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Microstructural characterisation of hybrid cement after exposure to high temperatures

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HIGHLIGHTS

- Hybrid alkaline cement (HYC) exposed to high temperatures.
- Better post-thermal performance of HYC than OPC at $T^{\circ} > 800^{\circ}\text{C}$ especially in water-cooled.
- Mineralogical and microstructural changes studied by XRD, SEM and ^{29}Si and ^{27}Al MAS-NMR.
- At $T^{\circ} > 800^{\circ}\text{C}$ in HYC recrystallisation of scanty hydraulic phases such as gehlenite and rankinite.

GRAPHICAL ABSTRACT

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ABSTRACT

This study was designed to determine the mineralogical and microstructural changes taking place in a hybrid alkaline cement (HYC = 30% Portland cement clinker + 70% (slag + fly ash + alkaline activator)) exposed to high temperatures. The cement pastes were heated for 2 h at 400 °C, 600 °C, 800 °C or 1000 °C and subsequently air- or water-cooled. Their mechanical strength was determined after cooling. The HYC pastes had higher residual strength than the reference portland cement (OPC). That better post-thermal performance in HYC and its failure to collapse when water-cooled after reaching temperatures of over 800 °C were attributed to the recrystallisation of scanty hydraulic phases such as gehlenite and rankinite.

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1. Introduction

Although portland cement-based construction materials are incombustible, they are subject to substantial structural damage

when exposed to high temperatures. The extent of damage depends on the chemical and physical changes taking place, in turn conditioned by temperature and exposure time. Earlier research on Portland cement (OPC) [1] has shown that portlandite ($\text{Ca}(\text{OH})_2$) decomposes, generating CaO, at approximately 460 °C; calcium silicate hydrate, C-S-H gel, releases water from its intermediate layer

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as well as hydroxyl groups at 50 °C to 600 °C; Ettringite (Aft) and calcium aluminate monosulfate (AFm) release water at ≤ 400 °C; and calcite decomposes at 600 °C to 800 °C [1–4]. Those chemical reactions induce microstructural changes and severe damage to the material.

OPC pastes exposed to high temperatures in the presence of high humidity or in contact with water may also rehydrate, generating portlandite and ettringite as well as neo-formed C-S-H. Rehydration prompts expansion and with it microcracking that causes structural damage in OPC mortars and concretes [5]. To avoid that harmful effect, Wang [6] added 20% ground granulated blast furnace slag (GGBFS) to OPC cements, which reduced cracking and raised their compressive strength at temperatures of over 400 °C.

Alkaline cements resulting from the alkaline activation of aluminosilicate materials are being intensively studied at this time, for less CO₂ is emitted in their, than in OPC manufacture [7–11]. They have also been shown to be more durable than conventional cement, particularly after exposure to high temperatures. Rashad et al. [12], studying the effect of temperatures of 200 °C to 800 °C on a sodium sulfate-activated slag paste, reported high residual strength up to 600 °C. Rovnanik et al. [13] observed akermanite crystallisation at 710 °C in sodium silicate-activated slag pastes and a decline in residual compressive strength at 800 °C, followed by a rise when the temperature was increased to over 1200 °C. Other researchers have also shown alkali-activated slag cements to be potentially apt for high temperature applications [14–18].

Fire and high-temperature resistance have likewise been studied in alkali-activated fly ash (AAFA) cements. Bakharev et al. [19] noted that at temperatures of around 800 °C AAFA pastes shrank, impacting their post-thermal treatment flexural strength, perhaps due to the formation of Na feldspars from the sodium, silicon and aluminium released during decomposition of their silicoaluminate gel. Fernández-Jimenez et al. [20,21] and Martín et al. [22] studied the high temperature performance of AAFA-based materials with in situ and post-thermal (200 °C to 1000 °C) tests. Their findings showed that AAFA pastes also exhibited pseudo-plastic behaviour attributed to the formation of a melted phase at temperatures of around 600 °C to 700 °C. After cooling, the solidification of that phase would help raise compressive strength. Crystalline nepheline was observed to form after exposure to 800 °C and crystalline albite after 1000 °C. Van Riessen et al. [23] compared the behaviour of AAFA and OPC concrete, both with compressive strengths of around 70 MPa. When one side of the materials was exposed to fire as described in Eurocode EN 1991-1-2, severe spalling was observed in the OPC concrete. In contrast, no detachment was found in the AAFA concrete, which exhibited high fire resistance. In short, most of the articles published to date on AAFA materials have reported that at around 600 °C to 800 °C these materials reach a critical turning point at which paste dimensional stability is severely affected [24–26].

