Acid resistance of calcium aluminate cement–fly ash F blends

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The short-term resistance to sulfuric acid at 90°C of four calcium aluminate cement (CAC)–fly ash class F (FAF) blends activated with sodium metasilicate (thermal shock resistant cements (TSRCs)), cured at 300°C, was compared to that of a calcium phosphate cement (CPC) (CAC–FAF blend activated with sodium hexametaphosphate) and a Portland cement class G/silica blend. The mechanical properties and compositions of the acid-exposed samples were evaluated by measuring their compressive strength and by means of x-ray diffraction, μ EDX (energy-dispersive x-ray spectrometry), thermogravimetric and Fourier transform infrared analyses. All calcium-containing hydrates were sensitive to the conditions of acid exposure. In the TSRC blends, these hydrates included hydrogrossular, feldspar family minerals and zeolites; in CPC, feldspar minerals and phosphate phases; and in the class G/silica blend, portlandite and tobermorite. Crystalline calcium sulfates formed in the acid-exposed surfaces with the exception of the most aluminium-rich TSRC samples where only potassium(sodium) aluminium sulfate, alunite, was detected. This sample underwent the least changes in weight, compressive strength and had the lowest sulfur permeation into the sample core. Calcium sulfates precipitated on sample surfaces limited sulfur penetration into the core of calcium-rich TSRC, CPC and G/silica blends.

Introduction

In geothermal wells, strongly acidic environments come from the dissolution of hydrogen sulfide (H_2S) with the formation of sulfuric acid (H_2SO_4). This leads to a very low pH (<1) hot-acid attack on the cement sheath (Alexander *et al.*, 2013; Lichti and Yanagisawa, 2015; Villasenor and Vicedo, 2010). The degradation of Portland cement by acid proceeds through decalcification of portlandite followed by calcium loss from calcium-silicate hydrate phases at a pH below about 12.4, causing an increase in porosity and decrease in mechanical strength (Beddoe and Dorner, 2005; Glasser *et al.*, 2008; Gutberlet *et al.*, 2015; Kudowski, 2004; Puertas *et al.*, 2012; Zivica, 2004). The acid diffusivity through the calcium-depleted hydrates is of an order of magnitude higher than that through the original material (Bentz and Garboczi, 1992). The calcium is replaced by acid protons linking the silicate chains and leaving just a silica residue at a pH below about 2 (Beddoe and Dorner, 2005; Chen *et al.*, 2004; Haga *et al.*, 2002). In the geothermal industry, silica polymerisation caused by low-pH environments is a known problem (Lichti and Yanagisawa, 2015). The precipitation of calcium–acid anions reaction products may either slow down acid attack (Zivica and Bajza, 2002) or enhance erosion and compromise the matrix integrity (Larreur-Cayol *et al.*, 2011).

The iron- and aluminium-containing hydrates of Portland cement dissolve slower and at lower pH values than calcium

hydrates (Beddoe and Dorner, 2005), so the addition of supplementary cementitious materials (SCMs) to Portland cement has been tested and shown to improve the cement's acid resistance by lowering the calcium content and decreasing porosity (Al-Akhras, 2006; Bakharev 2005; Bakharev *et al.*, 2002; Lee *et al.*, 2005; Ouyang *et al.*, 1988). In the case of attack by sulfate ions, SCMs also help to preserve matrix integrity since they do not form expanding reaction products. Using solely alkali-activated SCMs (Chindapasirt *et al.*, 2014) and incorporating them in reactive aluminium (Kandasamy and Shehata, 2014) has been reported to decrease ion diffusion and help enhance sulfate resistance. However, the gel hydration products of cements with alkali-activated SCMs such as fly ash undergo dealumination of aluminosilicates with the formation of the same final amorphous silica gel (Allahverdi and Skvara, 2001; Allahverdi and Skvara, 2005; Donatello *et al.*, 2013). Geopolymers with crystalline zeolites in the structure formed from activated fly ash were also shown to lose strength at 95°C in acidic media (Bakharev, 2005).

Calcium aluminate cement (CAC) has the advantage of a lower calcium content than Portland cement. The nature of its hydrates and the products of sulfuric acid reactions also help to slow down the degradation of CAC with sulfuric acid at pH levels of above ~ 3 (Lamberet *et al.*, 2008). At lower pH levels, however – although slowly – aluminium hydroxide dissolves in acid and eventually the acid degradation of cement proceeds.

