 1% gypsum to reach sufficient sulfate content. The rest (54%) of the binder was Cem I 42.5 N as used for the OPC mix. The amount of 10 ± 0.05 g of paste was placed in a glass ampule and put into the calorimeter together with a water reference sample (4.22 g of mass). The baseline was recorded 24 h before and after ampule placement.

The compressive strength of mortars was measured according the EN 196-1:2016 [14] using 450 kg/m³ of binder with the same combinations as aforementioned pastes and a 0.5 w/b ratio. Standardized quartz sand (0 - 4 mm) was used for 1350 kg/m³ of aggregate.

Results and Discussion

The differences between the limestone powders are visible through their particle sizes (Figure 2). The commercial LF shows the highest number of small particles with the smallest d_{50} value of 10.4 µm. The distribution of particles of this sample is in the size range from 215 to 0.15 µm. Sample LQW_AR seems to have a more evenly distribution of particles with an average d_{50} of 30.2 µm and a broader particle size range than the disc milled sample, from 894 to 0.18 µm. Surprisingly, LQW_DM has the highest d_{50} (68.8 µm) but a narrower particle size distribution with particle diameters in the range from 462 to 1.5 µm. This coarsening of particles could be explained by aggregation of limestone particles during short dry grinding caused by reversable particle adhesion [15].

Table 1: Chemical composition of limestone samples.

Sample	Content, wt.%										
	P_2O_5	Na_2O	K_2O	CaO	MgO	Al_2O_3	TiO_2	Fe_2O_3	SiO_2	MnO	SO_3
LQW	0.42	< 0.010	0.15	71.59	1.69	4.32	0.08	1.43	20.21	0.03	0.08
LF	< 0.01	< 0.01	0.05	91.35	1.86	3.03	0.07	0.73	2.85	< 0.010	0.05

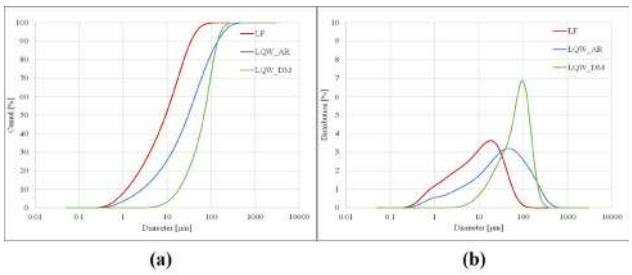


Figure 2: Particle size distribution of the three limestone powder materials: **(a)** cumulative and **(b)** differential distribution.

The results of the calorimetry measurement are shown in the normalized per gram of cement. The heat flow curve indicates the main kinetic reactions that happen during the early age hydration of cement and LC³ systems. The first most distinctive peak is attributed to the fast dissolution of alite, a slow ettringite formation and the start of C-(A)-S-H precipitation [16]. The second peak is referred to as the aluminate peak, is connected to the fast dissolution of C_3A and further ettringite formation [17]. The performed test showed slight differences between the samples. All LC³ samples show an enhancement and acceleration of the alite peak (curve shifted to the left) when compared to OPC, which is most likely due to the filler effect of the added SCMs. The additional nucleation from the limestone and clay promotes a higher rate of C-(A)-S-H precipitation and, with that, gypsum depletion. This reaction seems to be most pronounced with the LF sample. As expected, the aluminate peak of the LC³ systems is much more pronounced than the OPC one. This behavior is associated with the availability of sulfate (gypsum) which is rapidly depleted in the alite reaction. The earlier sulfate depletion triggers the aluminate reaction and, therefore, enhances the aluminate peak in these systems [18]. Again, the LF sample seems to have a slightly higher reaction than the other two limestone samples. This could be associated with a higher filler effect of this sample [17]. The acceleration trend is slightly different when comparing the two LQW samples. Within the LC³ mix the DM limestone shows slightly lower alite reaction but a higher aluminate reaction than the AR sample. The cumulative heat between all LC³ samples shows a relatively small difference of 2.5%. The LC³_LF sample has the highest heat release after 7 days while the LQW samples show almost the same reactivity at the end of the measured period (Figure 3).