Hybrid alkaline cement (HYC), a new type of binder presently under development [27–29], comprise a blend of ordinary portland and alkaline cements with a clinker content of around 20% to 30% and a large proportion of supplementary cementitious material (SCMs) laced with an alkaline activator. The present authors recently published a detailed study [30] of the physical and mechanical behaviour of HYC pastes after in situ exposure to temperatures of 200 °C to 1000 °C. The findings showed that after exposure, HYC pastes had higher compressive and flexural strength and fracture toughness than the reference OPC paste, as well as higher residual strength.

As a follow-up to that research, the present study analysed the mineralogical and microstructural changes taking place in HYC pastes after exposure to temperatures of up to 1000 °C, correlating the findings with post-treatment residual compressive strength.

An understanding of these processes could provide insight for the design of new, more heat/fire-resistant cementitious materials. In this study the post-treatment materials were characterised by X-Ray Diffractions (XRD), Scanning Electron Microscopy-Energy-Dispersive X-ray spectroscopy (SEM/EDX), ²⁹Si and ²⁷Al Magic-Angel Spinning Nuclear Magnetic Resonance (MAS NMR) and Mercury Intrusion Porosimetry (MIP).

2. Experimental

2.1. Materials

The binder used in this study was a preindustrial hybrid alkaline cement [30] containing 30% portland clinker + 32.5% ground granulated blast furnace slag (GGBFS) + 32.5% fly ash (FA) + 5% solid Na₂SO₄-based activator. The reference was a commercial portland cement (OPC) (CEM I 42.5R). Further to the XRF-determined (Bruker S8 TIGER) chemical composition in Table 1, the HYC had a lower CaO and a higher SiO₂ and Al₂O₃ content than the OPC. The mineralogical phases in the materials were identified on a Bruker AXS D8 Advance X-ray diffractometer (XRD) using Al₂O₃ as an external standard and TOPAS software. Rietveld refinement quantification showed that HYC contained a clinker content of slightly over 32.5% (somewhat higher than the 30% specified).

2.2. Methods

Cement pastes prepared with distilled water at a water / cement ratio of 0.3 were poured into stainless steel moulds to form 10x10x60 mm³ prismatic specimens [30], subsequently cured in a climatic chamber at 22 ± 1 °C and 95% relative humidity for 20 h [20–22]. After demoulding they were stored in the same chamber until 28 d, when they were measured, weighed, and exposed to temperatures of 400 °C, 600 °C, 800 °C or 1000 °C for 2 h in a laboratory oven. Thermal treatment consisted in placing the specimens in the oven preheated to the test temperature to simulate the conditions prevailing in accidental fires. Eight specimens were tested per cement type and temperature. Upon removal from the oven, four samples from each batch were air-cooled and four submerged in water for approximately 15 min [27]. The latter method was deployed given that water is an economic, non-toxic and commonly used fire extinguisher. Specimen compressive strength was determined on an Ibertest Autotest 200–10 test frame. The broken specimens were subsequently ground for instrumental characterisation, the air- and water-cooled materials with XRD and the air-cooled samples also with SEM/EDX, MIP and ²⁹Si and ²⁷Al MAS NMR.

The X-Ray Diffractograms for the powder samples were recorded on a Philips diffractometer using CuK α _{1,2} radiation and the following operating conditions: divergence slit, 6 mm (variable); 2 Θ angles 5° to 60°; step time, 0.5 s; and step size 0.02°. Scanning Electron Microscopy-Energy-Dispersive X-ray spectroscopy analyses were conducted on a JEOL JSM scanning electron microscope fitted with a solid-state BSE detector and a LINK-ISIS X-ray energy dispersion analyser. Porosity and pore size were found with a Micromeritics AutoPore IV 9500 mercury intrusion porosimeter at a maximum pressure of 227 MPa, a contact angle of 141.3° and a surface tension of 485·10^{−3}N/m. The ²⁹Si and ²⁷Al Magic-Angel Spinning Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance-400 spectrometer operating, for ²⁹Si, at a resonance frequency of 79.5 MHz and spinning speed of 10 kHz; single pulse excitation was used with a pulse length of 5 μ s and a 10 s recycle delay; 4912 scans were acquired; and chemical shifts were referenced to tetramethylsilane (TMS). The conditions for ²⁷Al were resonance frequency, 104.3 MHz; spinning

Table 1

Chemical composition (expressed as oxides in wt%) and mineralogical phases.