To the authors' knowledge the performance of high-temperature hydration products of blends based on CAC and SCMs in strong acids is not known.

This paper focuses on the short-time changes in the hydrate phase compositions and morphologies of CAC blends with sodium-metasilicate-activated fly ash class F (FAF) during an attack by sulfuric acid at 90°C. These blends were developed as thermal shock resistant cements (TSRCs) for geothermal wells (Sugama *et al.*, 2012). A Portland cement class G/silica 70/30 wt% blend was tested as a baseline. A CAC blend with FAF activated with sodium hexametaphosphate (calcium phosphate cement (CPC)), developed previously for applications in geothermal wells and tested for acid resistance (Sugama, 1997; Sugama *et al.*, 1999), was also investigated for comparison. To evaluate the role of calcium content, the studied formulations contained two types of CAC – low-calcium CAC#80 in blends TSRC-1 and TSRC-3 and high-calcium CAC#51 in blends TSRC-2 and TSRC-4 (Tables 1 and 2). To assess the effect of the SCM on acid resistance, the fly ash content of the blends was also varied, between 40 wt% (TSRC-1 and TSRC-2) and 60 wt% (TSRC-3 and TSRC-4). The pH value was chosen based on cement applications in geothermal wells with highly acidic environments where not only calcium but also ferrite and aluminate hydrates of Portland cement become soluble (Beddoe and Dorner, 2005). It was of interest to assess how the aluminium solubility at this pH affects the damaged layer composition and sample integrity, and it also allowed acceleration of the acid attack.

Experimental procedure

Table 1 lists the mix proportions of the tested blends and Table 2 gives the oxide compositions of their components determined by energy-dispersive x-ray spectrometry (EDX). The CACs for use in the TSRC blends were supplied by Kerneos Inc. The class G cement used was a Dyckerhoff North type.

Sodium metasilicate granular powder (supplied by PQ Corporation under the trade name Metso Beads 2048) was used as the alkali activator of FAF in the TSRC formulations. The sodium hexametaphosphate used in the CPC was supplied by Aldrich. X-ray powder diffraction (XRD) data showed three major crystalline phases in FAF – quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and hematite (Fe_2O_3). The CAC#80 encompassed crystalline corundum ($\alpha\text{-Al}_2\text{O}_3$), calcium monoaluminate ($\text{CaO} \cdot \text{Al}_2\text{O}_3$) and calcium dialuminate ($\text{CaO} \cdot 2\text{Al}_2\text{O}_3$), while CAC#51 had calcium monoaluminate as the major phase and gehlenite [$\text{Ca}_2\text{Al}(\text{Al},\text{Si})_2\text{O}_7$] and corundum as secondary phases.

The slurries were mixed by hand at a water to blend ratio of 0.4 for the class G/silica blend and at 0.44 for all the other blends. After mixing, the slurries were poured into 20 × 40 mm cylindrical moulds and left to set under 100% humidity at 85°C for 24 h, imitating placement temperatures in a geothermal well. Set samples were further cured for 24 h at 300°C in autoclaves, representing early curing under static conditions of high-temperature geothermal wells. The volumetric

	Cement: wt %	Class F fly ash (FAF): wt%	Other blend-forming reactants: wt%
TSRC-1	56.6 (CAC#80)	37.7	5.7 (sodium metasilicate)
TSRC-2	56.6 (CAC#51)	37.7	5.7 (sodium metasilicate)
TSRC-3	37.7 (CAC#80)	56.6	5.7 (sodium metasilicate)
TSRC-4	37.7 (CAC#51)	56.6	5.7 (sodium metasilicate)
Class G	70.0	—	30 (silica)
CPC	47.2 (CAC#51)	47.2	5.6 (sodium hexametaphosphate)

Table 1. Mix proportions of cement composites

	Aluminium oxide (Al_2O_3)	Calcium oxide (CaO)	Silicon dioxide (SiO_2)	Iron oxide (Fe_2O_3)	Sodium oxide (Na_2O)	Potassium oxide (K_2O)	Titanium dioxide (TiO_2)	Sulfur trioxide (SO_3)
Class G cement: atomic %	1.0	71	17	5.0	0.34	1.2	—	3.6
CAC#80: atomic %	75.2	24.7	—	0.1	—	—	—	—
CAC#51: atomic %	45.1	49.7	—	2.8	—	—	2.4	—
FAF: atomic %	35	2.7	50	7.1	0.30	3.1	1.6	—
Sodium metasilicate: wt%	—	—	46.6	—	50.5	—	—	—

