Research Paper

New developments in low clinker cement paste mineralogy

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ABSTRACT

The use of industrial waste as a cement addition often changes the composition and development of the hydrated phases and with them matrix performance and durability, in particular at later ages. The effect of the presence in blended cement of 20% to 50% kaolinite based activated carbon waste (ACW) on paste hydration has been characterized by means of XRD, SEM/EDX, TG/DTG, NMR and FTIR to identify and monitor the mineralogical phases forming in materials at ages of up to 180 d. The results showed that the main reaction products forming in the first 7 d included C-S-H gels, C_4ACH_{12} and C_4AH_{13} (hydroxy-AFm). Whilst monocarboaluminate (Mc) content declined with rising percentages of ACW, the amount of hexagonal phase hydroxy-AFm rose. Then microstructure of the C-S-H gels developing in the OPC and the 50% additioned paste differed. Compact C-S-H gel plates, and phyllosilicate-like laminar spongy microplates with high polymerised C-S-H gel formed in the blended cement paste.

1. Introduction

The cement industry's standard reuse of large amounts of industrial waste and by-products as supplementary cementitious materials has a very beneficial effect on its sustainability as well as on socio-economic development. Not only does the end product have a smaller environmental footprint (lower CO_2 emissions) and lower energy consumption which translates into lower costs, but also improves upon cement performance (Juenger and Siddique, 2015; Stark, 2011; Medina et al., 2017; Mohammed et al., 2016; Wang et al., 2016). In keeping with European legislation on commercial cement manufacture (European Committee for Standardization, 2011) thermally activated pozzolans, whether natural or industrial (such as fly ash, silica fume or blast furnace slag), have traditionally been added to cement at replacement ratios (alone or mixed) of up to 55%, depending on the type of cement. Given that worldwide cement production stands at around 4.2 billion tonnes/year, with demand predicted to rise substantially by 2050, natural pozzolan consumption is expected to be very high. The scientific community is consequently exploring industrial by-products as a possible source of other types of pozzolanic materials.

Kaolinite-based waste has been the object of a recent line of research as an alternative to the kaolinite extracted from natural quarries (Chakchouk and Samet, 2012; Rodríguez et al., 2013; Frías et al., 2013; Frías, 2006). The sludge generated by the paper industry, which

recycles paper into cellulose, is one such waste (Segui et al., 2012; Monte et al., 2009; Yan et al., 2011). Of the over 14.4 million tonnes produced in Europe yearly, 70% is generated during the manufacture of de-inked recycled paper. Earlier studies (Frías et al., 2015; Vigil et al., 2007; Vegas et al., 2014; Goñi et al., 2013) laid the scientific-technical grounds for converting kaolinite/calcite-based industrial waste to a high pozzolanicity product, identifying the main hydrated phases to be C-S-H gels, metastable hexagonal phases (hydroxy-AFm and C_2ASH_8), C_4ACH_{11} and layered double hydroxide (LDH)-like structures such as carbonate and metakaolinite (MK).

Research presently focuses on by-products such as coal mining waste (kaolinite/mica) (Fan et al., 2014; Modarres and Ayar, 2014; Frías et al., 2012), the stockpiling of which in areas around mines poses substantial environmental problems (Haibin and Zhenling, 2010; Dontala et al., 2015). According to the information available (BP Statistical Review of Wold Energy, 2017), worldwide coal output amounted to 19.350 Gt in 2016, and the respective waste to 40% of site production, depending on geology and mine conditions. When thermally activated at 500 °C to 900 °C for 2 h, such clayey waste can be converted to a metakaolinite-containing pozzolan, activated coal waste (ACW) (García et al., 2015; Vigil et al., 2017) although the activation conditions must be controlled to prevent the formation of quasi-stable dehydroxylated mica (Vigil et al., 2014).

To date, research has focused on the pozzolanicity of ACW/lime

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system, in which the hydrated phases identified include C-S-H gels, Hydroxy-AFm, C_2ASH_8 and LDH-like phyllosilicate/carbonate structures. The use of coal waste as a component in blended cements is a line of research scantly pursued by the scientific community, with the few papers available all dealing with its technical properties (Modarres et al., 2017; Beltramini et al., 2010; Vegas et al., 2015). In a previous paper, Frías et al., 2016 reported the reaction kinetics of blended cement pastes containing up to 20% ACW. They identified C-S-H gels, ettringite (Et), hydroxy-AFm and C_4ACH_{12} as the phases primarily involved in the synergies between cement hydration and the pozzolanic reaction.

Insight into the behaviour of such binary cements, presently unknown, would contribute to a deeper understanding of low cement content and hence low CO_2 systems.

This study, the first to explore 20% to 50% activated coal waste cement hydration used XRD, SEM-EDX, TG/DTG, FTIR and NMR techniques to identify and monitor the hydrated phases in 1 d, 7 d, 28 d, 90 d and 180 d pastes.

2. Experimental

2.1. Materials

Spanish coal mining waste from an open-pit mine (Sociedad Anónima Hullera Vasco-Leonesa, León) was thermally activated at what are generally regarded as optimal conditions (García et al., 2016): 600 °C for 2 h in an electric muffle furnace. The product (ACW) was subsequently ground to particle sizes of under 90 μm.

