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Calcination of art paper sludge waste for the use as a supplementary cementing material

Moisés Frías [a,*], Rosario García [b], Raquel Vigil [b], Sergio Ferreiro [a]

[a] Instituto Eduardo Torroja, CSIC, C/ Serrano Galvache, 4, 28033 Madrid, Spain
[b] Dpto de Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma, 28049 Madrid, Spain

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Abstract

This study shows the effect of calcination clay wastes from an art paper sludge for the use as supplementary cementing materials in blended cements.

The starting clay sludge rich in kaolinite and talc was calcined at 600, 650 and 700 °C between 2 and 5 h, kaolinite was transformed into amorphous metakaolinite.

This study reveals that calcination at 650 °C for 2 h is recommended to obtain a good supplementary cementing material for manufacture of blended cements.

Keywords: Art paper sludge; Clay minerals; Thermal activation; Metakaolinite; Supplementary cementing material

1. Introduction

The use of supplementary cementing materials for the manufacture of blended cements is well known during the last decades. According to the existing standards UNE-EN 197-1 (2005), these additions are generally natural pozzolans from volcanic and by-products like fly ash, silica fume, blast furnace slag. However, the thermally activated clayey minerals in cement manufacture are not used although they have excellent qualities. Furthermore, the previous researches are focused, mainly on kaolinite (Ambroise et al., 1985; Taylor, 1997; Palomo et al., 1999; Moropoulou et al., 2004; Ali and Wahid, 2006).

The reactivity of metakaolinite varies with thermal treatment (Rocha and Klinowski, 1990) during calcination (450 °C–600 °C) and turns into metakaolinite (Grim, 1968), a material with some degree of order. In metakaolinite, the Si–O network remains largely intact while the structure of Al–O network is reorganized, metakaolinite offers good properties as supplementary cementing material. It reacts particularly well with lime and forms hydrated compounds of Ca and Al silicates in water (Frías et al., 2000; Sabir et al., 2001; Frías and Sánchez de Rojas, 2003; Moropoulou et al., 2004; Saikia et al., 2006; Singh and Garg, 2006; Frías, 2006; Bacolas et al., 2006).

From the environmental point of view, paper sludge wastes should be recycled obtain metakaolinite. Previous studies have shown the good qualities of these calcined clay wastes as highly pozzolanic materials (Pera and Amrouz, 1998; Frías et al., 2004; Banfill and Frías, 2007; Vegas et al., 2006).

Due to the chemical and mineral composition of these clayey paper wastes, products calcined at 700–800 °C showed decreased reactivity as a consequence of the combination of three fundamental aspects: decarbonation, formation of new phases and less reactive surface (Vigil et al., 2007).

As no reports are available on the activation of this type of clay waste under 700 °C, the present study shows the morphological and mineralogical changes of the clay minerals 600–700 °C during 2 and 5 h.

* Corresponding author. Fax: +34 91 3020700.
E-mail address: mfrias@ietcc.csic.es (M. Frías).

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2. Materials and experimental methods

2.1. Art paper sludge

The starting clay waste was an art paper sludge from the Holmen Paper Madrid, S.L. This European industry is the only one that uses 100% the recycled paper as raw material.

The dry art paper sludge after 24 h at 105 °C has been calcined in a laboratory programmable furnace at 600, 650 and 700 °C during 2 and 5 h. The calcined products were ground in a mortar and then sieved below 45 µm. The samples were designed such as 600/2 (sample calcined at 600 °C from 2 h), 600/5 (sample calcined at 600 °C from 5 h) 650/2 (sample calcined at 650 °C from 2 h), 650/5 (sample calcined at 650 °C from 5 h) and 700/2 (sample calcined at 700 °C from 2 h).

2.2. Chemical, mineralogical and textural characterization

Chemical characterization was carried out by X-ray fluorescence (Philips PW 780, an anticathode tube of rhodium of 4 kW). The loss of ignition (L.O.I.) was calculated according to the existing European standard (EN 196-2, 1996).

The mineralogical composition was studied by X-ray diffraction (XRD) using random powder of the bulk sample and oriented slides of the <2 µm fraction (Moore and Reynolds, 1997). The X-ray diffractometer was a SIEMENS D-500 (Cu anode, 30 mA, 40 kV) the procedure proposed by Schultz (1964) was used to quantify the components.

Morphological characterizations were done using a SEM-EDX devise (PHILIPS XL30, W source, DX4i analyser and Si/Li detector). The analyser was calibrated with a multimineral sample: The USGS standard ADV-1 (Govindaraju, 1994). The chemical composition was obtained by an average value of ten analyses for each sample.

