Self-repairing properties of OPC clinker/natural zeolite blend in water and alkali carbonate environments at 270°C

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The 10 d recoveries of the mechanical properties and crack sealing of an ordinary Portland cement (OPC) clinker/natural zeolite (ferrierite (Fer)) blend modified or unmodified with silica were tested at 270°C in water and alkali carbonate environments. The recoveries of the samples depended on their modification with silica and the curing environment, but were more than 100% after repeated damage under some test conditions. The mechanical properties and phase compositions of recovered samples were evaluated by compressive strength measurements and x-ray diffraction, differential thermogravimetric analyses, Fourier transform infrared analyses and scanning electron microscopy coupled with energy dispersive x-ray spectroscopy. The sealing of 0.25 mm wide and ~2 mm deep cracks was visualised with a three-dimensional optical microscope. Fer decomposed under high-temperature alkaline conditions with the release of hydrolysates that, along with the hydrating clinker, participated in the formation of new phases contributing to strength recoveries. These phases included crystalline magnesium and aluminium-containing silicates, calcium and carbonated calcium silicates and amorphous hydrates. Crack sealing was complete for the silica-modified samples and partial for unmodified ones cured in carbonate environments. The sealing was very poor for samples cured in water. The main sealing phases included crystalline and amorphous silica, high-temperature-stable zeolites and talc mineral.

Introduction

For well cements, geothermal environments are among the most aggressive in terms of mechanical and chemical stresses, causing unavoidable concerns over short- and long-term cement sheath integrity. Cement failure can lead to the creation of micro-annuli or cracks, increased cement permeability and fluids migration, disbandment of cement from the casing and formations, casing corrosion by corrosive geo-fluids and collapse (Amin *et al.*, 2009; McCulloch *et al.*, 2003; Ravi *et al.*, 2002; Teodoriu *et al.*, 2013; Zhijun *et al.*, 2013). Repairs to failed well cements are expensive and time consuming and are complicated by the difficulties of locating and accessing damaged areas.

The development of cost-effective self-repairing cement technologies that allow recovery of the original cement properties without human intervention is an economical way to obtain durable well integrity. Among the major technical strategies for developing self-healing cements, autogenous healing relies on the hydration of residual non-hydrated and partially hydrated cement particles by permeation of water through cracks and the carbonation of hydrates with crack plugging by the hydration and carbonation reaction products (Edvardsen, 1999; Huang *et al.*, 2013; Talaiekhazan *et al.*, 2014). Another, autogenous healing approach involves the incorporation of pozzolan-latent cementitious materials such as fly ash (Sahmaran *et al.*, 2008, 2013; Termkhajornkit *et al.*, 2009),

ground granulated blast-furnace slag (GBFS) (Huang *et al.*, 2014) and silica fume (Qian *et al.*, 2010) as healing aids into cements. In contact with calcium- and sodium-containing alkaline fluids penetrating through the fractures, these non-reacted pozzolan materials form amorphous and crystalline calcium silicate, calcium aluminosilicate, sodium aluminosilicate and calcium(sodium) aluminosilicate products, which seal the cracks.

Aluminosilicate-based pozzolans can be natural, such as zeolites, metakaolin and clays, or industrial by-products including fly ashes and GBFS (Mertens *et al.*, 2009). Among the natural pozzolans, zeolites are abundant worldwide. In the USA, the US Geological Survey estimated the reserves of zeolite minerals and zeolite-rich deposits to be 120 million and 10 trillion tonnes, respectively (Virta, 2015). As economical materials, zeolites have a high potential for substitution of cement, gypsum, bentonite, montmorillonite, peat, perlite and silica sand, and their application in cements have increased in the past decade.

As is well-documented (Ahmadi and Shekarchi, 2010; Bilim, 2011; Habert *et al.*, 2008; Karadurt and Topcu, 2011; Mertens *et al.*, 2009; Ortega *et al.*, 2000; Perraki *et al.*, 2010; Uzal *et al.*, 2010; Yilmaz *et al.*, 2007), the crystalline clinoptilolite zeolite can totally or partially substitute ordinary Portland cement (OPC) in blends with OPC or lime where calcium hydroxide initiates the pozzolanic reactions of clinoptilolite.

Zeolites are crystalline hydrated aluminosilicate minerals and their structure is characterised by three-dimensional (3D) oxygen-linked $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral frameworks containing ion-exchangeable cations (Na^+ , K^+ and Ca^{2+}) and water molecules situated in their micropores and channels (Armbruster and Gunter, 1991; Curkovic *et al.*, 1997). Substantial amounts of iron may be intercalated in the crystal-line lattice of zeolite (Dubkov *et al.*, 2002; Kiwi-Minsker *et al.*, 2003; Perez-Ramirez *et al.*, 2003). Under alkali attack of calcium hydroxide from the hydration of lime and OPC, the aluminosilicate framework of zeolites disintegrates to form calcium silicates, calcium aluminates and/or calcium aluminium silicates in reaction with calcium cations (Liguori *et al.*, 2015; Özen *et al.*, 2016; Perraki *et al.*, 2005; Uzal and Turanli, 2012).

Compared with the properties of OPC-based cement, such pozzolan cements display improved resistance to sulfate-induced erosion and minimised water permeability; in addition, the formation of calcium-silicate-related swelling hydrogel is eliminated, thereby mitigating undesirable expansion-induced failure of concrete. On the other hand, they are slow to develop early strength and require increased water at mixing (Vejmelkova *et al.*, 2015). To mitigate these drawbacks, different treatment techniques involving ultrafine pulverisation (Alexander, 1960; Day and Shi, 1994), thermal, hydrothermal and acid treatments (Collepari *et al.*, 1976; Costa and Massazza, 1977; Hemings *et al.*, 1989; Seraj *et al.*, 2016) and chemical methods (Shi and Day, 1993) have been employed over more than three decades. These treatments enhance the pozzolanic reactivity of zeolites through de-alumination, resulting in a loss of crystallinity. Correspondingly, the silicon/aluminium ratio of untreated clinoptilolite significantly increases after treatment (Ates and Hardacre, 2012; Cakicioglu-Ozkan and Ulku, 2005; Elaiopoulos *et al.*, 2010; Misaelides *et al.*, 1996; Zhang *et al.*, 2002). Furthermore, under alkali conditions and elevated temperatures, zeolites undergo eventual decomposition of their crystalline structure as a result of silicon leaching (Bonilla *et al.*, 2009).

Among the various zeolites, ferrierite (Fer) is especially attractive for high-temperature hydrothermal applications in geo-thermal cements because of the high stability of its structure against hydrothermal and chemical treatments (Bonilla *et al.*, 2009; Wloch *et al.*, 2006) necessary for successful autogenous healing, relying on latent pozzolanic reactions.

