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Effect of Portuguese metakaolin on hydraulic lime concrete using different curing conditions

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ABSTRACT

Hydraulic lime concrete with the addition of metakaolin in various percentages and cured under different conditions was studied in order to evaluate the effect of the pozzolanic additions over time (7, 28, 90 and 360 days). This study was performed using NHL 5, a metakaolin of Portuguese origin, siliceous sand and calcareous coarse aggregate, with increasing percentages of substitution of hydraulic lime by metakaolin in weight. In order to evaluate the pozzolanic effect, compressive strength test were performed and analysed by relative strength–time plots and by the application of different indexes such as the index of specific strength and the pozzolanic index. Thermogravimetric analysis was performed at the age of 28 days in order to evaluate the phases present in the concrete specimens. As main conclusions metakaolin is an adequate material for application in concrete with hydraulic lime binder as a pozzolanic addition providing an increase in mechanical strength for the studied substitutions of 20% and 30%. Testing should be performed at 28 days when portlandite consumption is complete.

1. Introduction

Although currently concrete is made with the use of Portland cement as a binder, it is known that in ancient times the binders used in concrete were air lime and pozzolans. Taking into account this possibility and the fact that natural hydraulic lime and metakaolin are produced in Portugal, a concrete with these two products was designed and tested for its mechanical properties. Although it is expected that this concrete will have a lower performance and therefore limits to its use, it may be advantageous in the construction business due to lower CO_2 emissions and energy consumption in the production process. Sulphate attack caused by exposure to sulphate solutions is a common degradation factor in mortars and concrete. In the case of hydraulic lime concrete the absence of sulphates in the binder does not contribute to delayed ettringite formation in humid environments.

The use of metakaolin as a pozzolanic addition is growing and its influence on concrete with Portland cement as the main binder is well known, both in terms of mechanical strength and durability [1,2]. The reaction products of cement/metakaolin concrete or mortar have also been prone to several studies and it is known that apart from CSH there is a formation of calcium aluminate hydrates and also calcium silicate aluminate hydrates [3,4]. The reaction of air lime and metakaolin has also been the object of study [5,6]. However the use of pozzolanic additions with a hydraulic lime binder is complex as carbonation reaction is relevant and hydraulic reaction is slower than in ordinary Portland cement, due to the predominance of dicalcium silicate and very low contents of tricalcium silicate.

This study aims at identifying the mechanical evolution of concrete with natural hydraulic lime and the influence of metakaolin in its performance at various ages. It was executed using various curing conditions in order to evaluate their effect on the mechanical properties of hydraulic lime concrete.

2. Experimental

2.1. Composition and curing

Composition of hydraulic lime concrete was determined using a water/binder ratio of 0.45 with aggregates in a saturated condition. Aggregates and cement relative proportions were studied using a modified Faury method that takes into account the differences between cement (that served as basis of the method) and hydraulic lime. Three different compositions were studied. Mixture M0 is the reference mixture and uses only hydraulic lime as binder. Mixtures M2 and M3 had a partial replacement of hydraulic lime by metakaolin. This replacement, by weight, was 20% for composition M2 and 30% for composition M3. Grading of aggregates is presented in Fig. 1 that also shows the resulting final grading curve. The final mix proportions for all types of studied concrete are shown in Table 2 including hydraulic lime percentage in the binder (p).

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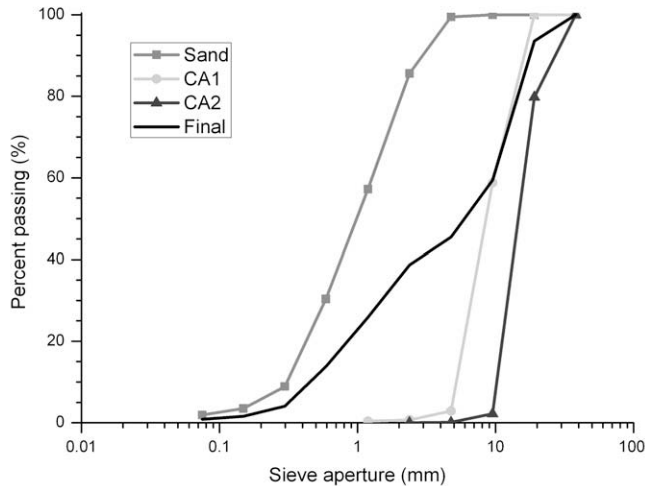

Fig. 1. Aggregate grading curves (sand, CA1, CA2) and final grading curve.

The developed experimental program was designed in order to incorporate the assessment of the effect of different curing conditions on the properties of hydraulic lime concrete with metakaolin. Three different curing conditions at atmospheric pressure were used where the relative humidity, RH, of the environment was changed. Concrete specimens were cured immersed in water, at 95% RH and at 65% RH. The temperature was kept constant at 20 °C in all cases. Specimens were preserved in the same curing conditions until the date of testing (up to 1 year).

2.2. Properties in fresh and hardened state

Fresh properties of concrete such as density and workability (measured using the slump test according to NP EN 12350-2:2002 standard) were measured. In the hardened state, the compressive strength (tests on 15 cm cubes) were performed at 7, 28, 90 and 360 days for original specimens.

