Micro-Raman study of stable and metastable phases in metakaolin/Ca(OH)$_2$ system cured at 60 °C

Sagrario Martínez-Ramírez [a,*], Moisés Frias [b]

[a] *Instituto de Estructura de la Materia (CSIC), C/Serrano 121, 28006 Madrid, Spain*
[b] *Instituto de Ciencias de la Construcción "Eduardo Torroja" (CSIC), C/Serrano Galvache, 4, 28033 Madrid, Spain*

A B S T R A C T

The kinetics of hydration reactions between MK and Ca(OH)$_2$ depends directly on the cementing matrix and curing temperature. For example, as the temperature increases in the metakaolin (MK)/calcium hydroxide system causes formation of the metastable hexagonal phases (C$_2$ASH$_8$ and C$_4$AH$_{13}$) that evolve into a thermodynamically stable cubic phase belonging to the hydrogarnet family (C$_3$ASH$_6$). This transformation will reduce the volume (approx. 9%) and a loss of durability of these cementing matrices. Although it is known that there are hydrated phases involved in the reaction, there is still an important scientific gap which occurs during the intermediate steps. For this reason, the micro-Raman spectroscopy is used for the first time as a suitable technique in order to study the conversion reaction in the MK/Ca(OH)$_2$ system cured at 60 °C. The results show that at short curing periods C–S–H gel as well as metastable phases with different AlO$_4^{5-}$ environments are present; this is the first time that these metastable phases have been observed by Raman spectroscopy. As hydration proceed C–S–H gel decreases, with a total disappearance at 30 h. After longer hydration stages the metastable phases transform to stable hydrogarnets identified by two broad bands in the OH and AlO$_4$ vibration region respectively (3670–3650 cm^{-1} and 520–540 cm^{-1}) with no C–S–H gel formation.

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1. Introduction

For many years, the importance of incorporating active additions in blended cement matrices is well known (Taylor, 1997). Currently, these additions are gaining greater importance due to problems with the environment and the need to include sustainability in the cement manufacturing process. So, cement producers have a wide range of additions for the manufacture of commercial cements such as traditional pozzolans (silica fume, fly ash and slag) and thermally-activated products such as metakaolin (MK) obtained by dehydroxylation of natural kaolinite under controlled temperature conditions (Sánchez de Rojas et al., 1999; UNE-EN, 2005; Lea, 1998; Fortes et al., 2006; Cara et al., 2006) and nontraditional additions such as activated paper sludge (Frías et al., 2008a,b; Banfill and Frías, 2007), sugar cane bagasse ashes (Frías et al., 2007), ceramic waste (Sánchez de Rojas et al., 2007), etc. Metakaolin, a commercial pozzolan, is an amorphous reactive aluminosilicate obtained by thermal treatment of kaolin or kaolinite (Sanz et al., 1988; Kristof et al., 1993; Moya, 1998). The heat treatment (600–800 °C) alters the structure of kaolinite, breaking the bonds and collapsing the clay structure (Shi, 2002).

It is well known that the kinetics of pozzolanic reaction between MK and Ca(OH)$_2$ depends directly on the matrix and curing temperature (Ríos et al., 2009; Siddique and Klaus, 2009; Frías, 2006). In this regard in previous works based on XRD and TG/DTA analysis, Frías and Sánchez de Rojas, 2003 and Frías and Cabrera, 2002, revealed the different hydrated phases coexistence: C–S–H, C$_2$ASH$_8$, C$_4$AH$_{13}$ and C$_3$ASH$_6$ (hydrogarnet family) in MK/Ca(OH)$_2$ systems cured at 60 °C. However, in MK blended cement matrices the kinetics varied substantially, mainly in the null stratlingite crystallinity and in the non formation of C$_3$ASH$_6$ (traces only).

Currently, there are still significant gaps with respect to the stability and evolution of these metastable hydrated phases with curing temperature and its importance in the evolution of the final performance of MK blended matrices which studies by the traditionally used XRD and TG/DTA techniques cannot solve.

As a result, in recent years other techniques are emerging, such as Raman and NMR, both of which are more suitable in getting a deeper knowledge about the kinetics of hydration reactions (Martínez-Ramírez et al., 2006 and Ferreiro et al., 2009) specifically in MK blended matrices. Raman spectroscopy provides information on the short-range order and local bonding in materials. Thus, Frías and Martínez-Ramírez, 2009, reported the identification of stratlingite (3692 and 531 cm^{-1}) by Raman spectroscopy in MK/white cement paste system. However, there is no literature evidence of the use of this technique in pure MK/Ca(OH)$_2$ pastes.

* Corresponding author. Tel.: +34915616800.
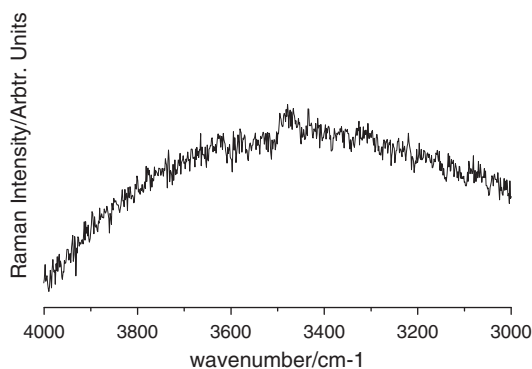*E-mail address:* sagrario@iem.cfmac.csic.es (S. Martínez-Ramírez).

Fig. 1. Raman spectrum of initial MK.