The work reported here evaluated the performance of an OPC clinker/Fer blend under the high-temperature hydrothermal conditions relevant for geothermal wells. Based on the reported performance of zeolite-modified cements, self-healing behaviour may be expected from the blend at high temperatures where zeolite may become reactive under the alkaline conditions of cement slurries. The purpose of the work was to establish the strength recoveries and fracture sealing of the

clinker modified with Fer and to understand the underlying mechanisms of the material's healing.

Experimental procedure

A blend of OPC clinker (type I/II)/Fer/gypsum (65/30/5 wt% respectively) was prepared by intergrinding (without grinding aids) unground clinker and the natural zeolite to a final composite with a mean particle size of 24 μm (the zeolite component, being softer, was ground to finer particles than the clinker in the final blend). The blend was provided by Trabits Group. OPC type I/II modified with silica powder (30% by weight of cement) was used as a reference material in the strength recovery tests. The addition of crystalline silica to cement is commonly carried out for subterranean cementing at temperatures above about 90°C to avoid strength retrogression.

Carbon microfibres (7–9 μm in diameter and 100–200 μm long) were added to ensure controlled crack formation. The fibres, supplied by Asbury Carbon, had a density of 1.73–1.79 g/cm^3 , carbon content of more than 94%, tensile strength of 2.0–3.8 GPa and Young's modulus of 180–240 GPa. Silica powder (average particle size $\sim 15 \mu\text{m}$) was added to half of the Fer-modified samples. The compositions of the tested blends are listed in Table 1.

The slurries were hand mixed at a water-to-blend mass ratio of 0.54, poured into 20 $\times$ 40 mm cylindrical polyacrylic moulds and left to set for 24 h at room temperature and then under $99 \pm 1\%$ humidity at 85°C for a further 24 h, imitating well-placement temperatures. The set samples were further cured for 24 h at 270°C in autoclaves filled with water or sodium carbonate solution, representing early curing under the static temperature of a hot geothermal well. The volumetric proportion of cement-to-solution was 1:3.5 and the pressure in the autoclave was 8.27 MPa.

A solution of sodium carbonate at 0.05 M was used to simulate the conditions of alkali carbonation in geothermal wells.

After curing, samples were crushed at their stress-strain yield point used to calculate the compressive strength and Young's modulus of the control and then autoclaved for a further 5 d at 270°C in carbonate or water environments to heal the damage. The crush tests and the 5 d autoclave-healing process were repeated, followed by final compressive strength measurements. Additionally, crack filling was examined on pre-cracked

Table 1. Tested formulations

	OPC/silica	Clinker/Fer	Clinker/Fer/silica
Clinker/Fer	—	94.3	66
OPC	66	—	—
Silica	28.3	—	28.3
Carbon microfibres	5.7	5.7	5.7

samples with cracks of 0.25 mm width and ~2 mm depth made by inserting Teflon tabs into the slurries before their curing for 24 h at 270°C as described above. After the initial curing, the Teflon tabs were removed and crack sealing was examined after 5 and 10 d of autoclaving in carbonate or water at 270°C using a Nikon Eclipse LV 150 3D microscope.

After the final compressive strength measurements, the cores and surfaces of the samples were ground into very fine powder and dried at 90°C for 24 h before thermogravimetric analyses, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and x-ray diffractometric (XRD) characterisation. The samples were examined by taking four FTIR scans for each spectrum using a 40 kV, 40 mA copper anode x-ray tube with a 0.02° step, 1.2 °/min scan speed, $2\theta = 3\text{--}51^\circ$.

The results were analysed using the PDF-4/Minerals 2015 database of the International Center for Diffraction Data (ICDD). The morphologies of the selected formulations were explored on typical spots of freshly fractured and chromium-coated samples with a Jeol 7600F scanning electron microscope (accelerating voltage of 15.0 kV, 11 μA).

Results and discussion

Mechanical properties and microscope study of fracture filling

Figure 1 summarises the results of mechanical property measurements of samples of the silica-modified OPC and clinker/Fer blends. Outstanding compressive strength recoveries were achieved: 134% by the blend containing Fer without silica even after two crush tests in the water environment and

Figure 1. Mechanical properties and their recoveries in water or alkaline carbonate solution at 270°C for OPC/silica and clinker/Fer blends

Figure 2. Photographs and 3D images of 0.25 mm crack in clinker/Fer silica-modified or non-modified samples before and after exposure to water or alkali carbonate environments at 270°C for 1 d (control), 5 d or 10 d

111% by the sample modified with silica in the carbonate environment. These compressive strength recoveries were accompanied by a progressive increase in Young's modulus, especially conspicuous for the sample without silica cured in water.

For the sample without silica cured in carbonate, the strength recovery was 170% after the first crush but only 70% after the second crush. The sample with silica cured in water showed strength recoveries very close to those of the OPC/silica blend (60% after the first crush and 56% after the second). The Young's modulus of these samples mirrored the compressive strength behaviour with strong recovery after the first crush and low recovery after the second crush for non-modified samples in carbonate and low recoveries for the sample with silica in water. Low strength recoveries were generally associated with the formation of large, long cracks.

Since the major role of a cement sheath in a subterranean well is zonal isolation, healed cement should possess low permeability along with recovered strength. The efficiency of crack filling was studied by taking images and reconstructing the 3D structure of pre-cracked (0.25 mm width) samples after 5 or 10 d of curing in water or carbonate (Figure 2). The crack filling was noticeably better in samples cured in the carbonate environment than those cured in water. For the sample modified with silica, the crack was completely sealed after 5 d. The crack in the unmodified sample was partially filled after 10 d in carbonate solution, but additional curing time would complete the crack plugging. The water-healed samples had some minor solid depositions in the fractures but they were not sufficient to seal the large cracks.

The results clearly showed that the strength recovery and crack filling in the tested samples differed. Crack filling was

unambiguously better in samples cured in carbonate than those in the water. The clinker/Fer sample modified with silica showed the best combination of strength recovery and fracture sealing when cured in the alkali carbonate environment.

Analyses of degraded samples – crystalline phases and XRD patterns

Tables 2–4 list the crystalline phases identified in the samples cured for 1 d (control), 5 d or 10 d in different environments, along with their ICDD numbers and chemical formulas. Figure 3 shows the XRD patterns of cores of the 10 d cured samples after water or carbonate solution curing (Figure 3(a)) and surfaces for carbonate-cured specimens (Figure 3(b)).

Both the control and 10 d cured samples showed some non-reacted clinker peaks (C_3S , ICDD 04-014-9801; C_2S , ICDD 00-033-0302) and peaks of crystalline silica for the

silica-modified samples. The intensities of the residual clinker peaks were higher for the samples without silica and those cured in water compared against those cured in alkali carbonate (the dramatic difference in peak intensities at $\sim 2\theta = 29.4^\circ$, 32.2° and 32.6° could not be accounted for by the lower amount clinker in the silica-modified samples), indicating acceleration of clinker hydration by carbonate in the presence of silica. Fer peaks disappeared after 1 d of curing in all the specimens, suggesting fast alkaline decomposition of the zeolite.