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	Other	^a Lol
HYC	39.67	32.53	12.2	3.83	0.94	3.12	1.04	0.78	0.5	3.07	2.32
OPC	62.52	19.50	5.60	2.31	0.77	3.33	0.05	1.03	0.24	1.56	3.09
Mineralogy	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Limestone	Gypsum/basanite	Activator	Quartz	Mullite	Amorphous	
HYC	20.05±2.37	5.45±1.40	3.98±0.78	3.02±0.70		1.70±0.5	2.03±0.02	3.00±0.1	6.27±0.8	54.5±2.3	
OPC	66.65±0.21	11.64±0.47	10.43±0.23	6.79±0.24	3.05±0.31	3.46/0.34±0.29	/	/	/	/	

^a Lol: loss on ignition.

speed, 10 kHz; recycle delay, 5 s; single pulse excitation with a 2 μ s pulse length; 400 scans acquired; chemical shifts referenced to Al (H₂O)₆³⁺. ²⁹Si MAS NMR spectra were deconvoluted with Origin pro 2016 software.

3. Results and discussion

3.1. Physical characterisation of pastes after thermal treatment

The photographs in Fig. 1 depict the paste specimens cooled in water after exposure to 800 °C and 1000 °C. The OPC pastes disintegrated upon contact with water after having been heated to 800 °C. The HYC specimens, in contrast, remained intact, with no obvious surface cracking. Such clearly different behaviour infers that the mineralogical and microstructural changes taking place in the two materials must differ.

The post-treatment residual compressive strength in the air- and water-cooled OPC and HYC pastes is graphed in percentage in Fig. 2. Strength declined by approximately 30% at 400 °C and 40% at 600 °C in the OPC samples, whilst at those temperatures water cooling appeared to have no further effect on their compressive strength. The water-cooled OPC samples could not be tested after heating to 800 °C or 1000 °C, however, for they had disintegrated completely (Fig. 1). In the air-cooled OPC specimens, strength declined by approximately 60% at 800 °C and 80% at 1000 °C. In contrast, strength varied very little between the air-

Fig. 2. Relative compressive strength of water (W) and air (A) -cooled OPC and HYC pastes.

and water-cooled HYC samples and was even slightly higher in the latter, with declines of 10% at 400 °C and 30% at 600 °C. After exposure to 1000 °C, irrespective of the cooling method, the residual strength in the HYC pastes declined by approximately 70% of the initial ambient temperature value.

Specimen weight loss is plotted against exposure temperature in Fig. 3. Most of the loss was observed between 25 °C and

Fig. 1. OPC and HYC water-cooled paste samples after exposure to temperatures of 800 °C and 1000 °C.

Fig. 3. Variation in weight in OPC and HYC pastes with exposure temperature by cooling method (A - air; W - water).

400 °C and related to the release of bound and unbound water from the matrix [3,5,31]. Weight loss at 1000 °C in the air-cooled samples was on the order of 25% in OPC and 24% in HYC. Both materials underwent smaller weight loss when water- than when air-cooled, due primarily to paste rehydration when the cements were submerged, for the lime generated with portlandite dehydration (at around 460 °C) may rehydrate to form $\text{Ca}(\text{OH})_2$ [5]; and to the presence of reabsorbed unbound water in the paste, given the rise in porosity.

3.2. Mineralogy

The diffractograms for the raw materials and for the 28 d hydrated pastes before and after exposure to 600 °C, 800 °C and 1000 °C are reproduced in Fig. 4, along with the XRD patterns for the water-cooled samples after exposure to 800 °C and 1000 °C.

The diffractogram for anhydrous OPC contained the lines characteristic of clinker (alite, belite, calcium aluminates and ferrite phases) and gypsum. In addition to the clinker phases, the HYC diffractogram included reflections indicative of the mullite and quartz present in fly ash and a wide hump with 2Θ values of 25° to 35° attributable to the vitreous/glassy component in the slag and fly ash [27–30].

