Cement and Concrete Research 85 (2016) 39–47

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Novel high-resistance clinkers with 1.10 < CaO/SiO$_2$ < 1.25: production route and preliminary hydration characterization

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ARTICLE INFO

Article history:
Received 3 August 2015
Accepted 24 March 2016
Available online xxxx

Keywords:
Clinker
Amorphous material
Thermal treatment
Hydration products
Compressive strength

ABSTRACT

New amorphous calcium silicate binders, hydraulically active, were produced by a process consisting in fully melting and rapid cooling of a mixture of typical raw materials (limestone, sand, fly-ash and electric furnace slag) with overall CaO/SiO$_2$ molar ratios (C/S) comprised between 1.1 and 1.25. Pastes were produced from these materials by mixing them with water in a water/binder ratio of 0.375. Compressive strength was determined at the ages of 7, 28 and 90 days and the hydration of these pastes was followed during this period by XRD, FTIR and ^{29}Si MAS-NMR. Tobermorite-like structures with low C/S and semi-crystalline character were observed to develop upon hydration of these new amorphous calcium silicate hydraulic binders. Moreover, no Portlandite was formed during hydration of these materials. The maximum compressive strength after 90 days is above 40 MPa. TGA was performed in order to determine the amount of structural water present in the pastes and their content related to the amount of hydrated products obtained. The relation between compressive strength and the amount of hydration products was investigated and some considerations about the mechanical properties of the hydration products and paste microstructure were inferred.

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1. Introduction

The production of cement has been following the evolution of modern society as it provides a cost-effective, durable and strong material to nearly all types of infrastructural installations, buildings and houses [1]. As a consequence, the volume of cement production has been increasing year after year and is expected to reach a value of 4 billion metric tons annually in the next decade [2]. Although this growth is a positive factor for economic and social development, its environmental impact is an issue that deserves particular attention since for every ton of cement produced, nearly 800 kg of CO_2 are emitted to the atmosphere. Because of this, nowadays, the cement industry is responsible for about 5% of the total anthropogenic CO_2 emissions [3,4].

Most of the CO_2 emitted in the process results from the decarbonation of the limestone used in the production of clinker (~55%), being around 45% of the total CO_2 emitted distributed by the burning of fuel (~35%), grinding, mining and transportation [4]. The need for the reduction of carbon dioxide emissions in cement industry has led to a remarkable process optimization, resulting also in several eco-friendly solutions, as energy recovery from waste valorisation or the incorporation of by-products generated by other industries. Furthermore, the subject of CO_2 emissions reduction drove the development of new alternatives that went beyond the optimization of existing process. Among these alternatives are, for example, the developments of belite-rich clinkers or sulfoaluminate clinkers [5–12].

In a recent publication [13], the authors presented a new family of amorpho-dendrictic clinkers hydraulically active with a CaO/SiO$_2$ ratio (C/S from now on) of 1.4. In this work, we went further on the decrease of the C/S ratio by proposing a different route: full amorphization of the clinker. This approach will impact on the CO_2 emitted in the production process, namely, in the decarbonation stage, reducing about 33% of the amount of CO_2 originating from the raw mix. The results presented in this paper are protected by PCT/PT2015/000006 "Amorphous Low Calcium Content Silicate Hydraulic Binders and Methods for Their Manufacturing".

2. Experimental section

2.1. Materials and processing conditions

Two new amorphous calcium silicate hydraulic binders were produced by using a combination of raw materials common in the cement industry in such a way that the obtained overall C/S molar ratios were 1.1 and 1.25. Table 1 shows the composition of the raw materials used

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http://dx.doi.org/10.1016/j.cemconres.2016.03.006
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Table 1
Raw materials composition and raw mix combinations used for the production of the amorphous hydraulic binders with C/S molar ratios of 1.1 and 1.25.

C/S molar	1.1	1.25	Composition (wt%)												
Raw materials	wt%	wt%	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	MnO	Cr_2O_3
Fly-ash	2.28	2.24	4.54	54.48	22.82	8.29	3.78	1.49	0.11	1.76	0.59	–	–	––	–
Sand	32.93	30.11	0.37	97.30	1.29	0.16	0.00	0.02	0.00	0.52	0.11	–	–	–	–
Limestone	62.67	65.56	43.34	0.92	0.17	0.13	54.83	0.22	0.01	0.01	0.07	–	–	–	–
Slag	2.12	2.08	0	13.90	8.26	43.54	21.18	6.06	0.40	0.00	0.00	0.46	0.46	3.76	1.98
1.1 Clinker (sample A)	100	–	–	46.85	1.70	1.75	48.03	0.43	0.02	0.30	0.13	0.01	0.01	0.11	0.06
1.25 Clinker (sample B)	–	100	–	43.84	1.66	1.75	51.07	0.44	0.02	0.28	0.13	0.01	0.01	0.11	0.06

(limestone, sand, electric furnace slag and fly-ash) and the final theoretical composition of the two prepared amorphous calcium silicate hydraulic binders.

After mixing these raw materials, approximately 120 g of raw meal was pressed with a force of around 100 kN to a disc shape with 10 cm diameter and 1.5 cm height. The disc was then broken into four pieces and placed in platinum crucibles which were moved inside and outside the furnace by means of a platinum crucible holder.