After 10 d of curing, the major types of crystalline reaction products included: calcium silicates and aluminium-modified calcium silicate hydrates (CSHs) (xonotlite, tobermorite and aluminium-substituted tobermorite, pseudowollastonite (Mitsuda and Banno, 1977), kilchoanite); carbonated CSHs (scawtite and spurrite); magnesium (calcium, iron) silicates;

Table 2. Crystalline compositions of cements cured for 1 d (control)

Water curing, no quartz	Water curing, quartz	Carbonate curing, no quartz	Carbonate curing, no quartz
<p><i>Principal:</i></p> <ul style="list-style-type: none"> Kilchoanite $Ca_6(SiO_4)(Si_3O_{10})$ (00-029-0370) Silica SiO_2 (04-015-7165/04-006-2057/04-012-1320) Scawtite $Ca_7(Si_6O_{18})(CO_3).2H_2O$ (00-031-0261) Katoite $Ca_3Al_3.5O_4.5(OH)_{7.5}$ (04-017-1503) Hibschite $Ca_3Al_2(SiO_4)_2(OH)_4$ (00-042-0570) Larnite Ca_2SiO_4 (01-083-0461) <p><i>Secondary:</i></p> <ul style="list-style-type: none"> Spurrite $Ca_5(SiO_4)_2(CO_3)$ (00-029-0307) Tobermorite 11A $Ca_{2.25}Si_3O_{7.5}(OH)_{1.5}(H_2O)$ (04-011-0271) Akermanite $Ca_2Mg(Si_2O_7)$ (04-016-1459) Magnesium silicates Mg_2SiO_4 (01-087-2040/01-074-1683) Akermanite-gehlenite $Ca_2Mg_{0.08}Al_{1.84}Si_{1.08}O_7$ (04-015-7935) Andradite $Ca_3Fe_{1.5}Al_{0.5}(SiO_4)_2(OH)_{0.8}$ (04-012-1320) 	<p><i>Principal:</i></p> <ul style="list-style-type: none"> Xonotlite $Ca_6Si_6O_{17}(OH)_2$ (00-023-0125) Tobermorite 11A $Ca_{2.25}Si_3O_{7.5}(OH)_{1.5}(H_2O)$ (04-011-0271) <p><i>Secondary:</i></p> <ul style="list-style-type: none"> Anorthite $Ca(Al_2Si_2O_8)$ (01-086-1705) Diopside $CaMgSi_2O_6$ (04-011-6812) Larnite Ca_2SiO_4 (01-077-0388) Cesantite $Ca_{1.31}Na_{4.32}((OH)_{0.94}(SO_4)_3)$ (01-075-1387) Anhydrate $CaSO_4$ (01-086-2270) Hematite Fe_2O_3 (04-006-9058) 	<p><i>Principal core:</i></p> <ul style="list-style-type: none"> Quartz SiO_2 (04-008-8440) Scawtite $Ca_7(Si_6O_{18})(CO_3).2H_2O$ (00-031-0261) Kilchoanite $Ca_6(SiO_4)(Si_3O_{10})$ (04-009-7055) Hatrunite $Ca_3(SiO_4)O$ (04-014-8419) Calcio-olivine Ca_2SiO_4 (04-006-2363) Tobermorite aluminium $Ca_{4.95}(Si_{5.5}Al_{0.5}O_{16.3})(OH)_{0.7}(H_2O)_5$ (01-074-2878) Dolomite $CaMg(CO_3)_2$ (04-015-9842) <p><i>Principal surface:</i></p> <ul style="list-style-type: none"> Kilchoanite $Ca_6(SiO_4)(Si_3O_{10})$ (00-029-0370) Xonotlite $Ca_6Si_6O_{17}(OH)_2$ (00-023-0125) Silica SiO_2 (04-015-7164) Scawtite $Ca_7(Si_6O_{18})(CO_3).2H_2O$ (00-031-0261) Tobermorite aluminium $Ca_{4.95}(Si_{5.5}Al_{0.5}O_{16.3})(OH)_{0.7}(H_2O)_5$ (01-074-2878) Dolomite $CaMg(CO_3)_2$ (01-081-8225) <p><i>Secondary core:</i></p> <ul style="list-style-type: none"> Huntite $CaMg_3(CO_3)_4$ (04-007-8886) Diopside $CaMgSi_2O_6$ (01-071-1067) Tobermorite 11A $Ca_{2.25}Si_3O_{7.5}(OH)_{1.5}(H_2O)$ (04-011-0271) Anhydrate $CaSO_4$ (04-007-9727) <p><i>Secondary surface:</i></p> <ul style="list-style-type: none"> Andradite aluminian $Ca_3Fe_{1.5}Al_{0.5}(SiO_4)_2(OH)_{0.8}$ (04-012-1320) Akermanite $Ca_2Mg(Si_2O_7)$ (01-077-9261) Diopside $CaMgSi_2O_6$ (01-071-1067) 	<p><i>Principal core:</i></p> <ul style="list-style-type: none"> Xonotlite $Ca_6Si_6O_{17}(OH)_2$ (00-023-0125) Tobermorite aluminium $Ca_{4.95}(Si_{5.5}Al_{0.5}O_{16.3})(OH)_{0.7}(H_2O)_5$ (01-074-2878) Diopside $CaMgSi_2O_6$ (01-071-1067) <p><i>Principal surface:</i></p> <ul style="list-style-type: none"> Quartz SiO_2 (01-070-3755/01-073-1748) Xonotlite $Ca_6Si_6O_{17}(OH)_2$ (00-023-0125) Tobermorite aluminium $Ca_{4.95}(Si_{5.5}Al_{0.5}O_{16.3})(OH)_{0.7}(H_2O)_5$ (01-074-2878) Calcite $CaCO_3$ (01-81-9560/04-015-7182) Akermanite $Ca_2Mg(Si_2O_7)$ (04-014-7679) <p><i>Secondary core:</i></p> <ul style="list-style-type: none"> Scawtite $Ca_7(Si_6O_{18})(CO_3).2H_2O$ (00-031-0261) Anhydrate $CaSO_4$ (04-007-9727) Calcite $CaCO_3$ (04-008-0213) Valerite $CaCO_3$ (00-033-0268) <p><i>Secondary surface:</i></p> <ul style="list-style-type: none"> Enstatite $Ca_{0.035}Mg_{0.965}SiO_3$ (04-013-1910) Scawtite $Ca_7(Si_6O_{18})(CO_3).2H_2O$ (00-031-0261) Diopside, sodian, ferroan $(Ca_{0.76}Na_{0.24})(Fe_{0.23}Mg_{0.77})(Si_2O_6)$ (01-082-3675)