The 28 d OPC pattern contained a hump at (2Θ) 20° to 35° associated with the main hydration product, C-S-H gel [2,3]. The intensity of the C_3S lines declined after hydration, whilst new reflections denoting crystalline phases appeared for portlandite, ettringite and calcite. The 28 d HYC diffractograms also contained reflections indicative of new crystalline phases such as portlandite, ettringite, calcite and carboaluminates, along with a hump at (2Θ) 25° to 35°, possibly attributable to the formation of a mix of C-S-H, C-(A)-S-H and C-A-S-H gels [27–30,32].

The following variations were observed in the diffractograms for the post-exposure materials.

- **OPC:** after heating to 600 °C, the intensity of the portlandite reflection clearly declined. The line did not disappear altogether, probably due to the presence of non-decomposed portlandite particles in the matrix or even more likely to CaO rehydration with the ambient humidity. Ettringite, which is unstable at over 100 °C, decomposed and disappeared entirely. C-S-H gel also dehydrated with temperature and began to decompose at >450 °C [4,5], as attested to by a hump between 2Θ 32° and 35° (Fig. 4). The calcite reflections practically disappeared when the sample was exposed to 800 °C and 1000 °C, at which temperatures CaO sourced from portlandite and calcite decomposition was clearly identifiable. Brownmillerite and belite were also present.

The former, a low reactivity phase probably present in the starting cement, had not reacted after 28 d and remained stable at the test temperatures (the intensity of the main line barely varied). In contrast, the intensity of the C_2S reflections rose at 800 °C and 1000 °C. As that phase, present in OPC, is characterised by a low 28 d hydration rate, part of the intensity may be due to the anhydrous C_2S in the starting material. Nonetheless, the rising intensity suggests that some C_2S formed at 800 °C and especially at 1000 °C. The α' - C_2S polymorph, also detected at 800 °C, was the result of polymorphic transition across temperatures ranging from 670 °C to 840 °C [33]. The XRD patterns for the samples water-cooled after heating to 800 °C or 1000 °C exhibited α' - C_2S , brownmillerite, calcite and portlandite. The very intense reflection associated with lime in the air-cooled samples was not detected in the water-cooled materials, in which the CaO rehydrated, generating portlandite, $\text{Ca}(\text{OH})_2$ (Fig. 4). Such rehydration largely explains the specimen disintegration depicted in Fig. 1.

- **HYC:** the ettringite and portlandite reflections disappeared when the sample was exposed to 600 °C, whilst the lines for calcite, mullite and quartz remained unchanged. No new crystalline phases were identified at that temperature. The hump (2Θ 25°–35°) associated with the mix of C-(A)-S-H and C-A-S-H gels [27–30,32] was still visible, very likely an indication that up to 600 °C the gel may have remained thermally stable. At 800 °C the hump associated with the cementitious gels changed substantially, tending to disappear and give rise to new crystalline phases, namely α' - Ca_2SiO_4 and gehlenite. The latter, a calcium aluminosilicate, often appears in alkali-activated slag cements after exposure to high temperatures (of around 800 °C) [12,13] as well as in heated vitreous slag (at 1450 °C) [34]. The mullite and quartz present in fly ash continued to appear as inert phases. When the temperature was raised to 1000 °C, β - C_2S and α' - Ca_2SiO_4 decomposed into rankinite, wollastonite and pseudo-wollastonite and the intensity of the gehlenite lines increased substantially. The diffractogram for the water-cooled HYC samples heated to 800 °C and 1000 °C exhibited the same reflections as observed in the patterns for the air-cooled specimens. The crystalline phases forming at high temperatures in HYC were scanty hydraulic and fairly stable in water.

