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Mineral phases formation on the pozzolan/lime/water system

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ABSTRACT

In Spain, the paper industry recycles large amounts of waste paper in the new paper production process. Paper sludge thermal activation (calcination at 700 °C for 2 h) is an environment-friendly alternative source for metakaolinite (MK) to be used for the manufacture of blended cements or cement based materials.
This paper could contribute to standardization of the use of new pozzolanic products in cement based materials and its use mixed with saturated lime dissolution. In this process are obtained zeolite, CSH gel, hydrotalcite-like compounds, hydrated aluminate tetracalcium and stratlingite.
These materials are formed in different times of pozzolanic reaction.

1. Introduction

Cement is composed of numerous minerals, which react at different rates with water. This process results in hydration products of varied composition and crystallinity that influence the properties of the concrete. Water in the cement matrix is composed of evaporable and non-evaporable water. Evaporable water is defined as the water held in both capillary and gel pores. Non-evaporable water refers to water that is structurally combined in the hydration product.

Pozzolans from industrial by-products and waste have received much greater impetus ever since their use has been associated with additional technical advantages and environmental benefits. The cement industry has been the first in recycling and valuing industrial by-products and wastes as well as natural materials, incorporating them to the different production stages of the manufacture of blended cements (Taylor et al., 1985; Lilkov and Stoitchkov, 1996). Experiments using palm oil, rice husk and fly ash are reported in the literature (Chindaprasirt et al., 2007). The term "pozzolana" is associated with all siliceous/aluminous materials, which, in finely divided form and in the presence of water, react chemically with $Ca(OH)_2$ to form compounds that possess cementitious properties (Sabir et al., 2001).

Calcined paper sludge made from deinked paper sludge produced in the paper recycling industry is classified as an inert waste, and in most cases it is destined either for the rubbish tip or for use as an alternative fuel in the ceramic and cement sector (Frías et al., 2007). Over recent years, many research projects have centred on a variety of new applications for this industrial waste. The use of its two principal mineral compounds, kaolinite and calcite, as mineral admixtures in cement and the most appropriate conditions for their production are now key research areas of enormous interest (Pera and Amrouz, 1988; Frías et al., 2000, 2007; Vigil de la Villa et al., 2004; Sabador et al., 2007), which form the starting point for this project.

Pozzolan/lime/water system is very simple and helping the interpretation of behaviour cement with the pozzolan. The knowledge of the hydration products generated during the pozzolanic reaction, by its morphological characteristics as well as by its chemistry and structural composition will be determinant for the use of the pozzolan.

The aim of the present work is identified the mineral phases present, by reactions on the metakaolinite (MK)/CaO saturated dissolution system cured at 40 °C and 1, 7, 28, 90, 180 and 360 days of reaction, when the MK comes from the calcination of the paper sludge to 700 °C for 2 h (Frías et al., 2004, 2008a; Bakolas et al., 2006; García et al., 2008).

The present research is a part of an experimental study about the obtaining of recycled metakaolinite from a Spanish paper sludge waste as complementary cementing material.

2. Materials and methods

Press-paper sludge was used in this work. It came from the company Holmen Paper Madrid, S.L., located in Madrid; a company

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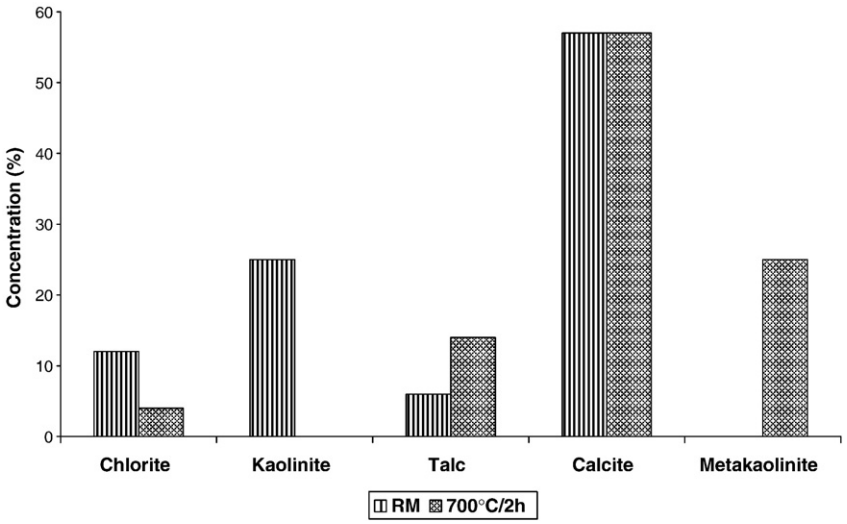

Fig. 1. Mineralogical composition by XRD for raw material (RM) and calcined paper sludge from 700 °C/2 h.

exclusively using 100% recycled paper as raw material. The dry paper sludge was thermal treated in an electrical laboratory furnace at a heating rate of 20 °C/min to 700 °C for 2 h. The calcined product was cooled at room temperature in desiccators. Then, it was ground and sieved to a particle size of under 45 μm. Further information concerning paper sludge pozzolanic activation is reported by authors in other scientific contributions (Vegas et al., 2006; Vigil de la Villa et al., 2007).