Table 3. Crystalline compositions of cements cured for 5 d

Water curing, no quartz	Water curing, quartz	Carbonate curing, no quartz	Carbonate curing, no quartz
<p><i>Principal:</i></p> <ul style="list-style-type: none"> Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (00-023-0125) Scawtite $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ (00-042-1436) Coesite SiO_2 (04-015-7168) Larnite Ca_2SiO_4 (04-013-6293) Jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ (04-017-4421) <p><i>Secondary:</i></p> <ul style="list-style-type: none"> Kilchoanite $\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$ (00-029-0370) Akermanite $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ (04-016-1459) Andradite aluminian $\text{Ca}_3\text{Fe}_{1.5}\text{Al}_{0.5}(\text{SiO}_4)_{2.8}(\text{OH})_{0.8}$ (04-012-1320) Calcite CaCO_3 (01-080-2803) Bassanite $\text{Ca}_3(\text{SO}_4)_3(\text{H}_2\text{O})_{1.8}$ (04-011-1766) 	<p><i>Principal:</i></p> <ul style="list-style-type: none"> Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (00-023-0125/04-017-1287) Tobermorite 9A $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ (04-012-1761) Tobermorite –MDO2 $\text{Ca}_{4.5}\text{Si}_6\text{O}_{16}(\text{OH})(\text{H}_2\text{O})_5$ (04-017-1028) <p><i>Secondary:</i></p> <ul style="list-style-type: none"> Diopside $\text{CaMgSi}_2\text{O}_6$ (04-015-8340) Protoenstatite MgSiO_3 (04-008-5467) Clinoenstatite, calcian $\text{Mg}_{0.944}\text{Ca}_{0.056}\text{SiO}_3$ (01-076-0525) Hedenbergite $(\text{Fe}_{1.5}\text{Ca}_{0.5})\text{Si}_2\text{O}_8$ (01-082-8083) 	<p><i>Principal core:</i></p> <ul style="list-style-type: none"> Spurrite $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$ (04-011-9708) Scawtite $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ (04-011-9710) Xonotlite-Ma2bc $\text{Ca}_6(\text{SiO}_3)_6(\text{H}_2\text{O})$ (00-023-0125) 22 % Kilchoanite $\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$ (00-029-0370) Tobermorite aluminium $\text{Ca}_{4.95}(\text{Si}_{5.5}\text{Al}_{0.5}\text{O}_{16.3})(\text{OH})_{0.7}(\text{H}_2\text{O})_5$ (01-074-2878) <p><i>Principal surface:</i></p> <ul style="list-style-type: none"> Xonotlite-Ma2bc $\text{Ca}_6(\text{SiO}_3)_6(\text{H}_2\text{O})$ (01-074-7586) Scawtite $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ (01-081-1918/00-042-1436) Gismondine $(\text{Ca},\text{Na}_2)\text{Al}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ (00-021-0840) Calcite CaCO_3 (01-080-2791) Pseudowollastonite CaSiO_3 (04-011-3072) <p><i>Secondary core:</i></p> <ul style="list-style-type: none"> Calcium carbonate CaCO_3 (04-015-4109) Andradite $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ (04-009-8467/01-073-6297) Andradite, aluminian $\text{Ca}_3\text{Fe}_{1.6}\text{Al}_{0.4}(\text{SiO}_4)_{2.6}(\text{OH})_{1.6}$ (04-012-1320) Pseudowollastonite CaSiO_3 (01-080-9543) Calcium magnesium silicate $\text{MgCa}(\text{Si}_2\text{O}_6)$ (01-076-6732) <p><i>Secondary surface:</i></p> <ul style="list-style-type: none"> Lawsonite $\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2(\text{H}_2\text{O})$ (01-073-6449) Enstatite $\text{Ca}_{0.035}\text{Mg}_{0.965}\text{SiO}_3$ (04-013-1909) Cancrinite $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24} \cdot 2\text{H}_2\text{O}$ (00-048-1862) Dolomite $\text{CaMg}(\text{CO}_3)_2$ (00-011-0078) 	<p><i>Principal core:</i></p> <ul style="list-style-type: none"> Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (00-023-0125) Silica SiO_2 (04-007-0522/01-075-8322) Tobermorite $\text{Ca}_{2.25}\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5}(\text{H}_2\text{O})$ (04-014-8455) Calcite CaCO_3 (04-019-3759/01-086-2340) Riversideite $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ (00-029-0329) <p><i>Principal surface:</i></p> <ul style="list-style-type: none"> Coesite SiO_2 (04-015-7168) Tridymite-M SiO_2 (00-018-1170) Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (00-023-0125) Scawtite $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ (00-042-1436) Tobermorite $\text{Ca}_{2.25}\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5}(\text{H}_2\text{O})$ (04-014-8455) Lithosite $\text{K}_3(\text{HAl}_2\text{Si}_4\text{O}_{13})$ (01-073-8490) <p><i>Secondary core:</i></p> <ul style="list-style-type: none"> Bassanite $\text{Ca}_3(\text{SO}_4)_3(\text{H}_2\text{O})_{1.8}$ (04-011-1767) Protoenstatite MgSiO_3 (04-009-2093) Diopside, ferrian $\text{CaMg}_{0.95}\text{Fe}_{0.1}\text{Si}_{1.95}\text{O}_6$ (04-013-61-03) Ilmenite MgSiO_3 (04-017-1488) Magnesite MgCO_3 (04-012-4919) <p><i>Secondary surface:</i></p> <ul style="list-style-type: none"> Calcium carbonate CaCO_3 (04-014-1601) Magnesium silicate MgSiO_3 (01-076-6771) Analcime – C $\text{Na}(\text{Si}_2\text{Al})\text{O}_6 \cdot \text{H}_2\text{O}$ (00-041-1478) Andradite, aluminian $\text{Ca}_3\text{Fe}_{1.6}\text{Al}_{0.84}(\text{SiO}_4)_3$ (04-015-1327) Gismondine $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ (00-039-1373)

magnesium and calcium carbonates; high-temperature-stable zeolites such as mordenite, analcime and thomsonite-calcium; calcium sulfates such as bassanite and anhydrate. Crystalline silica was dominant in the surfaces of specimens cured in alkali carbonate even for the unmodified samples.