Table 2. Oxide compositions of blend-forming components

proportion of cement to water was 1 to 3.5; the pressure in the autoclave was 8.27 MPa. Three cured samples of each type were weighed, measured and placed into solutions of sulfuric acid at 90°C (pH 2.5) for 6 d. Although the reactions' kinetic depends on the temperature, technical limitations did not allow acid experiments to be performed at geothermal temperatures of 300°C. After this treatment the samples were visually examined for signs of erosion and spallation. Since the TSRC samples did not show any visual degradation they were immersed into the acid at pH 0.5 for a further 12 d. The volume of the acid solution was twice the volume of the sample and the solutions were replaced with fresh ones every 3 d to maintain <15% increase in pH during the treatment.

After acid exposure the specimens were rinsed with water, weighed, measured and tested for compressive strength. They were then ground into very fine powder and dried at 90°C for 24 h before conducting thermogravimetric analyses (TGA), attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR), μ EDX measurements and XRD characterisation. The samples were examined using a 40 kV, 40 mA copper anode x-ray tube. The results were analysed using the International Centre for Diffraction Data (ICDD) PDF-4/Minerals 2014 database. 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 (SEM). The goal of the study was to obtain information on the TSRC–sulfuric acid reaction products and phase transformations of the original hydrates formed at early ages. These reaction products could either inhibit or accelerate the acid-induced erosion and spallation of geothermal cements.

Results and discussion

Appearance and mechanical properties

As shown in Figure 1, the TSRC-1, TSRC-2 and CPC samples exposed to acid resembled the control samples; there were some brownish areas on the TSRC-2 and TSRC-4 specimens but the rim structure was not clearly visible; the class G/silica samples formed a well-defined white layer that partially eroded the densified underlying zone.

Table 3 summarises the mechanical properties of the samples before and after acid exposure. The decreases in weight and diameter may result from sample dissolution, erosion and spallation, while the precipitation of acid–cement reaction products may increase these parameters. The processes of weight and diameter gain or loss may partially or completely compensate each other if they happen simultaneously. All the TSRC samples experienced some weight loss, shrank in diameter and had a small corrosion depth, suggesting that product accumulation was less important than cement dissolution in the acid. The CAC-rich samples lost the least weight (TSRC-1) and diameter, possibly by forming expansive calcium salts (TSRC-2). An increase in FAF to 60 wt% (TSRC-3 and TSRC-4) caused further weight and diameter losses.

The compressive strength of the TSRC samples was not compromised by the acid exposure: the strength of TSRC-1 remained unchanged, while the strengths of TSRC-2, TSRC-3 and TSRC-4 increased by 17%, 31% and 67%, respectively. Continuous hydration and FAF reactions that are slower than

Figure 1. Appearance of samples after 18 d exposure to sulfuric acid at 90°C (pH 2.5 for 6 d followed by pH 0.5 for 12 d): (a) TSRC-1; (b) TSRC-2; (c) CPC; (d) class G/silica

	Weight change: %	Diameter change: %	Compressive strength: MPa		Corrosion depth: mm
			Before acid exposure	After acid exposure	
TSRC-1	−0.3	−0.79	18.0 ± 0.7	18.0 ± 2.0	0.68
TSRC-2	−1.12	−0.02	13.9 ± 1.3	16.3 ± 1.7	0.44
TSRC-3	−1.79	−1.65	11.2 ± 1.9	14.7 ± 2.3	<0.5
TSRC-4	−3.17	−0.85	12.7 ± 2.1	21.2 ± 4.5	<0.5
Class G/silica	+3.83	+1.88	17.4 ± 0.7	20.5 ± 0.6	1.97
CPC	−3.20	−1.7	25.3 ± 1.6	24.6 ± 6.5	0.86

Table 3. Sample properties after 18 d exposure to sulfuric acid at 90°C (pH 2.5 for 6 d followed by pH 0.5 for 12 d)

Figure 2. XRD patterns of TSRC-1 and TSRC-2 samples exposed to sulfuric acid for 18 d compared with control samples before exposure: B, boehmite; K, katoite; Q, quartz; G, gehlenite; P, perovskite; H, hematite; CC, calcium carbonates; An, analcime;

Ba, bassanite; CS, anhydrite; Al, alunite; D, dmisteinbergite; Ye, ye'elimite; M, mullite; HS, hydroxysodalite; Ga, garronite; A, anorthite; C, corundum

the hydration of CAC could be responsible for the increased compressive strength, especially in the FAF-rich samples (TSRC-3 and TSRC-4).