2.3. Pozzolanic activity method

An accelerated method was used to study the pozzolanic activity of calcined sludge. The test consisted of introducing these calcined clay wastes in a saturated lime solution at 40 °C for 1, 7, 28 and 90 days. At the end of each period, the CaO concentration in the solution was analysed (Frías et al., 2004). The adsorbed lime (mMol/L) was obtained as difference between the concentration in the saturated lime control solution and the CaO found in the solution in contact with the sample. A commercial metakaolinite was also used as reference.

3. Results and discussion

3.1. Chemical and mineralogical composition of starting paper sludge

The starting paper waste was composed mainly of SiO_2 (10.7%), Al_2O_3 (6.7%) and CaO (24.2%) (Table 1). The ignition loss was of 55.7% and the rest of oxides were below 1% in weight. Traces of chloride ions (0.06%) could be detected in the starting paper sludge, depending on the origin of the recycled paper.

According to the XRD patterns (Fig. 1) and chemical composition, the clayey waste was mainly formed by kaolinite (12.3%) and calcite (43%) and, in minor proportions some phyllosilicates such as chlorite, micas and talc (with a total percentage of 7.1%). An organic matter content of 34.9% was determined.

Table 1
Chemical composition of starting and calcined art paper sludges by XRF

Composition (%)	Raw sludge	600 °C/ 2 h	600 °C/ 5 h	650 °C/ 2 h	650 °C/ 5 h	700 °C/ 2 h
SiO_2	10.69	20.24	20.65	21.06	21.44	22.32
Al_2O_3	6.74	13.11	13.38	13.58	13.87	14.55
Fe_2O_3	0.41	0.52	0.52	0.54	0.54	0.56
CaO	24.15	36.39	37.20	37.81	38.55	40.21
MgO	0.96	2.15	2.20	2.24	2.30	2.35
SO_3	0.30	0.28	0.28	0.29	0.29	0.32
K_2O	0.22	0.34	0.34	0.35	0.35	0.37
Na_2O	0.24	0.08	0.08	0.09	0.09	0.09
TiO_2	0.21	0.24	0.25	0.25	0.25	0.26
P_2O_5	0.16	0.17	0.17	0.17	0.18	0.18
L.O.I.	55.71	26.24	24.68	23.36	21.93	18.52

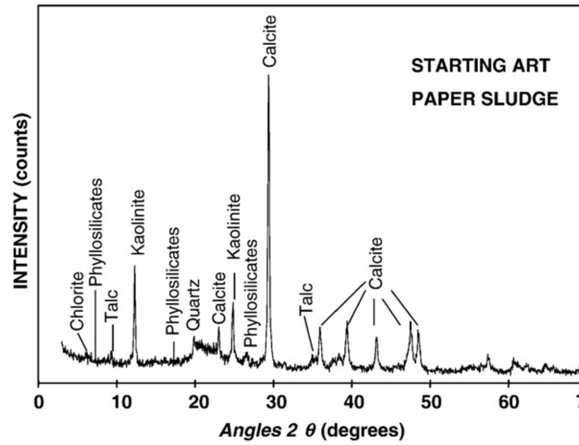

Fig. 1. XRD pattern for the starting art paper sludge.

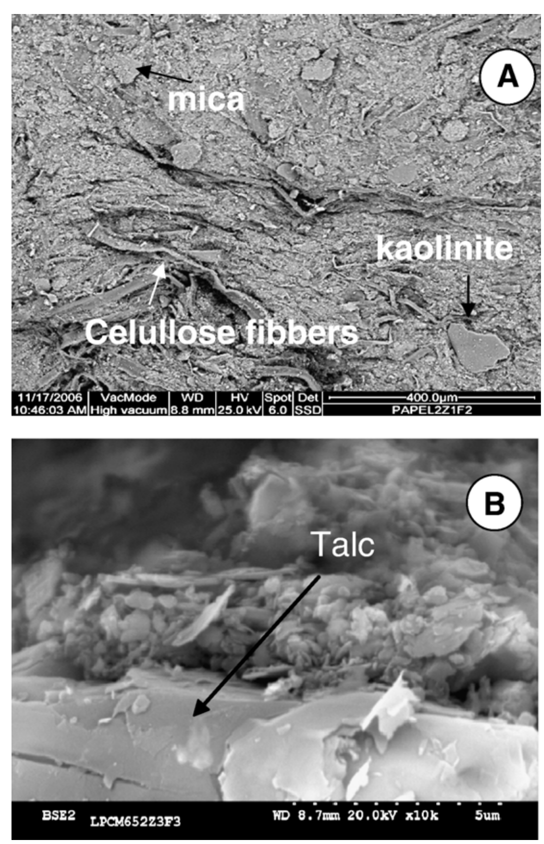

Fig. 2. A) Cellulose fibbers, kaolinite and micas in the raw sludge. B) Talc crystals in the raw sludge.