The crystalline compositions of the silica-modified and unmodified samples varied noticeably. Calcium silicates with a calcium/silicon ratio between 0.7 and 1 (such as tobermorite and predominantly xonotlite) formed as the major crystalline products in both environments for samples modified with

Table 4. Crystalline compositions of cements cured for 10 d

Water curing, no quartz	Water curing, quartz	Carbonate curing, no quartz	Carbonate curing, no quartz
<p><i>Principal:</i></p> <ul style="list-style-type: none"> ■ Orthoenstatite (01-082-3784) MgSiO_3 ■ Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (00-023-0125) ■ Scawtite $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ (00-042-1436) ■ Spurrte $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$ (04-011-9708) ■ Kilchoanite $\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$ (00-029-0370) ■ Andradite aluminian $\text{Ca}_3\text{Fe}_{1.5}\text{Al}_{0.5}(\text{SiO}_4)_{2.8}(\text{OH})_{0.8}$ (04-012-1320) ■ Jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ (04-017-4421) <p><i>Secondary:</i></p> <ul style="list-style-type: none"> ■ Bassanite $\text{Ca}_3(\text{SO}_4)_3(\text{H}_2\text{O})_{1.8}$ (04-011-1766) ■ Anhydrate CaSO_4 (04-007-9727) ■ Magnesite MgCO_3 (04-012-4918) 	<p><i>Principal:</i></p> <ul style="list-style-type: none"> ■ Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (04-017-1287) ■ Pseudowollastonite CaSiO_3 (04-011-3072) <p><i>Secondary:</i></p> <ul style="list-style-type: none"> ■ Anorthite $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$ (01-086-1705) ■ Diopside aluminian $(\text{Ca}_{0.5}(\text{Ca}_{0.4}\text{Mg}_{0.1}))(\text{Mg}_{0.86}\text{Al}_{0.14})(\text{Al}_{0.15}\text{Si}_{1.85}\text{O}_6)$ (01-075-9999) ■ Tobermorite 11A $\text{Ca}_4(\text{Si}_6\text{O}_{15})(\text{OH})_2(\text{H}_2\text{O})_5$ (01-077-8367) ■ Magnesite MgCO_3 (04-012-4918) ■ Calcium magnesium silicate $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ (04-014-7678) ■ Bassanite $\text{Ca}_3(\text{SO}_4)_3(\text{H}_2\text{O})_{1.8}$ (04-011-1767) ■ Anhydrate CaSO_4 (04-007-9727) ■ Scawtite $\text{Ca}_7\text{Si}_6(\text{CO}_3)\text{O}_{18} \cdot 2\text{H}_2\text{O}$ (00-042-1436) 	<p><i>Principal core:</i></p> <ul style="list-style-type: none"> ■ Spurrte $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$ (04-011-9708) ■ Scawtite $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ (01-081-1918) ■ Xonotlite-Ma2bc $\text{Ca}_6(\text{SiO}_3)_6(\text{H}_2\text{O})$ (01-074-7583) ■ Pseudowollastonite CaSiO_3 (01-080-9543) ■ Calcite CaCO_3 (01-078-3262) <p><i>Principal surface:</i></p> <ul style="list-style-type: none"> ■ SiO_2 (04-017-1027/04-007-2191/04-001-7249/04-008-7824/04-013-9484/04-007-2468) ■ Talc-1A $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (04-013-2941) ■ Mordenite $\text{Na}_3\text{Al}_3\text{Si}_{21}\text{O}_{48}(\text{H}_2\text{O})_{9.2}$ (04-017-1315) <p><i>Secondary core:</i></p> <ul style="list-style-type: none"> ■ Andradite aluminian $\text{Ca}_3\text{Fe}_{1.5}\text{Al}_{0.5}(\text{SiO}_4)_{2.8}(\text{OH})_{0.8}$ (04-012-1320) ■ Thomsonite $\text{CaNaCa}_2\text{Al}_5\text{Si}_5\text{O}_{20}(\text{H}_2\text{O})_6$ (04-013-3051) <p><i>Secondary surface:</i></p> <ul style="list-style-type: none"> ■ Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (00-023-0125) ■ Analcime $\text{Na}(\text{AlSi}_2\text{O}_6)(\text{H}_2\text{O})$ (01-072-0445) ■ Tobermorite –MDO1 $\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2(\text{H}_2\text{O})_5$ (04-017-1027) 	<p><i>Principal core:</i></p> <ul style="list-style-type: none"> ■ Xonotlite-Ma2b2c $\text{Ca}_6\text{Si}_6\text{O}_{18}(\text{H}_2\text{O})$ (01-074-7584) ■ SiO_2 (01-075-8322/01-072-4568/04-008-8696) ■ Pseudowollastonite (04-011-3072) CaSiO_3 ■ Tobermorite $\text{Ca}_{2.25}\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5}(\text{H}_2\text{O})$ (04-014-8455) ■ Calcite CaCO_3 (01-081-9560) <p><i>Principal surface:</i></p> <ul style="list-style-type: none"> ■ SiO_2 (01-089-3607/04-012-1126/01-077-8631) 49% ■ Xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (00-023-0125) ■ Talc-1A $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (04-013-2941) <p><i>Secondary core:</i></p> <ul style="list-style-type: none"> ■ Calcium magnesium silicate (diopside) $\text{CaMgSi}_2\text{O}_6$ (04-011-6812) ■ Calcium magnesium silicate $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ (04-014-7678) ■ Anhydrate CaSO_4 (01-072-0916) <p><i>Secondary surface:</i></p> <ul style="list-style-type: none"> ■ Mordenite $\text{Na}_3\text{Al}_3\text{Si}_{21}\text{O}_{48}(\text{H}_2\text{O})_{9.2}$ (04-017-1315) ■ Magnesium iron silicate $\text{MgFe}(\text{SiO}_4)$ (04-014-7729)

silica. Tobermorite persisted up to 10 d of curing and its calcium-to-silica content decreased as the curing time in carbonate solution increased, suggesting calcium removal through carbonation. Aluminium dissociated from decomposed Fer was included in tobermorite detected in the control samples in the carbonate environment. In addition to aluminium, zeolite decomposition supplied silicon and magnesium for further reactions.

The crystalline composition of the silica-rich samples cured in water closely resembled those of the OPC/silica blend, with the principal products being the clinker high-temperature hydrates.

In the case of unmodified samples, kilchoanite and dicalcium silicate were the major CSHs with calcium/silicon ratios of 1.5

and 2, respectively, formed after 1 d at 270°C (control). The hydrothermal formation of dicalcium silicates and transformation to kilchoanite at temperatures above 220°C were reported by Mitsuda *et al.* (1985). Kilchoanite persisted in the water-cured samples after 10 d, coexisting with xonotlite, which became the major calcium silicate phase in both the water- and carbonate-cured samples.

Carbonated CSHs were the main hydration products in the absence of silica in both the water-cured samples and especially in the carbonate-cured samples. They formed in the control samples and the intensity of their peaks steadily increased at the longer curing times of 5 d and then 10 d. These were scawtite and spurrte, possibly contributing to the increased crack sealing rate (see the section on ‘Mechanical properties and

Figure 3. XRD patterns of clinker/Fer blends after curing for 10 d at 270°. (a) Sample cores: trace A, silica-modified sample cured in water; trace B, non-modified sample cured in water; trace C, silica-modified sample cured in carbonate; trace D non-modified sample cured in carbonate. (b) Sample surfaces: trace A, silica-modified sample cured in carbonate; trace B non-modified sample cured in carbonate. T = tobermorite, X = xonotlite, O = orthoestatite, K = kilchoanite, Sc = scawtite, Sp = spurrite, Th = thomsonite, Ad = andradite aluminian, Ah = anhydrate, Q = quartz, CC = calcium carbonates, An = analcime, Mo = mordenite, Tc = talc

microscope study of fracture filling'). The hydrothermal formation of carbonated calcium silicates from dicalcium silicate and silica has been reported previously (Kalousek and Nelson, 1978). Scawtite persists under high-temperature hydrothermal conditions; it was found to be present in natural rocks exposed to carbonates, forming a stable layer during the carbonation of CSH-bearing rocks from Northern Ireland (Milodowski *et al.*, 2011). It was also reported to be commonly encountered in high-temperature wells where aqueous solutions of carbon dioxide entering pores of hydrating cement form scawtite and release silica that may partially seal fractures (Bensted, 1988).