3.3. Microstructure

Fig. 5 shows the pore size distribution in the 28 d HYC and reference OPC pastes by temperature. Pore diameter, porosity and mercury intrusion volume are summarised in Table 2. At all the

Fig. 4. XRD patterns for OPC and HYC: anhydrous materials, 28 d cement pastes and specimens heated at 600 °C, 800 °C and 1000 °C. (Legend: **A**: alite, C_3S ; **AI**: C_3A , 031-0301; **An**: anhydrite, $CaSO_4$, 032-1048; **B**: belite, C_2S , 033-0302; **C**: calcite $CaCO_3$, 083-0578; **E**: ettringite, $C_6AS_3H_{32}$, 041-1451; **F**: brownmillerite, $Ca(Al, Fe)_2O_5$, 030-0226; **I**: lime, CaO , 074-1497; **P**: portlandite, $Ca(OH)_2$; **Q**: quartz, SiO_2 , 046-1045; **M**: mullite, 084-1205; **G**: gehlenite, $Ca_2Al_2SiO_7$, 035-0755; **H**: hematite, Fe_2O_3 , 033-0664; **R**: rankinite, $Ca_3Si_2O_7$, 022-0539; **W**: wollastonite-2 M, $CaSiO_4$, 043-1460; **b**: calcium silicate, α - Ca_2SiO_4 , 036-0642; **g**: gypsum, $CaSO_4 \cdot 2H_2O$, 037-1496; **w**: pseudo-wollastonite, $Ca_3(Si_3O_9)$, 074-0874; **α**: hemicarboaluminate, $C_3A \cdot Ca[OH \cdot (CO_3)_{0.5}] \cdot H_{11.5}$, 041-0221).

test temperatures, total porosity in HYC was similar to or greater than in OPC. Total porosity, observed to rise in both cements with rising temperature, was closely related to the decline observed in OPC and HYC compressive strength. Pore size distribution differed clearly in the two cements. At ambient temperature, the 28 d HYC pastes exhibited a higher percentage of small pores (<50 nm) than the OPC materials. Thermal treatment enlarged pore size, much more significantly in the OPC than in the HYC cements. The fraction

under 100 nm declined while the percentage of the largest pores (>100 nm), associated with the presence of capillary pores, grew [35–37]. Pore size in HYC covered a very wide and irregular range, with diameters from 10 nm to 2000 nm. Whilst high temperature crystallisation and phase transformation in the matrix may induce an increase in pore diameter, the presence of a sintered phase might explain the pore size refinement in HYC cements, a topic discussed in greater detail in a later section.

Fig. 5. MIP-determined pore size distribution of (a) OPC, and (b) HYC paste exposed to high temperature, cooled in air.

Table 2

MIP-determined porosity parameters in OPC and HYC pastes exposed to high temperature, cooled in air.

Sample	Exposure temperature (°C)	Median pore diameter (nm)	Mean pore diameter (nm)	Porosity (%)	Total intrusion volume (ml/g)
OPC	25	17.9	38.2	16.53	0.083
	600	60.7	92.6	31.43	0.173
	800	150.3	221.7	44.29	0.279
	1000	606.4	653.1	41.88	0.236
HYC	25	13.2	21.9	19.67	0.105
	600	34.4	73.3	35.53	0.206
	800	123.4	200.5	43.17	0.263
	1000	1028	1040	43.25	0.265

SEM micrographs of the HYC matrix after exposure to 800 °C and 1000 °C are reproduced in Fig. 6. The microstructure was observed to comprise fairly well compacted small particles. The SEM analysis did not show a high degree of crystallinity. Although XRD identified crystalline phases such as gehlenite, their presence could not be clearly detected with SEM, suggesting that they were very small or embedded in a scanty crystallised solid phase. Further to the chemical composition, the mean Ca/Si in the matrix was around 1.7 and Al/Si < 1.

3.4. Nanostructure: MAS NMR spectroscopy

The MAS ^{29}Si NMR spectra for HYC after exposure to ≥ 800 °C and the anhydrous and 28 d pre-treatment cements are repro-

duced in Fig. 7, whilst the position and area of the deconvoluted signals are given in Table 3. The ^{29}Si MAS NMR spectrum for anhydrous HYC contained a narrow symmetrical signal at -71.6 ppm with two shoulders at -69 ppm and -73 ppm. The narrow signal was attributed to belite and the two shoulders to alite. The deconvoluted signals at -66.9 ppm, -74.3 ppm and -77.7 ppm were associated with the vitreous phase of the slag [38,39] and the signals centred at around -107 ppm and -89 ppm with fly ash [7–9]. The spectrum for the 28 d HYC exhibited very intense peaks at -79.6 ppm (Q^1 , end of chain) -82.3 ppm ($\text{Q}^2(1\text{Al})$) and -85.6 ppm ($\text{Q}^2(0\text{Al})$), all characteristic of C-(A)-S-H gels [40–42]. The resonances at -87.9 ppm, -92.4 ppm and -97.8 ppm (Fig. 6 and Table 2) may be attributable to the presence, respectively, of the $\text{Q}^3(2\text{Al})$, $\text{Q}^3(1\text{Al})$ and $\text{Q}^3(0\text{Al})$ units generally detected in C-A-

Fig. 6. Backscattered SEM micrographs and EDX analysis of selected points in the HYC paste after exposure to: (a) 800 °C, (b) 1000 °C.

