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Characterisation of pre-industrial hybrid cement and effect of pre-curing temperature

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ABSTRACT

This study aimed to determine the physical-mechanical, mineralogical and microstructural properties of a pre-industrially manufactured hybrid cement (HYC) containing 5% alkaline activator and less than 30% clinker. The effect of the initial curing temperature (25 ± 1 or 85 °C for 20 h) on hydration kinetics and the development of compressive strength were also explored. The hydration products formed were characterised using XRD, SEM/EDX and ^{27}Al and ^{29}Si MAS-NMR. The findings showed that pre-industrial hybrid cement sets when hydrated with water and hardens to a 28-day mechanical strength of 35 MPa. The main reaction product formed was a mix of cementitious gels: C-(A)-S-H and C-A-S-H. Curing at 85 °C for 20 h, shows a behaviour similar to OPC, inhibited ettringite formation and generated more polymerised gels, enhancing 3-day but not 28- or 90-day mechanical strength.

1. Introduction

Since Portland cement (OPC) was patented in the nineteenth century, its use has spread worldwide, making it one of humanity's most prevalent structural materials. That predominance is attributable to its low cost, high mechanical strength and universal availability [1,2]. Today, however, the cement industry is faced with higher production costs due to: i) rising energy prices the worldwide, which are mirrored nearly linearly in cement costs; ii) shortage of supply of quality raw materials; and iii) the need to reduce CO_2 emissions (OPC manufacture generates nearly two billion tonnes/year of CO_2 emissions, accounting for 8–10% of anthropogenic emissions worldwide [3]). As a result, both the scientific and technical communities are working to develop alternative cements and binders [1,4–6].

One effective way of lowering the CO_2 emissions associated with OPC manufacture is to use the so-called alkaline cements or geopolymers [4–7] developed in recent decades. Any contention that alkaline cements can replace OPC in all of its many applications at this time is hardly realistic, however. One possible intermediate solution (with scant technical, logistic or economic implications) might consist in reducing the clinker content in cement as far as possible and expanding the use of supplementary cementitious materials (SCMs) such as natural pozzolans or industrial by-products (fly ash or slag) [8–11]. The problem posed by using large amounts of SCMs, however, is that they lengthen setting times and lower the initial mechanical strength of mortars and concretes. As in alkaline cement production, solid or liquid activators (new admixtures developed for this purpose) can be used to circumvent that problem. The combination of traditional OPC and alkaline cements yields what are known as hybrid cements (HYC) [5,12,13].

Hybrid cements are the result of alkali-activating low (20–30%) clinker content blended cements with an alkaline activator added in a proportion of approximately 5%. The remaining 65–75% of the blend consists of supplementary cementitious materials (SCMs), either natural pozzolans or industrial by-products such as fly ash from coal-fired power plants or blast furnace slag. In Europe, the amount of supplementary materials (SCMs) that can be used as additions in Portland cement is limited by the existing legislation (EN 197-1). Elsewhere, however, such as in the USA (ASTM standard C1157/C1157M-11) and certain Latin American countries (as Colombia, NTC 121), neither the chemical composition of cements nor of their components are restricted. As the standards in place there classify cements on the grounds of prescriptive and performance requirements, hybrid cements meeting those requirements could be commercialised immediately in such countries.

Alkaline activators (admixtures) are used in hybrid cements to

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hasten the initial SCM reactions. Moreover, solid alkaline activators such as deployed in this study feature an important additional technological advantage, for with them hybrid cement can be produced using traditional Portland cement manufacturing processes. Jointly milling clinker + SCMs + activator yields a powdery material that has merely to be mixed with water to set and harden [13,14]. The production of such cements (hereafter “hybrid cements”) therefore calls for an in-depth understanding of both traditional (OPC) and alkaline cement behaviour.

The type of reaction products formed in alkaline cement would be expected to depend largely on the reaction conditions: chemical composition of the starting materials, type and concentration of the alkaline activator and initial curing conditions, among others [4–7]. Two types of alkaline cements can be distinguished. ***a)*** In the alkaline activation of blast furnace slag (AABFS), temperature hastens initial strength development (as in OPC), although strength declines at more mature ages [15–17]. The C-A-S-H gel formed, as well as the secondary reaction products, are more crystalline than when heat is not applied. ***b)*** In the alkaline activation of fly ash (AAFA), curing temperature (between 65 and 90 °C) plays a very important role, as heat accelerates early age reactions, with the product exhibiting 1-day mechanical strength upward of 30 MPa [18,19].

Curing at a higher temperature, for instance, is known to expedite initial OPC hydration. The C-S-H gel formed during OPC hydration at temperatures >65 °C is more highly polymerised than when it forms at ambient temperature [20–22].