Decomposed Fer was the main source of magnesium while clinker provided calcium for calcium magnesium silicates crystallised after the first day of curing (akermanite, diopside and enstatite). At longer curing times in the alkali carbonate solution, the intensities of their peaks strongly decreased even in cores of the samples, likely because of calcium removal through carbonation. Dolomite crystallised as one of the principal phases in unmodified samples through the calcium hydroxide attack of Fer, but its peaks weakened strikingly after 5 d of curing and were completely replaced by talc in the

surfaces after 10 d through skarnification reactions with silica accompanied by calcium carbonate formation, which was a major crystalline phase in the surface of the unmodified samples. Talc is a soft, clay-type mineral, and is unlikely to play any significant role in strength recovery; however, it may aid the sealing of small crevices.

In the case of the water-cured silica-modified samples, calcium magnesium silicate formed after 1 d of curing and persisted in the samples for 10 d. However, the peak intensities of this product were significantly lower than those of calcium silicates, indicating that this phase was not a major contributor to the strength recovery. In the sample without silica, magnesium silicate formed after the first day and became a major crystalline hydration product after 10 d. This phase likely played the key role in the outstanding strength recovery of the unmodified water-cured sample.

High-temperature-stable zeolites formed mostly in the surface layer of carbonate-cured specimens after 10 d of curing. In the presence of silica, the silica-rich zeolite mordenite was predominant (silicon/aluminium ratio = 7). For the sample without silica, peaks of thomsonite-calcium with lower silica content

were detected (silicon/aluminium ratio = 1). Notably, there were no zeolites among the principal core products in any of the specimens. Zeolites could be crystallising from the silica aluminate amorphous phase after the decomposition of Fer and magnesium reactions with calcium, silica and carbonate or could crystallise from solution with high dissolved sodium, aluminium and silicon contents at the solids' surfaces. In both cases, sodium and carbonate ions of the solution would play a major role in zeolite crystallisation, explaining their presence in the surfaces of the samples.

Some iron-containing hydrates formed, with the iron associated with Fer, and likely assisted in strength recovery. After 10 d of curing, they included andradite aluminian in both environments and magnesium iron silicate in the surface of the modified samples cured in carbonate solution.

In summary, the XRD analyses showed high-temperature alkaline Fer decomposition after 1 d of curing, the persistence of unreacted clinker and silica phases for 10 d and faster clinker loss for the silica-modified samples cured in alkali carbonate. The reactions of calcium from the clinker with magnesium from the Fer led to the formation of calcium magnesium silicates or dolomite. These products were not stable in the carbonate solution, transforming to calcium-free magnesium silicates and talc at longer curing times. The major identified crystalline phases contributing to the strength recovery were calcium silicates (xonotlite, tobermorite, kilchoanite and pseudowollastonite), magnesium silicate (orthoestatite) and calcium iron aluminate (andradite). The phases participating in sealing the cracks were mostly formed in the carbonate environment and included crystalline silica, talc and high-temperature-stable zeolites (mordenite, analcime and thomsonite-calcium). Carbonated calcium silicates, scawtite and spurrite, formed in unmodified samples as principal phases in the sample cured in carbonate and to a lesser extent in the water-cured samples, contributing to the strength when present in small amounts. Sodium carbonate played an important role in the formation of reaction/hydration products stable after 10 d of curing through the interactions of calcium, magnesium, sodium, carbonate and bicarbonate ions, creating conditions favouring silica precipitation.

Differential thermogravimetric (DTG) measurements

Table 5 lists the weight losses in different temperature ranges for specimens cured in water and carbonate solution and Figure 4 shows the DTG curves for the control samples (cured for 24 h at 270°C) and the samples cured for 10 d. The weight losses up to 400°C can be associated with (sodium, calcium) silica aluminate and CSHs; zeolite decomposition may also contribute to the weight loss in that temperature range (analcime, mordenite and thomsonite (Foldvari, 2011)). Between about 400 and 550°C, calcium-rich CSHs contribute to the weight loss (Ishida *et al.*, 1993), along with calcium hydroxide; the recrystallisation of aragonite to calcite occurs at around

Table 5. Thermal decomposition temperature ranges and associated weight losses for specimens cured under different conditions

Sample	Weight loss: %		
	70–400°C	400–550°C	600–850°C
Water curing, no quartz			
1 d (control)	2.7	1.6	3.4
10 d	1.5	1.4	3.3
Water curing, quartz			
1 d (control)	4.1	1.0	2.5
10 d	3.8	0.8	2.4
Carbonate curing, no quartz			
1 d (control)	2.7	1.6	4.8
10 d	1.4	1.2	8.2
Carbonate curing, quartz			
1 d (control)	4.2	0.7	3.0
10 d	3.6	0.6	3.0

450°C. The weight losses at temperatures above 550°C are, for the most part, due to the decomposition of carbonates such as calcite (~600°C), magnetite (~620–650°C), calcium magnesium carbonates (600–650°C, huntite), magnesium iron calcium carbonate (~700–750°C) and dolomite (750–800°C) (Foldvari, 2011). Calcium silicate carbonate, scawtite, decomposes to CaCO₃ at ~790°C and de-carbonates in the temperature range between ~830 and 850°C (McConnell, 1955; Stevula and Petrovic, 1981). The sulfate-containing mineral jarosite decomposes at ~610°C (Frost *et al.*, 2005) contributing to the mass loss in the range 550–850°C for the water-cured unmodified samples. Talc decomposition also takes place in this temperature range (~800–840°C) (Ewell *et al.*, 1935).

The decomposition peaks of various hydrates overlap strongly, thus not allowing the identification of separate phases. However, the following general trends supported the findings of the XRD analysis. The weight losses below 400°C were about twice as high for the samples with silica as for those without it in both water and carbonate curing environments, confirming the formation of CSHs in the presence of silica and faster clinker reactions for the silica-modified samples. On the other hand, the decomposition rate in the range 400–550°C associated with the calcium-rich hydrates and calcium hydroxide was greater for the samples without silica (0.6–1.0% with silica; 1.2–1.6% without silica). These hydrates are likely to be amorphous for the most part with some contribution of kilchoanite, as identified by XRD. The specimen without silica cured in the carbonate solution experienced the greatest weight loss above 550°C (>8%). This result is in agreement with the XRD study, suggesting the decomposition of carbonated calcium silicate (scawtite) along with the possible decompositions of dolomite and talc (a wide decomposition band above 800°C). The decomposition peaks of silica-containing specimens at ~785°C are likely associated with calcium magnesium carbonates.