Fig. 7. ^{29}Si MAS NMR spectra for anhydrous HYC and specimens heated at 800 °C and 1000 °C.

S-H gels forming during slag alkaline activation [42–44]. Those resonances are an indication that more polymerised gels formed in HYC than in OPC.

Substantial change was observed in the ^{29}Si NMR for the HYC exposed to 800 °C. The intensity of the signals for the Q^1 and Q^2 units declined drastically to near disappearance as a result of the dehydration and decomposition of the ‘drierketten’-like structure characteristic of C-A-S-H gel at that temperature [13]. After deconvolution, signals were detected at –71.5 ppm (26.90%) associated with the formation of beta- C_2S ; –70 ppm (18.23%), with the presence of α' - C_2S [45]; and –72.5 ppm, with the Q^1 units in gehlenite [46]. Those data were consistent with the XRD findings for the 800 °C material. The signals at the most negative values (–92.4 ppm and –97.8 ppm) disappeared, whereas the signal at –87.8 ppm, associated with the formation of low crystallinity phases, probably Q^3 units, widened. The decline in intensity of the signals associated with Q^4 units at –107 ppm / –108 ppm after exposure to 800 °C may be attributable to unreacted fly ash sintering. Richard et al. [47,48] reported that unreacted fly ash particles

released amorphous aluminosilicate at temperatures of >500 °C in an alkali-activated fly ash geopolymer.

Substantial change was also observed in the ^{29}Si MAS NMR spectrum for the HYC exposed to a temperature of 1000 °C. The intensity of the Q^0 signals (–69.8 ppm and –71.7 ppm) associated with C_2S (beta- and α - C_2S) declined considerably (Table 3). The resonance at –73.4 ppm remained unchanged, the intensity of the signal at 74.8 ppm rose and a new signal appeared at –76.2 ppm. All three were associated with the formation of the two main phases detected with XRD, crystalline gehlenite and rankinite. Florian et al. [49] found that gehlenite generated two signals on ^{29}Si MAS NMR spectra, at –72.5 ppm and –74.7 ppm. Rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$) may give rise to signals at around –74.8 ppm and –76.2 ppm [50,51], whilst the signal at –83.9 ppm was related to the Q^2 units in pseudo-wollastonite (α - $\text{Ca}_3\text{Si}_3\text{O}_9$) and the resonances at –86.3 ppm, –88.9 ppm and –90.3 ppm to wollastonite (β - $\text{Ca}_3\text{Si}_3\text{O}_9$) [47,48]. The signals at –77.6 ppm, –78.8 ppm and –80.0 ppm may be assigned to low crystallinity phases, i.e., vitreous phases with longer structural units than the dimers precipitat-

Table 3
Deconvolution of ^{29}Si MAS-NMR spectra, showing signal position, area and tentative assignment.