The effect of curing temperature on hybrid cements has not yet been studied, however. The present survey therefore pursued a dual objective. i) On the one hand, it aimed to verify the mechanical properties, composition and structure of the reaction products formed during the hydration of pre-industrially manufactured hybrid cement; ii) and on the other, to determine whether pre-curing temperature (25 ± 1 or 85 °C) plays a significant role in hydration.

2. Experimental procedure

2.1. Materials

The pre-industrial hybrid cement used was manufactured in at Latin-American cement plant (about 20 tons were manufacture). The process, consisting in the joint milling of Portland clinker, slag, fly ash and activator, is depicted in Fig. 1. The proportions used were 30% Portland cement clinker +32.5% BFS +32.5% FA +5% solid activator.

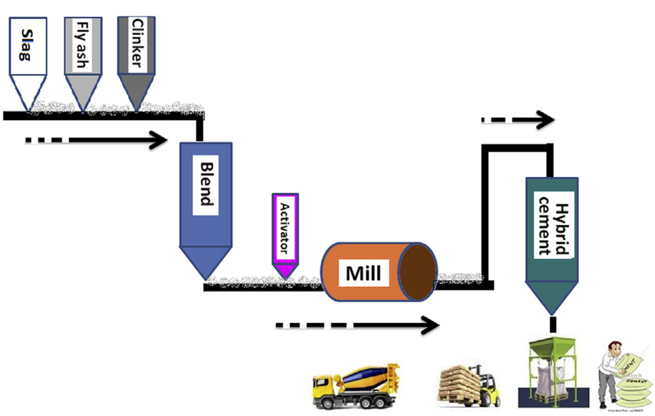

Fig. 1. Stages in HYC manufacture.

Table 1 gives the chemical composition of the pre-industrial hybrid cement (denominated CEM CC5) as determined on a Bruker S8 TIGER X-ray fluorescence analyser. Its mineralogy was found with a BRUKER AXS D8 ADVANCE X-ray diffractometer (XRD) and quantified using Rietveld refinement. Given the high vitreous content of pre-industrial hybrid cement, its quantification was based on an external standard (30% corundum) [23]. Particle size distribution was determined by laser granulometry using a *SYMPATEC* diffractometer with a measuring range of 0.90–175 μm. The powdery samples were dispersed with isopropyl alcohol to eliminate inter-particle Van der Waals and electrostatic forces.

The Rietveld-refined XRD pattern for the hybrid cement (CC5) is reproduced in Fig. 2 (30% corundum was used as a standard [23]). The quantification findings are given in Table 2. The clinker content in the pre-industrial hybrid cement appeared to be slightly higher than stipulated (on the order of 32.5% rather than the 30% specified).

Further to the particle size distribution findings shown in Fig. 3, 95% of the particles measured under 45 μm and 40% under 10 μm, meeting an important requirement for reactivity.

2.2. Method

In some Latin-American countries as Venezuela, Mexico, Colombia the standards are more similar to ASTM than the EN standards. For example in Colombia, the performance specification for hydraulic cement, standard NTC 121 (equivalent to ASTM C1157/C1157M.11), was approved in 2014. This standard classifies cement types by their features and performance. General purpose cement, UG, for instance, must exhibit a Vicat needle-determined initial

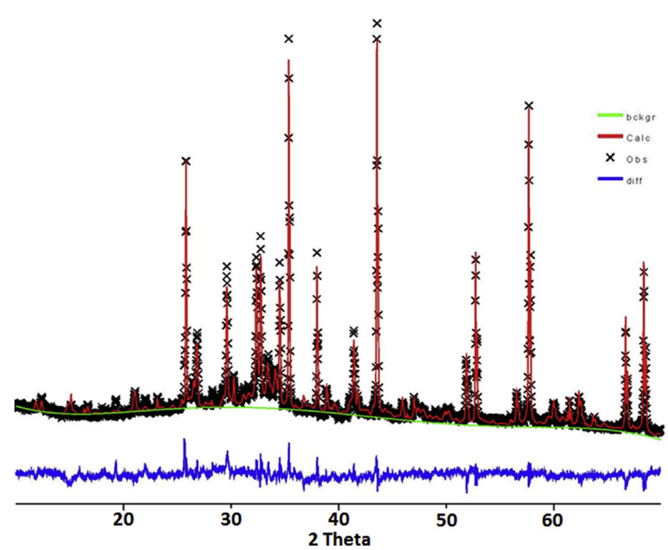

Fig. 2. Rietveld quantification of the cement CC5 studied using 30% corundum as a standard.

Table 1
Chemical composition of the pre-industrial hybrid cement (% by mass).

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MnO/Mn_2O_3	MgO	SO_3	Na_2O	K_2O	TiO_2	Other	[b]LoI
[a]CEMCC5	39.67	32.53	12.2	3.83	0.804	0.94	3.12	1.04	0.78	0.5	1.899	2.32

[a] CEM CC5 = pre-industrially manufactured hybrid cement.
[b] LoI, loss on ignition.