Figure 4. DTG curves of cement blends cured for 1 d (control; dashed lines) or 10 d (after two crush tests; solid lines) at 270°C in water or alkali carbonate solution

ATR-FTIR measurements

Figure 5(a) shows the FTIR absorption spectra in the region of 1800 to 650 cm^{-1} for the water-cured control samples (24 h at 270°C) and for the non-hydrated clinker/Fer blend. The spectrum of the blend encompassed the following 11 absorption bands.

- A wide band around 1043 cm^{-1} and a weak one at 669 cm^{-1} from T–O (T = silicon or aluminium) bond-related anti-symmetric ($V_{\text{as T-O}}$) and symmetric ($V_{\text{s T-O}}$) stretching vibrations in 3D oxygen-linked $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral frameworks of zeolite.
- Two other bands of T–O bonds at 1225 (Si–O ($V_{\text{as Si-O}}$)) and 707 cm^{-1} (Al–O ($V_{\text{s Al-O}}$)) (Christidis *et al.*, 2003; Elaiopoulos *et al.*, 2010; Joshi *et al.*, 1997; Mozgawa, 2001).
- The prominent doublet at 921 and 889 cm^{-1} from the cement clinkers, namely, Si–O bond stretching ($V_{\text{as Si-O}}$) in orthosilicate of calcium silicates (C_3S and C_2S), and the band at 707 cm^{-1} from Al–O ($V_{\text{s Al-O}}$) in tricalcium aluminate (C_3A) (Fernandez-Carrasco *et al.*, 2012; Gaki *et al.*, 2007; Mollah *et al.*, 2000; Taddei *et al.*, 2014).
- The five bands at 1486, 1451, 853, 829 and 707 cm^{-1} associated with the carbonate (CO_3^{2-}) group in carbonated compounds: the two bands at 1486 and 1451 cm^{-1} from C–O bond stretching ($V_{\text{as C-O}}$) and the last three bands from O–C–O bond bending ($\delta_{\text{O-C-O}}$) (Gunasekaran *et al.*, 2006; Xyla and Koutsoukos, 1989; Ylmen and Jaglid, 2013), so both Al–O and C–O contributed to the 707 cm^{-1}

band. The shoulder and weak bands at 1158 and 669 cm^{-1} , respectively, are attributable to S–O stretching ($V_{\text{as S-O}}$) and O–S–O bending ($\delta_{\text{as O-S-O}}$) of the sulfate (SO_4^{2-}) tetrahedral group in gypsum (Fernandez-Carrasco *et al.*, 2012; García-Lodeiro *et al.*, 2011; Ylmen *et al.*, 2009). Finally, the band at 1624 cm^{-1} was from H–O–H bending ($\delta_{\text{H-O-H}}$) in water.

The spectrum of the cement autoclaved in water for 24 h at 270°C showed the following new features: (a) the appearance of three new bands at 1204, 1073 and 959 cm^{-1} ; (b) the attenuation in absorbance and disappearance of Fer-related bands (Otero Areán *et al.*, 2008); (c) the enhanced peak intensity of carbonate-associated bands. The new band at 1204 cm^{-1} was attributed to Si–O stretching ($V_{\text{as Si-O}}$) in the amorphous silica gel (Almecida and Pantano, 1990) and the other two new bands were Si–O ($V_{\text{as Si-O}}$) in CSH and calcium silicate anhydrate formed during C_3S and C_2S hydration (Mollah *et al.*, 2000; Taddei *et al.*, 2014), resulting in the band frequency shift from 921 cm^{-1} of orthosilicate to 959 cm^{-1} of polymerised silicate.

The attenuation in absorbance and the disappearance of Fer-related bands strongly suggested zeolite decomposition in reactions, with Ca^{2+} and OH^- released during clinker hydration under high-temperature hydrothermal conditions (Colleparidi *et al.*, 1976; Costa and Massazza, 1977). As a result of hot alkali dissolution and hydrothermal disintegration, Fer partially disappeared and partially converted to an amorphous phase.

Figure 5. FTIR spectra of non-hydrated clinker/Fer blend, and control samples cured for 1 d (a) or 10 d (b) in water at 270°C; samples cured in alkali carbonate solution at 270°C for 10 d (c)

The enhanced intensity of carbonate-associated bands corresponds to a large amount of carbonated CSH such as scawtite formed in cement. As is obvious from the presence of bands at 921 and 889 cm^{-1} , some non-hydrated clinker still remained after autoclaving for 1 d. This fact was one of the reasons why the non-modified samples had a lower compressive strength at an early hydration age. However, importantly, cement damaged in the crush tests recovered its compressive strength during an extended autoclave period, at least partially because of the hydration of non-reacted clinker. Additionally, the bands at 1158 and 669 cm^{-1} were interpreted as sulfate-related reaction products (Al-Hosney and Grassian, 2005; Thompson and Palmer, 1988).

The spectrum of the silica-modified sample clearly differed from that of the unmodified sample with even more striking decay of the absorbance related to Fer, clinker and carbonates, with the band at 959 cm^{-1} representing the hydrated silicate compounds becoming the principal one along with the emergence of a new band at 1073 cm^{-1} attributed to Si–O stretching in silicate. Relating this information to the XRD study, it can be suggested that the silica not only promoted the formation of CSHs (tobermorite and xonotlite) responsible for developing the early strength of cement, but also reacted with ionic species (Na^+ , Mg^{2+} , and Al^{3+}) liberated from the hot alkali dissolution of Fer to form anorthite and diopside in the presence of calcium ions from the clinker. In agreement with the XRD results, the FTIR spectra did not show the additional formation of carbonated compounds in the silica-modified samples cured in water.

The spectra of the samples cured in the alkali carbonate environment at 270°C for 1 d were similar to those of the water-cured samples except for the incorporation of carbonate-related bands. Again, the intensity of these bands in the unmodified samples was much higher than in the samples modified with silica.

Figure 5(b) shows the FTIR spectra of the damaged samples after 10 d of curing in water at 270°C. In agreement with the XRD results, the spectra of the unmodified samples indicated the presence of both carbonated and non-carbonated silicate compounds with the principal and secondary bands at nearly 959 cm^{-1} and at 1073 cm^{-1} , corresponding to Si–O bond stretching, and several carbonate-related C–O stretching bands at 1486, 1451, 853 and 829 cm^{-1} . Relating this evidence to the XRD reveals that the major crystalline non-carbonated silicates would be orthoenstatite, xonotlite (Mostafa *et al.*, 2009), kilchoanite and andradite aluminian, while the carbonated silicates involve scawtite and spurrite. There were still Fer- and clinker-related bands present in the samples, clearly indicating that the hydration of the clinker and the dissolution of zeolite were not completed after 10 d of exposure.