For this reason, this work uses Raman spectroscopy for the first time, to study in depth the effect of curing temperature on reaction kinetics in a pure MK/Ca(OH)$_2$ system (50:50 in weight), cured at 60 °C until 123 days of hydration.

2. Experimental

2.1. Materials

The chemical composition of the metakaolin (MK) and lime used in the study has been described previously (Frías and Sánchez de Rojas, 2003). MK and lime were mixed in the ratio 1:1 by weight and the water/solid ratio was 2:37. After mixing the samples were placed in a plastic airtight container and then left in a water bath at 60 °C for different time periods: 2 h; 6 h; 21 h; 30 h, 34 days and 123 days. This curing temperature was selected according to the heating results reported previously in MK–cement mortars (Frías et al., 2000). After the appropriate hydration time the samples were taken from the plastic containers and dried in an oven at 105 °C for 24 h.

2.2. Techniques

Micro-Raman measurements were taken with an RM 1000 Renishaw Raman Microscope System equipped with a laser 514 nm, a Leica microscope and an electrically refrigerated CCD camera. The spectra shown here were obtained with 50× magnification objective lenses. The laser output was 50 mW. Time acquisition was 10 s. The software employed for data acquisition and analysis was WIRE for Windows and Galactic Industries GRAMS/32TM. Five scans were recorded to improve the signal-to-noise ratio. Spectra at five different points were taken for each sample to minimize problems arising because of the possible lack of sample uniformity. The Raman spectra presented are the representative measurements of the 5 points.

3. Results and discussion

The vibration band characteristics of starting materials have been described in a previous work (Frías and Martínez-Ramírez, 2009). It is important to note that the MK spectrum showed a broad band with a small peak at about 3480 cm^{-1} due to OH vibrations (Fig. 1).

3.1. MK/Ca(OH)$_2$ system cured at 60 °C for 2 h

Fig. 2 shows the micro-Raman spectrum of the blend hydrated for 2 h. Main Raman bands of portlandite at 3616 cm^{-1} (O–H stretching) and 353 cm^{-1} (Ca–O lattice vibrations) cm^{-1} were identified. There is also a small signal at 1084 cm^{-1} ($\nu_4[CO_3]$) due to a carbonation reaction of the Ca(OH)$_2$ during handling and storage. There are three additional small signals at 3471; 3353 and 3224 cm^{-1} attributed to OH stretching vibrations of water molecules, the first one can be attributed to unreacted MK. A small broad band at ~680 cm^{-1} is generated by the Si–O–Si symmetrical bending vibrations in C–S–H gel indicating the small amount formation of this silicate.

3.2. MK/Ca(OH)$_2$ system cured at 60 °C for 6 h

The spectrum interval for 4000–3000 cm^{-1} shows a predominant signal at 3616 cm^{-1} attributed to the non-consumed portlandite (spectra not showed) and in some parts of the sample a band with a maximun at 3648 cm^{-1} and a shoulder at 3595-3516 cm^{-1} was observed. The first signal is due to OH present into C$_4$AH$_{13}$ (Frías and Sánchez de Rojas, 2003) and the second one can be due to OH from calcium aluminium hydrate phases (C$_4$AH$_{19}$, C$_2$ASH$_8$, etc.) that is confirmed by the broad band at 534 cm^{-1} $\nu_1[AlO_4^{5-}]$ (Fig. 3). The broadness of this band can confirm the presence of different AlO$_4^{5-}$ environments. According to Black et al. (2006), after C$_3$A hydration the initial band at 505 cm^{-1} shifts to 510, 530 and 540 cm^{-1} due to different hydration products, the first one is due probably to C$_4$AH$_{13}$ the second one to a calcium carboaluminate and the third one to C$_3$AH$_6$. At these ages a very small C–S–H band (about 680 cm^{-1}) is observed, according to previous results up to 12 h the predominant phase was C–S–H gel. Ríos et al. (2009) indicated that several poor crystalline materials occurred at shorter reaction times that can explain the broad band.
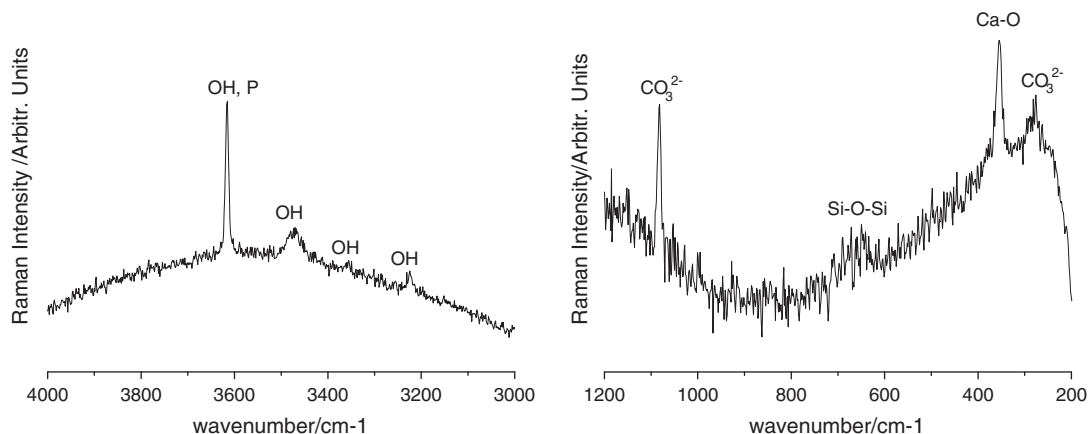

Fig. 2. Micro-Raman of the paste MK/Ca(OH)$_2$ cured at 60 °C for 2 h (p: portlandite).