Further to the requirements laid down by the European Committee for Standardization (2011) for the manufacture of type II A/B commercial cements, a CEM I 52.5R commercial Portland cement was used in this study. The D_{90} (diameter through which 90% of the product passes) for the cement was 35.9 μm and 32.6 μm for the waste. The chemical composition of the starting materials is given in Table 1;

while the mineralogy by Rietveld of the starting materials is collected inTable 2 and the datasets for phase identification in Table 3, using X^2 as an index of disagreement or goodness of fit to the quotient between Rwp and Rexp.

The blended cements contained 0%, 20%, 30% or 50% ACW. Prismatic (1x1x6 cm) cement paste specimens were prepared at a water/binder ratio of 0.5, to which 40% solid Sikament FF superplasticiser was added to attain the same fluidity as in the reference paste. The mixing water was corrected for the admixture water to maintain a constant water/binder ratio. All the specimens were cured in water for up to 180 days. After each curing period they were immersed in acetone for 24 h and vacuum dried for a further 24 h to stop cement hydration.

2.2. Methods

The chemical composition of the starting ACW and OPC samples was analysed on a Philips (Eindhoven, Netherlands) PW 1404 X-ray fluorescence analyser fitted with an Sc−Mo X-ray tube and Super-Q Manager analytical software.

The mineralogical composition of the bulk samples was determined by random powder X-ray diffraction (XRD) on a Siemens D-5000 (Munich, Germany) X-ray diffractometer fitted with a Cu anode. Their operating conditions were 30 mA and40 kV and divergence of 2 and

0.6 mm with reception slits, respectively. The samples were scanned in (2θ) 0.041 steps with a 3-scount time.The characterization of bulk samples was carried out using the random power method operating from 3° to 70° 2θ at a rate of 2°/min (Moore and Reynolds, 1997). The XRD patterns were analysed with the Match 3 Rietveld Fullprof software (Match; Fullprof) using the Inorganic Crystal Structure Database (ICSD) (Allmann and Hinek, 2007) and the Crystallography Open Database (COD) (Grazulis et al., 2012). Rietveld quantification (Rietveld, 1967, 1969) accuracy is typically presented in terms of constants R and X^2. While, R only compares peak intensities calculated from the spectra of the material to the intensity of the experimentally line, the X^2 calculation in phase weight as well. Ideally, both constants should be equal to 1. Due to discrepancy between observed and calculated data, however, which are particularly significant for materials comprising more than three phases, X^2 values of 20 to 5 are generally accepted as satisfactory for valid results.

In light of the optics of all the data gathering instruments used (including Bragg Brentano geometry, Cu Kα1 wavelength, fixed divergence and Soller slits), the pseudo-Voigt function was chosen as the most suitable to describe peak shape in the preliminary fit performed. The information on the structural parameters listed for the phases on their COD or ICSD cards was entered. The parameters were refined in the recommended order (McCusker et al., 1999): first the global parameters, i.e., background functions (the Chebyshev polynomial function, using three variable coefficients), zero shift and scale factors, followed by the unit cell parameters for each phase. The March-Dollase function, normally apt for correcting preferred orientation in flat-plate specimens, was applied (Dollase, 1986). The instrumental polarisation factor (0.7998) and optics used in these diffraction trials were applied to modify peak shape and isotropic and anisotropic factors. Two corrections to optimise the fit were introduced during the refinement cycles: for micro-absorption (Brindley, 1951) to minimise the effect of different absorption coefficients for the phases present in the mix and for diffraction peak alternations using the Caglioti equation (Caglioti et al., 1958).

Sample morphology and microanalysis were determined with SEM/EDX on an Inspect FEI electron microscope (Hillsboro, OR, USA), fitted with a W source, DX4i energy dispersive X-ray analyser and a Si (Li) detector. Freshly cut samples were observed using a backscattered electron (BSE) detector, whereas the gold-sputtered field samples were examined with a high-vacuum imaging secondary electron detector (resolution: 3.0 nm at 30 kV [ETD],10 nm at 3 kV [ETD], and 4.0 nm at 30 kV [BSE]). The accelerating voltage was 26–30 kV and the working distance 10 mm. Sample microanalysis was conducted on an Oxford Instruments INCA Energy 200 energy dispersive X-ray spectrometer, running at 20 kV. SEM-EDS precalibration tests were conducted with internal standards to improve ZAF correction. The chemical composition, found as the mean of 10 scans per sample, is shown in Table 4 together with the standard deviation. These semi-quantitative analyses were performed on clean surfaces to prevent contamination as far as possible. The findings are expressed in wt% of oxides.

Sample particle size distribution was determined with a Malvern Mastersizer 3000 laser granulometer(Great Malvern, UK), with air as the dispersing medium (Frías and Sánchez de Rojas, 1997).

Thermogravimetric studies (TG/DTG) were conducted with an SDT Q600 V20.9 Build 20 analyser on 45 mg to 50 mg powder samples, heated at a rate of 10 °C/min in an N_2 (100 mL/min) atmosphere.

Pellets in which 1.2 mg of hydrated paste sample were mixed with

Table 1
Chemical compositions (%) of OPC and ACW.

Materials	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	K$_2$O	Na$_2$O	SO$_3$	TiO$_2$	P$_2$O$_5$	LOI
OPC	20.80	5.70	2.89	58.99	1.89	1.36	0.93	4.11	0.15	0.26	2.79
ACW	52.63	25.29	4.64	4.20	0.77	3.09	0.17	0.27	1.17	0.14	3.09