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Research paper

Long-term behavior of lime–metakaolin pastes at ambient temperature and humid curing condition

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S-SiO_2

ABSTRACT

This paper presents the reaction behavior of lime and metakaolin (MK) pastes submitted to long term aging at ambient temperature and relative humidity of 95 ± 5%. The results presented are the basis for an extensive research pointing towards the formulation of lime based mortars for conservation of historic buildings, namely in humid environments.

MK, when mixed with calcium hydroxide, in the presence of water, originates a set of major hydrated compounds, specifically, stratlingite, monocarboaluminate and calcium aluminate hydrate. The type of hydrated compounds formed is dependent on the lime/MK ratio, being some of them unstable over time. This instability can compromise the mechanical properties of lime–MK mortars. From this work different reaction kinetics with aging were perceived, being the best results in terms of the pozzolanic reaction obtained with 50% MK content. Pastes with less than 25% of MK also present reliable stability.

1. Introduction

The importance of studying the use of lime based binders for employment in conservation of historic masonry has become one of the major challenges regarding the built heritage conservation theme (Ball et al., 2012; Gameiro et al., 2012a,b; Papayianni and Konopissi, 2005; Veiga et al., 2010).

A variety of advantages arises from the application of lime based binders in this field in contrast to what has been seen for cement mortars. These advantages include low manufacturing temperature of binders, high vapor permeability and the ability to accommodate movement due to a low modulus of elasticity and through micro-cracking, as well as the ability of self-healing of the mortars.

Although pure air lime binders can offer strength and durability, this is mainly achieved after a long period of time, through carbonation (Ball et al., 2012).

However, air lime durability and resistance to water action, as well as short term strength, can be improved by adding pozzolanic materials to the mixture, leading to a pozzolanic reaction. In this case, initial strength is obtained by a hydration reaction between lime, a pozzolanic material and water. Pozzolanic materials could be of natural, industrial and sub-product origin, and are mainly composed by amorphous silica and alumina compounds.

In this study the pozzolanic material used was metakaolin (MK), which is a material with great potential in Portugal, since there is a large abundance of kaolinitic clay reserves, waiting to be exploited, in order to produce metakaolin (Gameiro et al., 2012a,b). Nowadays, the main pozzolanic material employed in Portugal is coal fly ash; however its use is expected to decrease due to environmental restrictions.

MK is known by its high pozzolanicity, being important to study its influence on the performance and durability of lime mortars to be applied for conservation and restoration of historic masonries (Aggelakopoulou et al., 2011; Bakolas et al., 2006; Ball et al., 2012; Gameiro et al., 2012a,b; Konan et al., 2009; Moropoulou et al., 2004; Papayianni and Konopissi, 2005; Rojas-Frías, 2006; Siddique and Klaus, 2009; Veiga et al., 2010).

The phase formations of lime–MK mixtures with different CH amounts were first reported by Serry et al. (1984), showing that

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stratlingite was the main crystalline phase obtained. Several other studies stated the occurrence of calcium aluminate hydrate C_4AH_{13} or monocarboaluminate ($C_4A\overline{C}H_{11}$), as well as stratlingite and calcium silicate hydrate (CSH) at 20 °C (Aggelakopoulou et al., 2011; Ambroise et al., 1985; Fernández et al., 2010; Martínez-Ramírez and Frías, 2011; Murat, 1983; Rojas-Frías, 2006; Sepulcre-Aguilar and Hernández-Olivares, 2010; Serry et al., 1984, 1987).

In a precedent paper Gameiro et al. (2012a) have presented the results of six months' evaluation of different lime–MK pastes, cured at relative humidity (RH) of 95 ± 5% and at a temperature of 23 ± 2 °C, showing that major crystalline phases formed are stratlingite, tetracalcium aluminate hydrate, monocarboaluminate, portlandite and calcite. The principal difference observed between the lime–MK pastes studied is the decrease of hydraulic crystalline phases formed with the lowest MK content, namely pastes with less than 17% of MK as lime substitution. Another aspect to be mentioned is the instability over time of the calcium aluminate hydrate species formed. This instability could interfere in strength development of lime–MK materials with aging, which can limit the use of lime–MK binders for conservation purposes.

The present paper presents the results obtained until 1.5 years of curing, following the mineralogical compounds formed and their changes and further stability at long curing times. These results are considered vital when aiming at the formulation of air lime based mortars for conservation of historic buildings, namely in environments where the contact with CO_2 is difficult or in the presence of water.

2. Experimental

2.1. Materials, pastes compositions and conditioning

Pastes were prepared using a pro-analysis calcium hydroxide reagent (CH) and a commercial metakaolin (ARGICAL M1200S from Imerys), MK, in different lime by MK replacement ratios (mass%).