HYC		HYC 28d 25 °C		HYC 28d 800 °C		HYC 28d 1000 °C	
Pos.(ppm)	A(%)	Pos.(ppm)	A(%)	Pos.(ppm)	A(%)	Pos.(ppm)	A(%)
-66.9 (Slag)	4.65	-67.9	2.83	-68.1	1.24	-67.8	1.15
-69.9 (OPC)	10.76	-69.6	3.74	-70.0	18.23	-69.8	4.82
-71.6 (OPC)	11.92	-71.6	11.61	$\text{Q}^0, \alpha'-\text{Ca}_2\text{SiO}_4$	26.90	$\text{Q}^0, \alpha'-\text{Ca}_2\text{SiO}_4$	5.75
-73.1 (OPC)	9.94			$\text{Q}^0, -\text{Ca}_2\text{SiO}_4$	16.20	$\text{Q}^0, -\text{Ca}_2\text{SiO}_4$	12.41
-74.3 (Slag)	10.34	-73.8	6.45	Q^1 , gehlenite		Slag+ Q^1 , gehlenite	
				-74.5 Slag+ Q^1 , gehlenite	10.08	-74.8 Q^1 , gehlenite + Q^1 , rankinite	19.67
						-76.2 Q^1 , rankinite	19.86
-77.7 (Slag)	16.75	-77.4	8.09	-77.6 Q^2 , glassy phase	7.41	-77.6 Q^2 , glassy phase	9.67
		-79.6 Q^1 (0Al)	9.49			-78.8 Q^2 , glassy phase	1.99
		-82.3 Q^2 (1Al)	21.68	-81.1 Q^2 , glassy phase	4.42	-80.0 Q^2 , glassy phase	4.99
		-85.6 Q^2 (0Al)	13.37			-83.9 Q^2 , pseudo- wollastonite	11.02
		-87.9 Q^3 , (2Al)	5.48	-87.8 Q^2 , glassy phase	12.13	-86.3 Q^2 , wollastonite	2.13
-89.0 (FA)	13.36					-88.6 Q^2 , wollastonite	3.77
		-92.4 Q^3 , (1Al)	2.71			-90.3 Q^2 , wollastonite	2.77
		-97.8 Q^3 , (0Al)	3.91				
-107.1 (FA and quartz)	22.28	-108.3 Q^4 (FA and quartz)	10.58	-107.0 Q^4	3.37		

ing with crystalline phase formation. Such polymerisation may be due to the role of alumina, which converts non-bridging oxygen (NBO) into bridging oxygen (BO) by forming Si-O-Al bonds. [52,53].

The ^{29}Si NMR spectra for HYC after exposure to 800 °C and 1000 °C denoted significant change, primarily yielding low hydraulicity calcium silicates and aluminates. Both the reaction products formed and the unreacted slag and fly ash were significantly affected by exposure to 800 °C and 1000 °C, as attested to by the data in Fig. 7 and Table 3. The signals associated with a C-A-S-H/C(A)-S-H gel in the 28 d reference spectrum exhibited similar behaviour. The Si and Al sourced from the slag and fly ash and the Al, Si and Ca from the other phases formed with HYC hydration gave way to new (crystalline and glassy) phase formation. Park et al. [54] described a similar crystallisation pathway in alkali-activated fly ash/slag blended cements exposed to high temperatures.

The ^{27}Al MAS NMR spectra for the HYC paste before and after exposure to high temperatures are reproduced in Fig. 8. Aluminium may exhibit three coordination environments, Al^{IV} for chemical shifts of +80 ppm to +50 ppm, Al^{V} for shifts of +40 ppm to +30 ppm and Al^{VI} for shifts of +15 ppm to -10 ppm. The spectrum for anhydrous HYC contained a wide signal centred over +60 ppm attributed to the aluminium in the slag + fly ash [38–44,54], along with a narrow signal at +79 ppm associated with the aluminium in the clinker. After hydration, the 28 d HYC spectrum exhibited new resonances in the Al^{IV} region centred over

Fig. 8. ^{27}Al MAS NMR spectra for anhydrous HYC and specimens heated at 800 °C and 1000 °C.

+12.4 ppm, associated with the presence of ettringite, and +9.2 ppm, with carboaluminates [38–41], phases identified as well with XRD. The intensity of the signal at +79 ppm disappeared with cement hydration, whilst the signal at +60 ppm shifted slightly. A series of small shoulders observed between +75 ppm and +60 ppm that might be attributed to $q^2(I)$, $q^2(II)$ and q^3 species (Fig. 7) were associated with aluminium tetrahedra surrounded by silicon atoms in C-(A)-S-H/C-A-S-H-like gels [39,55,56]. That was consistent with the presence of the $Q^2(1Al)$, $Q^3(1Al)$ and $Q^3(2Al)$ units detected in the ^{29}Si MAS NMR spectra for the same sample.

The signals for octahedrally coordinated Al (ettringite and carboaluminates) disappeared on the ^{27}Al MAS NMR spectra for the HYC exposed to 800 °C and 1000 °C due to phase decomposition at those temperatures [3–6,35]. A wide signal ranging from –70 ppm to +30 ppm and centred over +58/59 ppm was associated with the overlap of aluminium in Al^{IV} and Al^V environments, partially associated with gehlenite-like new phases [49] and Al present in a low crystallinity phase (vitreous phases with Si-O-Al bonds).