The production process used consisted in the following procedure and is schematically exemplified in Fig. 1:

A. Heating the raw mix at a rate $R_1 = 25$ °C/min to a temperature T_1 of 1500 °C
B. The temperature T_1 (in the liquid region) was maintained constant for a period $t_1 = 60$ min allowing the homogenization of the composition
   Cooling the system to room temperature naturally in air at cooling rate R_2 of approximately 300 °C/min, which can be achieved by simply removing the sample from the furnace and let it to cool in air under laboratory ambient.

After quenching, the obtained amorphous hydraulic binders were mechanically removed from the crucibles, by breaking the bulk sample in the interior and tapping its bases with a flat rigid object, and ground in a ring mill for 180 s with propanol, followed by a drying step at 50 °C in a stove for about 1 h. The grinding process did not introduce any changes of microstructure detectable by XRD. The ground powder had a particle size below 35 μm and was used to produce pastes by mixing it with water at a water/binder weight ratio of 0.375. The pastes were poured into proper moulds with dimensions of $20 \times 20 \times 40$ mm^3 and cured in a moisture-controlled environment with a relative humidity over 95%. The prisms were demoulded at 7 days immediately before the compressive strength test. At 1 and 2 days of age, the pastes didn't gain enough consistency to be demoulded and tested. Additionally, a clinker paste prepared from a clinker powder ground to a Blaine fineness of about 350 m^2/kg was produced under the same conditions. This paste was used only for mechanical behaviour comparison with the new amorphous hydraulic binders. The clinker main phases were estimated by XRD using Rietveld method, with the following values being obtained: C_3S ~78%, C2S ~4%, C_3A ~3% and C_4AF ~14%. Hydration evolution and compressive strength measurements were performed at the ages of 7, 28 and 90 days, so that a relationship between hydration products development and mechanical properties could be established over time.

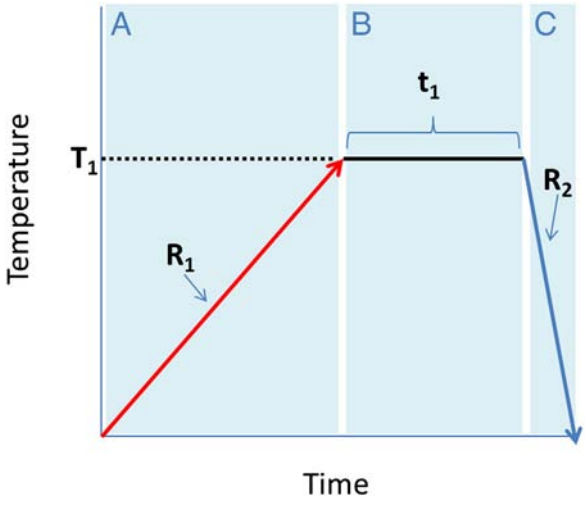

Fig. 1. Procedure used in the production the amorphous hydraulic binders.

2.2. Characterization methods

Both the anhydrous clinkers and their respective pastes, at the ages of 7, 28 and 90 days, were characterized for the purpose of structural assessment, phase development and mechanical performance.

Compressive strength tests were performed at 7, 28 and 90 days of hydration in paste prisms with dimensions $20 \times 20 \times 40$ mm^3 in an Ibertest Autotest 400/10 equipment using standard test procedures, namely, a 2.4 kN/s force rate was applied during the compression tests. Three prisms per sample were tested at each age. After compressive strength testing, the pieces of the pastes with 28 and 90 days were ground in an agate mortar, dried at 105 °C and sealed in vacuum for further utilization in other characterization procedures, with exception for the thermogravimetric analysis (TGA) on which all the samples (7, 28 and 90 days) were used immediately after the compressive tests in order to assess the amount of water contained in the structure of the hydrated products. TGA experiments were performed in an ELTRA equipment running at constant heating rates between fixed temperature steps that evolved until constant mass at temperatures of 105 °C, 250 °C, 500 °C and 950 °C. A heating rate of 4 °C/min was applied in the first step (from room temperature to 105 °C), while in the second step (between 105 °C and 250 °C) a heating rate of 10 °C/min was used. The two last steps (from 250 °C to 500 °C and between 500 °C and 950 °C) ran at a heating rate of 15 °C/min.

X-ray diffraction was performed in a X'Pert Pro (PANalytical) diffractometer using monochromatic CuKα1 radiation ($\lambda = 1.54059$ Å) and working in reflection geometry ($\theta/2\theta$). The optics configuration was a fixed divergence slit (1/2°), a fixed incident anti-scatter slit (1°), a fixed diffracted anti-scatter slit (1/2°) and X'Celerator RTMS (Real-time Multiple Strip) detector, working in scanning mode with maximum active length. Data for each sample were collected from 5° to 70° (2θ). The samples were rotated during data collection at 16 rpm in order to enhance particle statistics. The X-ray tube worked at 45 kV and 40 mA. The amorphous content of the samples produced, both anhydrous and hydrated, was determined by adding 20% in weight of corundum (99.9% α-Al_2O_3 from Alfa Aesar) as an internal standard, whose peaks are identified in Figs. 3 and 4 as (*). Phase quantification was performed through Rietveld analysis using the Panalytical software Highscore Plus, following the same procedure adopted by these authors in a previous article [13] and whose theoretical basis can be found elsewhere (e.g. see Bish and Howard [14]).

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