The chemical composition of metakaolin (major elements) was accomplished by XRF analysis (Table 1), using a Panalytical Axios X-ray fluorescence spectrometer with CrKα radiation. Loss on ignition was determined by sample calcination at 1000 °C for 3 h. Specific surface area was obtained by Blaine method.

The particle size distribution was: d(10%) = 1.53 μm, d(50%) = 4.35 μm and d(90%) = 11.97 μm.

MK pozzolanic activity was checked by the modified Chapelle (AFNOR, 2012) and Fratini test methods (CEN, 2011). These two methods measure the amount of CH fixed by the pozzolan. According to NF P 18-513 standard (AFNOR, 2012) the value of the MK pozzolanic activity should not be less than 700 mg $Ca(OH)_2$/g of metakaolin, being obtained in this case a result of 1342 mg $Ca(OH)_2$/g of pozzolan. The result obtained in the Fratini method confirms the high pozzolanic activity of this MK.

The pastes' mixing process as well as the storing and curing conditions used was accomplished in the same manner as previously reported (Gameiro et al., 2012a,b,c), consisting in mixing different lime–MK pastes (lime replacement by MK, wt.%) using a 1:1 water/solid ratio.

Pastes were stored at relative humidity of 95 ± 5% and at temperature of 23 ± 2 °C, with the purpose of favoring the hydration reaction in detriment of the carbonation reaction (Cizer, 2009).

At specific curing ages samples were analyzed by XRD and TG–DTA. Table 2 illustrates all sample identification and corresponding mixes.

2.2. Methods

After drying (temperature 40 °C) the samples were ground and sieved at 106 μm. X-ray diffractograms were obtained on a Philips PW3710 X-ray diffractometer, with 35 kV and 45 mA, using Fe-filtered CoKα radiation of wavelength λ = 1.7903 Å. Diffractograms were recorded from 3° to 74° 2θ, at an angular speed of 0.05° 2θ s^{-1}. The crystalline phases were identified by comparison with the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF).

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed in a SETARAM TG–DTA analyzer, under argon atmosphere, with a heating rate of 10 °C/min, ranging from room temperature up to 1000 °C. The free portlandite (CH) and CO_2 contents in the samples were determined from the mass losses in the range of 400–550 °C (CH dehydration) and 550–850 °C (decarbonation), respectively (Aggelakopoulou et al., 2011; Lawrence et al., 2006). The determination of the free portlandite content enables to obtain the extent of pozzolanic reaction, while CO_2 content gives information about the carbonation rate in each sample.

3. Results and discussion

3.1. XRD results

Fig. 1(a) to (g) presents the XRD patterns obtained. The main crystalline components detected are: stratlingite (C_2ASH_8), tetracalcium aluminate hydrate (C_4AH_{13}), monocarboaluminate ($C_4A\ \overline{C}\ H_{11}$), portlandite (CH) and calcite ($C\overline{C}$). Other minor phases are also present and include a calcium silicate hydrate (CSH), a calcium aluminate hydrate type ($Ca_2Al(OH)_7 \cdot 6.5H_2O$), katoite ($Ca_3Al2(SiO_4)(OH)_8$) and quartz ($SiO_2$).

Stratlingite (C_2ASH_8) is the main hydrated crystalline compound formed in pastes with high MK contents (MK50 to MK25)—Fig. 1(a) to (d). However, its presence is not detected in low MK content pastes (MK < 25%) up to 1.5 years of curing—Fig. 1(e) to (g). Since stratlingite is described by some authors (Ding et al., 1995; Heikal et al., 2004) as conferring mechanical strength to lime-based mortars, it can be inferred that high MK content should confer high mechanical strengths to lime–MK based mortars. However, a distinction is observed concerning

Table 1
Chemical composition and physical properties of the metakaolin.

Compounds	Chemical composition (mass%)
SiO_2	54.39
Al_2O_3	39.36
Fe_2O_3	1.75
MnO	0.01
MgO	0.14
CaO	0.10
Na_2O	–
K_2O	1.03
TiO_2	1.55
P_2O_5	0.06
Loss on ignition	1.90
Surface area (m^2/g)	3.38

Table 2
Paste sample identification, materials and mass ratios.

Paste	Materials (mass%)		Mass ratios (CH:MK)
	CH	MK	
MK50	50	50	1:1
MK38	62	38	1:0.6
MK33	67	33	1:0.5
MK25	75	25	1:0.3
MK17	83	17	1:0.2
MK9	91	9	1:0.1
MK5	95	5	1:0.05