Further to those findings, exposing an HYC cement to high temperatures yields a mineralogy and microstructure that differ from those in OPC. Such differences determine the higher post-thermal treatment performance in HYC, particularly when water-cooled.

When OPC pastes are exposed to high temperatures the main hydration products ($Ca(OH)_2$, ettringite and C-S-H gel) dehydrate and decompose. The release of water vapour raises porosity and pore size, adversely affecting mechanical strength and inducing cracking and spalling. The new phases formed, primarily CaO, may rehydrate in the presence of moisture or water (Fig. 4, XRD patterns) or carbonate, all to the detriment of strength. In such CaO rehydration-related deterioration, portlandite may exert such high crystallisation pressure in the matrix that the material may disintegrate, as in Fig. 1.

HYC exhibited better post-thermal treatment performance than OPC, whether air- or water-cooled (Fig. 1). That result may be attributed to different chemical and mineralogical composition-governed crystallisation pathways in the matrix. As the $Ca(OH)_2$ and ettringite contents were lower in HYC, that cement exhibited lower unbound water loss. C-A-S-H gel is more highly polymerised than the C-S-H gel found in OPC and therefore contains less water. The lower calcium content and the presence of alkalis also affected the products formed at high temperatures. Low hydraulicity crystalline phases such as gehlenite and beta- C_2S formed in HYC exposed to high temperatures.

Florian et al. [49] reported that beta- C_2S , gehlenite and wollastonite formation was favoured over beta- C_2S at 1000 °C to 1200 °C when the CaO/SiO_2 ratio was ≈ 2 . Conversely, beta- C_2S was favoured over wollastonite when the ratio rose to 3. The present findings confirmed those results: as the CaO/SiO_2 ratio was 3.2 in the OPC system, the phases primarily forming at 1000 °C were beta- C_2S and lime. Conversely, the CaO/SiO_2 ratio in HYC was 1.2 (<2), whereby at 800 °C gehlenite and wollastonite prevailed over beta- C_2S formation. In this study gehlenite formed in the hybrid cements at lower than the reference temperature, an observation attributed to the presence of alkalis, which lower crystallisation temperatures. Sourced from the solid activator used in HYC, such alkalis induced the formation of a solid phase where crystalline rankinite, wollastonite, pseudo-wollastonite (no Al) and gehlenite formed. The 2 h duration of thermal treatment may not have sufficed to generate well-defined crystals or those forming may have been small and embedded in the solid phase vitrified by abrupt cooling (Fig. 7, Table 3). All the aforementioned phases exhibited low hydraulicity.

The suite of changes described in the foregoing affected total porosity and pore size distribution, and consequently mechanical strength. Briefly, although compressive strength declined in both

OPC and HYC after exposure to high temperatures, the hybrid alkaline cement exhibited higher residual post-treatment compressive strength than OPC. In other words, HYC proved to be more thermally stable than OPC, particularly if in contact with water.

4. Conclusions

This article describes the mineralogical and microstructural changes taking place in a hybrid cement comprising 39.67% CaO, 32.53% SiO_2 and 12.2% Al_2O_3 after exposure to temperatures of up to 1000 °C. The major conclusions that can be drawn are set out below.

- Hybrid alkaline cement (HYC) exhibited higher residual compressive strength than the reference OPC after exposure to temperatures of up to 1000 °C, whether air- or water-cooled.
- Mineralogically, high temperature treatment of HYC induced the decomposition of hydration products, including a mix of gels, primarily at 600 °C to 800 °C, and the formation of new products, such as crystalline gehlenite and rankinite, along with a melted phase that vitrified when cooled.
- The crystalline gehlenite and rankinite forming in the HYC after exposure to temperatures of 800 °C to 1000 °C exhibited low hydraulicity. That, in conjunction with the absence of CaO, led to higher performance in HYC than OPC when in contact with water. When exposed to 800 °C and 1000 °C and water, OPC pastes decomposed very rapidly (in seconds or minutes), due primarily to CaO rehydration.
- Microstructurally, hydration product decomposition and the concomitant release of water raised porosity, redounding adversely to mechanical strength. The presence of a melted phase in HYC nonetheless refined porosity, leading to a lower percentage of large pores than in OPC.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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