The CPC sample had the largest losses in weight and diameter, and experienced a 3% decrease in compressive strength. The class G/silica sample increased in both weight and diameter by forming a large external layer that proved to be calcium sulfate in the XRD tests; the compressive strength of this sample increased by about 19%.

Analyses of degraded samples – crystalline phases, XRD patterns

Figures 2–4 show the XRD patterns of the tested cement formulations cured at 300°C before and after acid exposure.

Table 4 lists the crystalline phases identified in the samples, along with their ICDD numbers and chemical formulas. Tables 5–7 give more detailed information on 2θ values of the experimental peaks and the phases associated with them. The complex composites show patterns with split peaks, suggesting the contribution of several phases, so each peak on the XRD patterns is associated with a number of possible contributors in the tables.

Crystalline phases of the control TSRC samples included non-hydrated reactants (corundum, quartz, mullite, perovskite, gehlenite, hematite and some calcium carbonates), hydration products of CAC such as boehmite and hydrogossular minerals (katoite silician and katoite), and hydration and reaction products from FAF alone or from both FAF and CAC

Figure 3. XRD patterns of TSRC-3 and TSRC-4 samples exposed to sulfuric acid for 18 d compared with control samples before exposure: Ga, garronite; Go, gorgeyite; B, boehmite; K, katoite; Q, quartz; G, gehlenite; H, hematite; CC, calcium carbonates;

An, analcime; Ba, bassanite; Al, alunite; D, dmisteinbergite; M, mullite; Ha, harmotome; C, corundum; Ph, phillipsite; He, hedenbergite

(such as various zeolites and anorthite). (Other members of the garnet series, such as grossular and hirschildite, or the plagioclase feldspar series ranging from albite to anorthite may contribute to the XRD patterns but were not explicitly identified because of the blends' complexity and their overlapping XRD patterns.) In addition, calcium carbonates formed during sample mixing and curing since no special precautions were taken to avoid carbonation.

CAC hydrates (boehmite, katoite silician and katoite) crystallised as major phases in the cement-rich blends TSRC-1 and TSRC-2. In the higher calcium content blend (TSRC-2), katoite formed instead of katoite silician, and the intensity of boehmite peaks was significantly lower than in the patterns of the aluminium-

rich blend (TSRC-1). TSRC-1 hydrates included not only the faster hydrating CAC hydration products, but also a crystalline zeolite, hydroxysodalite, which is a product of fly ash reactions.

An increase in FAF content in the initial blends (TSRC-3 and TSRC-4) raised the intensities of the fly ash hydration products, zeolites, and weakened those of the CAC hydrates, hydrogrossular phases and boehmite.

During the 18 d acid treatment, curing of the samples continued but at a lower temperature of 90°C, causing changes mostly in compositions of the sample cores, and the acid reacted with the cement, mostly altering the surface layers. The following changes occurred in the cores of TSRC samples.

Figure 4. XRD patterns of CPC and class G/silica cement samples exposed to sulfuric acid for 18 d compared with control samples before exposure: T, tobermorite 9A; Q, quartz; CC, calcium carbonate; Br, brownmillerite; Pr, portlandite; FH, iron oxide hydroxide; Gy, gypsum; D, dmisteinbergite; K, katoite;

An, analcime; CP, calcium hydrogen phosphate; A, anorthite; CA, carbonated hydroxylapatite; HA, hydroxylapatite; HS, hydroxylapatite sulfation; Ph, phillipsite; Ba, bassanite; M, mullite; C, corundum

For CAC-rich blends TSRC-1 and TSRC-2, the feldspar family minerals, isomorphous dmisteinbergite and anorthite, replaced the garnet series hydrates, katoites; the intensities of boehmite peaks dropped, although it remained one of the major phases. Further reactions of FAF produced new zeolites such as analcime, garronite and harmotome (and, possibly, other zeolites with chains of double-connected four-membered rings, gismondine and phillipsite, which have overlapping XRD patterns). In addition, some calcium sulfates were identifiable in the core of TSRC-2, but not to any significant extent in the core of TSRC-1 (Table 4).

