



High temperature resistance of a very high volume fly ash cement paste



Shane Donatello^{a,*}, Carsten Kuenzel^b, Angel Palomo^a, Ana Fernández-Jiménez^a

^a Eduardo Torroja Institute of Construction Sciences (CSIC), C/Serrano Galvache 4, 28033 Madrid, Spain

^b Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, UK

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ABSTRACT

The physical and chemical changes taking place in a very high volume fly ash cement paste (FAN-4) following exposure to temperatures up to 1000 °C are presented. Tests were repeated with commercially available CEM II/A-M Portland composite-cement (MS). FAN-4 pastes showed impressive residual strengths after heat exposure which increased dramatically when heated previously at 800 or 1000 °C. This was in stark contrast to the MS paste, which showed a continual decrease in residual strength following heating and subsequent cooling. The increase in residual strength with FAN-4 paste coincided with a major shrinkage event, which was associated with sintering and the formation of the new mineral phases anorthite, gehlenite, wollastonite, diopside and albite. The MS cement formed generally non-hydraulic calcium silicate phases upon heating at ≥ 800 °C. The differences in phase formation were linked to different starting elemental compositions. The FAN-4 paste was considerably richer in Si, Al, Fe and alkalis but poorer in Ca. The elemental composition of the binder phase will be an important factor to take into account when determining the high-temperature performance of future cements and concretes, which are likely to contain significantly higher contents of supplementary cementitious materials than is presently the case.

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1. Introduction

1.1. Lowering the CO₂ footprint of Portland cement based materials

While significant improvements in the Portland cement (PC) manufacturing process have been made by shifting from the wet process to the dry process and introducing pre-heating and pre-calcining stages [1,2], it is unlikely that further major improvements in thermal efficiency of the process can be made [3]. It is widely regarded that the key to further major reductions in the CO₂ emissions associated with PC manufacture is to increase the quantity of blended materials in cements, i.e. to reduce the mass of clinker in a given mass of cement by blending with industrial by-products, natural pozzolans or calcined clays [2,4–5].

Arguably the most significant industrial by-product with regards to blended cements is coal fly ash. Rough estimates for global fly ash production in 2010 are around 800–1000 Mt although the exact figure is difficult to ascertain since in many countries coal power stations are not obliged to report this data. From a life cycle assessment perspective, it is feasible to consider available fly ash as a CO₂ free resource. Fly ash has been used in blended cements for decades at replacement rates of around 10–30% as is reflected by

various national and international standards [6–7]. More recently work has been carried out investigating the use of blended cements with significantly higher fly ash contents [8–10]. One major issue with high fly ash content cements is slow setting and low early strengths. One possible approach to minimising this problem, while maintaining high cement replacement rates, has been to create ternary blended cements with fly ash, limestone and PC [11,12]. Another approach has been to add a source of strong alkali to activate fly ash glassy phases much more rapidly than is the case with the typical pozzolanic reaction with portlandite at ambient temperature [13,14]. With regards to the latter approach, the blended cements can be termed as “hybrid alkaline cements”.

While drastically reducing the CO₂ emissions associated with the binder, the effect of the high fly ash content on durability aspects of pastes is uncertain. In a recent publication by the authors, the high fly ash content cement pastes and mortars were shown to present a similar resistance to Na₂SO₄, seawater and acid solutions as a commercially available sulphate resistant PC [15]. Another important durability aspect is resistance to high temperatures, which provides a useful indicator of the behaviour of a material during a fire event.

1.2. High temperature exposure of Portland cement and concretes

Cement based materials are non-flammable and offer significant safety advantages over wood and plastic and help protect

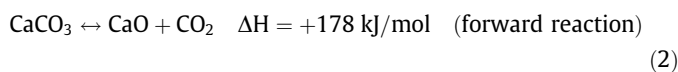
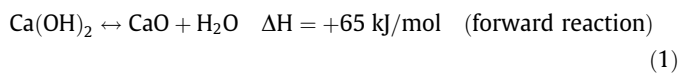
* Corresponding author.

E-mail address: shanedonatello@hotmail.com (S. Donatello).

steel rebar in structural concretes. However, fire events and high temperature exposure can nonetheless cause significant damage to PC based materials.

In a normal PC paste, pore water and crystalline hydration water can be lost from AFt and AFm type phases and C–S–H gel at temperatures below 300 °C [16]. Despite this, it is worth mentioning that some pastes can exhibit strength increases following heating at 105 °C [17,18]. Such unusual behaviour is likely to be due to trapped steam vapour creating conditions favourable for the in situ hydrothermal synthesis of C–S–H type phases.