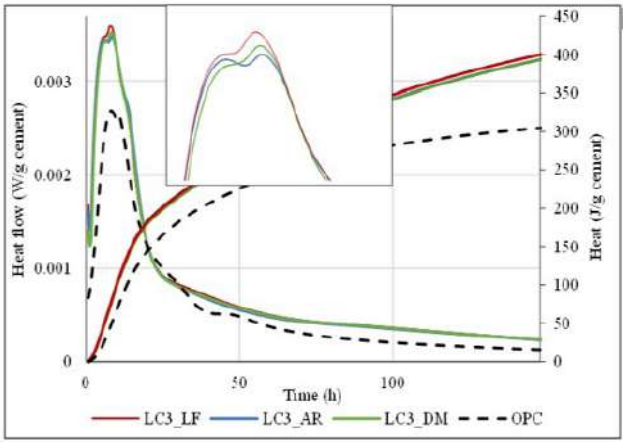


Figure 3: Heat flow and heat release of the LC³ and OPC mixes measured by isothermal calorimetry up to 7 days.

Table 2 shows the fresh properties of mortar, temperature and consistency measured with a flow table. The different limestone types seem to influence the mortar consistency, LF sample showing the lowest value which could be connected to the smallest particle size range. It has been seen in literature that finer particle size and, consequently, higher surface area, could lead to faster hydration rate and setting time [19]. This could influence consistency also.

Table 2: Fresh properties of mortar mixes.

Label	Temperature [°C]	Consistency [mm]
OPC	25.8	187.5
LC³_AR	25.3	153.5
LC³_DM	25.6	150.5
LC³_LF	25.3	147.5

The compressive strength of mortar mixes is shown in figure 4. All LC³ mixes show a reduction of the compressive strength (15 - 25% reduction of the OPC 28-day strength). The early (7 day) average strength is higher with the LQW sample and the highest for the disc milled limestone mix, which is opposed to the calorimetry measures. It should be noted that the standard error of the sample with the highest strength value is significant. After 28 days the LC³_LF shows the highest strength gain with 37.48 MPa, which is in accordance with the total heat of hydration measured by isothermal calorimetry. The "AR" sample of limestone shows the lowest strength gain, but only 2 MPa lower than the disk milled sample. All 3 binders could be characterized as grade 32.5 cement [11].

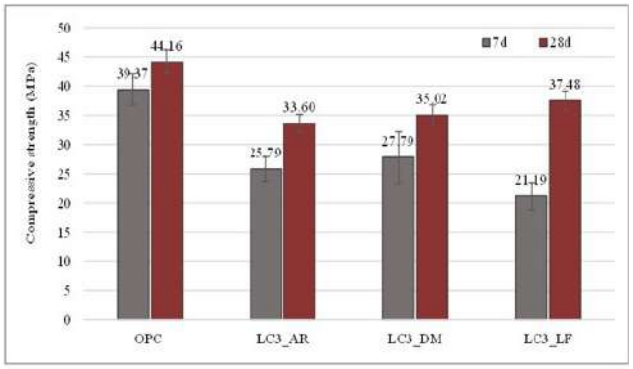


Figure 4: Compressive strength of mortar mixes after 7 and 28 days.

Conclusions

The research investigates and compares the differences between two types of limestone: the commercially available, high purity limestone and unrefined LQW. To investigate the potential of quarry waste, this material was utilized "AR" and disk milled. The conclusions of the study are as follows:

- The particle size distribution curves of the tree samples differ in size and shape. The LF sample seems to be

the finest material with the smallest d_{50} and the lowest number of bigger particles (> 0.1 mm). Milling the LQW in a DM seems to increase the d_{50} value due to the particle agglomeration but decreases the particle size range.

- The isothermal calorimetry measurement showed an enhancement of the aluminate reaction of the LC³ mixes compared to the OPC mix. Even though the sample containing LF showed the highest heat release after 7 days of measurement, the difference with the LQW samples seems neglectable (3%).
- The 28-day compressive strengths of mortar agree with calorimetry measurement. Even though all samples show a lower strength than the OPC, the LF sample shows slightly higher results than others, while the LC³_DM mix gives slightly higher compressive strength than the LC³_AR. Nevertheless, all samples satisfy the criteria of cement class 32.5 for 28-day compressive strength.

Considering the environmental burden of the concrete industry, it is essential to explore the possibility of quarry waste utilization and weigh the benefits and burdens of such actions. Based on the presented study, it can be concluded that it is possible to incorporate LQW as a part of the LC³ system with slight decline in the reactivity of the system compared to the use of pure limestone. Regardless, the difference could be considered negligible if the ecological and economic savings are significant. The future prospective would be to assess the rheological and durability challenges regarding the use of this type of LC³ cement which is essential for the commercialization of this type of binder.

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Conflict of Interest

None.

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