These materials were mixed with an CaO saturated dissolution and were curate in an electric oven at 40 °C during 1, 7, 28, 90, 180 and 360 days of reaction as these are the conditions required to achieve one of the mechanical requirements for the cement mortar strength (European Standard UNE EN 197-1, 2000).

Mineralogical analyses were carried out by X-ray diffraction (XRD) using a SIEMENS D-5000 analytical powder diffractometer with an automatic divergence slit, graphite monochromator and Cu Kα radiation. Non-oriented specimens were prepared for general XRD but for the characterization of starting clays oriented specimens were also prepared by sedimentation of the <2 μm fraction on a glass slide (Barahona, 1974; Brindley, 1984). The XRD data were collected in the angular range $3° \leq 2\theta \leq 65°$ with step 0.03° and counting time 3 s (Moore and Reynolds, 1997). The current and voltage intensity applied to the generating X-ray tubes has been of 30 mA and 40 kW and the divergence and receipt splits of 1 and 0.18°, respectively. For the checking of the phyllosilicates it is used the oriented and solvated aggregate with ethylene glycol method. The different minerals from the total percentage have been calculated by the relation between the characteristic peaks areas. To quantify the components in the bulk sample the procedure proposed by Schultz (1964) was used.

The textural study of the material was accomplished using electronic microscopy sweep in equipment PHILIPS XL-30 with wolfram source. The powder samples were fixed to the metallic slide through a graphite plate, in equipment BIO-RED SC-502. Also, it was accomplished with chemical analyses by EDX with silicon detector/lithium and analyzer DX41. Data shown in the tables are the average value of ten measures, carried out in different fields.

Systematic observations were performed using an SEM-EDX device (PHILIPS XL30, W source, DX4i analyzer and Si/Li detector). The analyzer was previously calibrated with a multimineral sample: the USGS standard ADV-1 (Govindaraju, 1994).

Chemical compositions were obtained from an average value of ten analyses for each sample; in this case the value is close to the standard deviation. These analyses were performed on clean surfaces to avoid, as far as possible, all sources of contamination.

3. Results and discussion

We have analysed by DRX two samples: raw material (RM) (paper sludge) and calcined paper sludge at 700 °C/2 h. The semiquantitative analysis is show in the Fig. 1. RM shows chlorite, kaolinite, talc and calcite. When the paper sludge is calcined to 700 °C/2 h the minerals stay, but the kaolinite disappear and is transformed in to metakaolinite (MK) (Frías et al., 2008b; García et al., 2008).

The XRD patterns of the calcined paper sludge at 700 °C/2 h elaborated (MK/saturated lime dissolution) and cured in furnace to 40 °C during 1, 7, 28, 90, 180 and 360 days of reaction are shown in the Fig. 2, and their semiquantitative mineralogical analysis are in the Fig. 3.

Talc, chlorite and calcite, minerals from the raw material, are shown to the all pozzolanic reaction age (Fig. 4). Talc concentration is constant but the calcite concentration decrease from the beginning just 28 days of reaction, and then it increases gradually until the finings pozzolanic reaction at 360 days. This fact is related to the incorporation of the carbonate group to the hydrotalcite type phases,

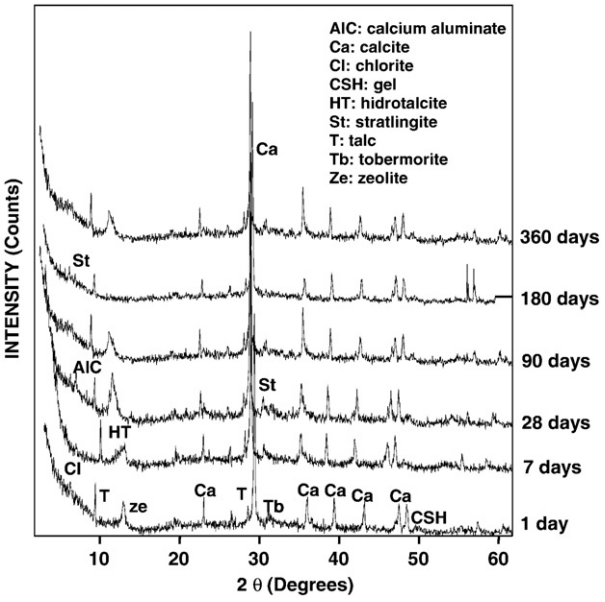

Fig. 2. XRD patterns of the 1, 7, 28, 90, 180, 360 days of pozzolanic reaction.