As the temperature increases, the dehydration of portlandite, another major product in PC pastes, generally occurs between 400 and 550 °C [19] and provokes a significant shrinkage effect [20]. The presence of dehydrated portlandite leaves the microstructure prone to expansion upon subsequent rehydration, which is an exothermic reaction, as indicated by the reverse reaction of Eq. (1) [19,21]. The rehydration of portlandite is well known to be detrimental to cement pastes and concretes and the degree of degradation can be directly linked to the sorptivity of heat exposed PC pastes and concretes [22]. Due to the restricted movement of water through the pore network of the solid matrix, water removed by C–S–H, AFt/AFm and portlandite dehydration can be retained within the matrix as steam vapour, with pressures building up to a point at which cracks are produced and surface spalling can occur as tiny pockets of high pressure vapour are explosively released. Considerable research effort has been focussed on trying to understand the key factors behind the spalling process [23,24]. The performance of cements and concretes containing pozzolanic additions has been shown to be beneficial in cases where blast furnace slag [25] or volcanic ash [26] were used. While this could simply be attributed to the lower portlandite content, such an explanation would fail to account for irregular results with silica fume blended cements [27,28].



Another aspect to consider is the decomposition of calcite to free lime, which generally occurs at temperatures of 600–850 °C (see Eq. (2)). The free lime produced by decarbonation, like that from portlandite dehydration, is liable to later hydrate into expansive Ca(OH)₂. At higher temperatures, sintering of silicate phases can occur and provoke major changes in sample density, dimension and crystalline components. The hybrid alkaline cement used in this study is likely to behave in a much different manner to a pure PC paste at sintering temperatures (typically 800–1100 °C) due to its high fly ash content. Another important consideration may be the significant quantity of quartz introduced with the fly ash component. Quartz is known to exhibit a sudden expansion at 573 °C following conversion from low α to high β type quartz [18,19].

The general effect of replacing cement clinker with a class F fly ash is to reduce the quantity of Ca in the paste and therefore the quantity of portlandite and calcite present. Any free Ca(OH)₂ will either carbonate or sooner or later be locked into C–S–H or C–A–S–H type gels via the pozzolanic reaction of portlandite with fly ash glassy phases [29]. According to Khoury [18], this should help improve resistance to degradation at high temperatures and was indeed reflected in a large number of tests carried out on cement pastes and concretes exposed to 600 °C [30]. However, many other aspects such as differences in the gel structure, Ca:Si ratios of gels, w/b ratios and the nature of any aggregates used may also be important.

As part of a larger set of trials, the objective of this work is to evaluate the resistance of a novel hybrid alkaline cement containing a very high content of fly ash (ca. 80% by mass) to high temperature environments in comparison with a PC based reference paste. Although many other factors such as aggregate type and specimen dimensions will undoubtedly be important, in order to focus solely on the behaviour due to the nature of the binder composition at high temperatures, tests were carried out with pastes, and then only with specimens of identical dimensions.

2. Materials and methods

2.1. Materials

The very high volume cement binder (FAN-4) consisted of a class F fly ash milled until $\geq 98\%$ of the sample passed a 45 μm sieve, a PC clinker milled until $\geq 85\%$ passed a 45 μm sieve and a laboratory grade Na₂SO₄ salt (Panreac). Further details of the hybrid blend composition and raw material compositions can be found in an earlier publication by the authors [14].

As a reference material, a commercially available Type II/A–M Portland-composite cement (MS) was also tested under the same conditions as used with the test hybrid cement (FAN-4). According to the EN 197-1 [7] definition of Type II/A–M cements, between 6% and 20% of cement by dry mass had been substituted by an unspecified pozzolanic material or blend of pozzolanic materials, such as coal fly ash, blast furnace slag or natural pozzolans. Furthermore, up to 5% content as limestone is also permitted. Due to obvious economic and environmental reasons, blended Portland cement is becoming more common on the market at the expense of pure (CEM I type) Portland cements. Type II/A–M cements are particularly attractive since they afford significant flexibility to the manufacturer in cement formulation and make it harder for competitors to copy any successful blends. In terms of total dry content as PC clinker, the hybrid FAN-4 paste contains only 18% clinker (Ca poor) whereas the reference Type II/A–M cement will contain around 80–90% clinker (Ca rich). The major elemental compositions, as determined by X-ray fluorescence (Philips PW 1404/00/01), of the two anhydrous cements are shown in Table 1.

2.2. Paste elaboration

Pastes were mixed together with distilled water using the minimum liquid to binder ratios possible while maintaining sufficient workability of the paste. The liquid to solid ratios were 0.36 and 0.32 for the FAN-4 and MS pastes respectively. Pastes were mixed manually for 3 min and cast into 1 × 1 × 6 cm stainless steel moulds with the aid of a jolting apparatus. Moulds were then placed in a curing chamber maintained at 23 ± 2 °C and $\geq 95\%$ relative humidity. After 24 h, samples were demoulded and left to continue curing in the humidity chamber for a period of 70 d before being subjected to the high temperature resistance tests.

2.3. High temperature resistance tests

Paste samples were weighed, measured and photographed prior to being exposed to either: 200, 400, 600, 800 or 1000 °C for a

Table 1
Major element composition determined by XRF (expressed as oxides in wt.%).

	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	LOI ^a
FAN-4	48.7	17.1	13.5	7.4	1.8	1.8	2.1	2.2	4.4
MS	26.3	6.8	46.6	2.5	4.8	1.0	1.0	6.4	4.0

^a LOI represents weight "loss on Ignition" at 1000 °C during 1 h in Pt crucibles.

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