The spectrum of the silica-modified cement after 10 d in water was similar to that of the 1 d autoclaved sample, highlighting

accelerated dissolution of Fer and reactions with clinker in the presence of silica.

The surface spectrum of the damaged non-modified cement exposed for 10 d to the alkali carbonate environment (Figure 5(c)) showed a new reaction product identified as silica based on the newly developed bands at 1023 and 785 cm^{-1} , respectively from Si–O ($V_{\text{as Si-O}}$) and ($V_{\text{s Si-O}}$) stretching vibrations (Ramasamy and Suresh, 2009; Saikia *et al.*, 2008). The formation of silica as the major reaction by-product was due to the precipitation of silica in carbonate after dissolution of silicate compounds. This spectrum also showed the presence of some silicate and carbonate reaction products coexisting with the residue of clinker. As expected, the core of this sample had two major bands at 959 and 921 cm^{-1} , attributed to silicate reaction products and clinker, but there were no quartz-related bands, indicating that, beneath the carbonated top surface layer, the cement remained intact. Thus, conceivably, the precipitation of silica may create a protective barrier layer abating the rate of further carbonation-induced erosion. For the silica-modified cement, the spectrum of the surface showed silica as a primary product in conjunction with the silicates (xonotlite and talc-1A) as secondary reaction products identified by XRD. The presence of residual clinker and carbonated compounds was negligible, supporting the XRD results. The underlying core area was composed of silicate- and sulfate-related reaction products.

Morphologies of silica-modified and unmodified samples cured in water or carbonate

The core morphologies of the damaged samples autoclaved for the total 10 d in water or carbonate were amorphous for the most part (see Figure 6 and Table 6) with some inclusions of needle-like crystals (points 1, 8, 9 and 12). The amorphous matrix was rich in silica for the silica-modified samples (points 6, 7 and 10) and rich in calcium for the water-cured unmodified sample (point 13). The needle-shaped crystals had compositions typical of xonotlite and scawtite (points 1 and 8) and kilchoanite (point 12), supporting the XRD findings. Silica-rich mordenite composition was detected in some spots on the surfaces of the samples (2, 5 and 14). The surface compositions of both the silica-modified and unmodified cements were, for the most part, typical of silica and the morphologies showed depositions of amorphous and crystalline silica (points 3, 4, 11 and 15), in agreement with XRD and FTIR results. The carbon detected in the samples resulted from their carbonation and from the presence of carbon microfibres.

Conclusions

OPC type I/II clinker/Fer, Fer/silica and non-silica blends were tested for compressive strength recoveries and fracture closure under hydrothermal conditions at 270°C in alkali carbonate or water environments after imposed mechanical

Figure 6. Scanning electron micrographs of typical cement microstructures of clinker/Fer samples cured for 10 d at 270°C

Table 6. Elemental compositions of the points shown in Figure 6

Point	Carbon	Sodium	Magnesium	Aluminium	Silicon	Calcium	Iron	Possible phase
1	5.4	0.39	0.42	4.6	14	14	0.81	Xonotlite, non-reacted Fer
2	—	1.6	—	1.6	31	—	—	Mordenite, silica
3	—	0.72	—	0.39	33	—	—	Silica
4	—	0.56	—	0.32	33	—	—	Silica
5	—	3.9	—	3.2	28	—	—	Mordenite
6	—	0.23	—	0.3	33	—	—	Amorphous matrix
7	8.8	0.43	—	1.0	14	13	0.23	Amorphous matrix
8	11	—	—	1.1	13	13	0.31	Xonotlite, scawtite
9	8.3	0.31	0.64	1.2	15	13	0.3	Fer, xonotlite,
10	19	—	—	0.73	14	—	—	Amorphous silica-rich matrix
11	5.2	—	—	—	28	—	—	Silica
12	12	—	0.19	0.63	10	14	0.24	Kilchoanite
13	2.9	—	0.13	0.52	14	23	0.26	Amorphous matrix
14	—	1.8	—	1.8	31	—	—	Mordenite, silica
15	9.9	0.47	—	0.22	23	—	—	Silica

damage. The following general conclusions can be drawn from the study.

- (a) Compressive strength recoveries were outstanding (above 100%) for repeatedly damaged silica-modified samples healed in carbonate and for unmodified samples healed in water at 270°C for 10 d. The strength recoveries of the unmodified samples in carbonate were comparable to those of the OPC/silica blends and those of the silica-modified samples were more than 100% after the first imposed damage and less than 60% after the second damage. The decrease in recovery was due to the increased sample brittleness after the first healing period, resulting in the formation of long,

wide cracks in the second damage that were difficult to repair.

- (b) The 0.25 mm cracks were closed after 10 d in carbonate for the silica-modified samples and partially closed for the unmodified ones. On the other hand, crack sealing was insignificant for the samples healed in water.
- (c) The recoveries of compressive strength were the result of continuous clinker hydration and fast high-temperature alkali decomposition and interactions of Fer. The crystalline structure of Fer was lost after the first 24 h of 270°C exposure for samples cured in carbonate or water. The decomposed zeolite released silicon, magnesium, aluminium and iron, which participated in the creation of new phases, contributing to the strength recoveries and

sealing of the fractures. The formation of mixed calcium aluminium silicates and calcium magnesium silicates suggests that decomposition and reactions of the zeolite and hydration of the clinker phases were concurrent.

- (d) The new crystalline phases responsible for strength recoveries included various magnesium silicates, calcium silicates, calcium aluminium silicates and calcium aluminium iron silicates. The crystalline products sealing the cracks were mostly silica, talc and high-temperature-stable zeolites (mordenite, analcime and thomsonite).
- (e) The decomposition of Fer was faster for samples cured in the alkali carbonate environment than for samples cured in water. This, along with the partial calcium removal as soluble calcium bicarbonate and the lower solubility of silicon, led to increased precipitation of crystalline and amorphous silica, resulting in more efficient sealing of the cracks in the carbonate-cured samples. The formation of talc through the transformation of calcium magnesium silicates (diopside and akermanite) to various magnesium silicates (protoenstatite and ilmenite) as a result of calcium removal by carbonation and through dolomite skarnification also contributed to the process of fracture filling.
- (f) The major crystalline hydration products of the clinker were xonotlite in the silica-modified samples and kilchoanite along with carbonated calcium silicates (scawtite and spurrite), which became the principal crystalline products in the carbonate environment, for the unmodified samples. Carbonated CSHs were persistent after 10 d of curing and likely responsible for the good initial strength build-up and first-time recoveries but increased the samples' brittleness and, consequently, decreased second-time recoveries.
- (g) The study showed that natural zeolites unstable under high-temperature alkaline conditions may serve as a latent source of aluminium, silica and other cations for new phases and the strength recovery of damaged cements under high-temperature geothermal conditions.

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