In order to evaluate the formation of different phases with metakaolin content of these concrete specimens, Differential Thermal Analysis was performed at the age of 28 days, using a Netzch STA 409 °C and a temperature range between 20 °C and 1000 °C, with a heating rate of 10 °C/min.

2.3. Materials

All the materials used in this study are commonly available in Portugal, although their use is not widespread due to the preferred use of Portland cement as a binder and fly ash that is still abundant as a pozzolan. Binders were characterised in terms of their chemical composition, taking into account major elements, by X-ray Fluorescence using a Philips PW 1400 X-ray Fluorescence Spectrometer and in terms of their mineralogical composition by X-ray Diffraction using a Philips X-Pert Pro X-ray Diffractometer. Aggregates were characterised in terms of their particle size distribution following standard EN 12620:2002, Aggregates for concrete.

2.3.1. Hydraulic lime

The binder used was hydraulic lime NHL 5 that is currently the only hydraulic lime produced in Portugal. Additionally, its compressive strength of 5 MPa at the age of 28 days is sufficient to be improved by the addition of a pozzolan, allowing the use of this type of concrete in low demanding structural applications such as urban equipment, cycling roads, blocks, among others. The predominant crystalline phase present in its composition is portlandite and other phases present are dicalcium silicate, tricalcium silicate, calcite and quartz. Chemical composition of Portuguese NHL 5 is shown in Table 1.

2.3.2. Metakaolin

Metakaolin is an artificial pozzolan obtained by the calcination of kaolinitic clays over a specific temperature range.

Table 2
Mixture composition including hydraulic lime percentage in the binder (p).

Name	Constituents (kg/m^3)						p (%)
	CA1	CA2	Sand	NHL 5	MK	Water	
M0	619	455	321	550	–	247.5	100
M2	619	455	321	440	110	247.5	80
M3	619	455	321	385	165	247.5	70

It is a very fine material, with a high specific surface that enhances pozzolanic reactivity. Pozzolanic reactivity was measured following "NP EN 196–5: methods of testing cement. Pozzolanicity test for pozzolanic cement", that is a testing procedure intended for application in pozzolanic cements, measuring $Ca(OH)_2$ consumption in a solution with a standard quantity of cement and pozzolan. However, and taking into account the various available methods for measurement of pozzolanic reactivity, it has proven to be the most adequate for this purpose when dealing with pozzolanic materials. When applied to metakaolin, this testing procedure classified the material as an active pozzolan. XRD results revealed the presence of quartz and kaolinitic minerals whilst in terms of chemical composition, shown in Table 1, there is a predominance of silica and alumina.

2.3.3. Aggregates

Aggregates used in this study were natural siliceous sand and calcareous coarse aggregate. The sand grading curve is in the range of 0–4 mm. Coarse aggregates were divided into two groups; one in the range 5–10 mm (CA1) and the other in the range 10–25 mm (CA2). Grading curves of sand and coarse aggregate are plotted in Fig. 1.

2.4. Assessment of the effect of metakaolin

Some strength indexes were used to assess the effect of metakaolin. Pozzolanic strength indexes as defined in [7] for cement concrete and previously used for hydraulic lime concrete [8] were used to assess the pozzolanic effect of metakaolin, while *k-value* efficiency factor [9] was calculated from compressive strength to measure the effect of metakaolin addition on the strength of concrete.

The specific strength ratio, R, is defined [7] as the contribution to concrete strength from unit binder and unit mineral admixture and is defined by

$$R = f_c/p \tag{1}$$

where f_c is the concrete compressive strength and p is the hydraulic lime or mineral admixture percentage of the cementitious materials (see Table 2). R_{HL} expresses the contribution of unit hydraulic lime to concrete strength without any mineral admixture, R_M expresses the contribution of unit hydraulic lime, when metakaolin is used, to concrete strength, and R_P is the contribution of the pozzolanic effect of metakaolin to concrete strength due to metakaolin, expressed by the equation:

$$R_P = R_M - R_{HL} \tag{2}$$

The index of specific strength, K, is the ratio of R_M to R_{HL}, and the contribution of pozzolanic effect to strength, P, can be assessed by the percentage value of the contribution of pozzolanic effect to concrete strength, which can be written as:

$$P = 100(R_P/R_M) \tag{3}$$

The pozzolanic index, P, relates to the favourable contribution of the pozzolan relatively to the usual binder.

The estimation of the *k-values* [9], follows the procedure described next. The compressive strength of a Portland cement concrete and generalized here for hydraulic lime concrete, can be estimated by the following empirical equation:

$$f_c = S\left(\frac{1}{W/HL} - a\right) \tag{4}$$

where f_c is the compressive strength (MPa), W is the water content in the initial concrete mix (kg/m^3), HL is the hydraulic lime content in concrete (kg/m^3), S is a parameter depending on the binder type (MPa) and a is a parameter depending mainly on time and curing. In the case of metakaolin concrete, expression Eq. (4) can be generalized and the following expression for compressive strength can be used, which involves the concept of *k-value*:

Table 1
Chemical composition of metakaolin and hydraulic lime (percentage in weight).

Oxides	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	Na_2O	TiO_2	Na_2O	LOI
MK	0.04	59.90	32.29	1.28	2.83	0.17	0.24	0.36	2.83	2.80
NHL 5	43.13	22.45	7.07	2.82	1.67	2.13	0.59	0.38	0.59	18.6