The cores of the FAF-rich TSRC-3 and TSRC-4 samples showed partial or complete disappearance of the originally formed zeolites. In both TSRC-3 and TSRC-4, sulfur

permeated into the cores of the samples with the formation of calcium sulfates in TSRC-4 (made with calcium-rich CAC#51) and potassium-aluminium sulfate in TSRC-3 (made with aluminium-rich CAC#80). Calcium carbonates persisted in the cores of all the samples but not in the acid-exposed surfaces.

In the surfaces of the acid-exposed samples, calcium sulfates and potassium-aluminium sulfate phases partially or completely replaced the peaks of most calcium-containing hydrates, including hydrogossular, plagioclase feldspar and zeolites. Exceptionally, there were no crystalline calcium sulfates in the surface layer of TSRC-1. Only potassium(sodium) aluminium sulfate, alunite, formed in the surface of this sample. In geothermal sites, alunite forms naturally as a result of

Principal phases	Secondary phases	Non-reacted phases
TSRC-1 before exposure Boehmite $\text{AlO}(\text{OH})$ (01-074-2895) Hydroxysodalite $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ (00-011-0401) Katoite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ (04-014-1869)	Calcium carbonate CaCO_3 (04-006-5444/01-085-0849)	Quartz SiO_2 (04-006-2057) Corundum Al_2O_3 (04-008-3293) Mullite $\text{Al}_6\text{Si}_{12}\text{O}_{13}$ (00-015-0776) Hematite Fe_2O_3 (00-001-1053)
TSRC-1 after exposure, core Dmisteinbergite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (04-011-5220) Boehmite $\text{AlO}(\text{OH})$ (01-074-2896)	Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (04-012-1276) Garronite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ (00-039-1374) Calcium carbonate CaCO_3 (04-006-5444/01-085-0849) Harmotome $\text{Na}_3\text{Al}_3\text{Si}_5\text{O}_{16}(\text{H}_2\text{O})_{6.5}$ (04-009-5432) Analcime $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_8$ (04-011-6233) Hydroxysodalite $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ (00-011-0401) Katoite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ (04-014-1869)	Corundum Al_2O_3 (04-005-4497) Mullite $\text{Al}_6\text{Si}_{12}\text{O}_{13}$ (00-015-0776) Quartz SiO_2 (01-077-8621) Hematite Fe_2O_3 (01-080-5407/08/09/ 04-002-5211)
TSRC-1 after exposure, surface Alunite $\text{KAl}_3(\text{SO}_4)(\text{OH})_6$ (00-047-1884) Boehmite AlOOH (01-073-9093)	Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (00-041-1486) Analcime $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_8$ (04-011-7963)	Corundum Al_2O_3 (04-005-4497) Mullite $\text{Al}_6\text{Si}_{12}\text{O}_{13}$ (01-079-1452) Quartz SiO_2 (01-083-0539) Hematite Fe_2O_3 (04-002-2983)
TSRC-2 before exposure Boehmite $\text{AlO}(\text{OH})$ (04-010-5683) Katoite $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (04-017-4319)	Calcite $\text{Ca}(\text{CO}_3)$ (01-083-0577)	Gehlenite $\text{Al}_2\text{Ca}_2\text{O}_7\text{Si}$ (04-015-7930) Quartz SiO_2 (01-083-0542/01-073-1748) Perovskite CaTiO_3 (00-022-0153) Hematite Fe_2O_3 (00-039-1346)
TSRC-2 after exposure, core Dmistenbeirgite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (00-051-0064) Bassanite $\text{CaSO}_4(\text{H}_2\text{O})_{0.67}$ (00-036-0617) Boehmite $\text{AlO}(\text{OH})$ (04-010-5683)	Katoite $\text{Ca}_{2.93}\text{Al}_{1.97}(\text{Si}_{0.64}\text{O}_{2.56})(\text{OH})_{9.44}$ (01-077-1713) Analcime $\text{Na}_{1.71}((\text{Al}_{1.806}\text{Si}_{4.194})\text{O}_{12})(\text{H}_2\text{O})_{2.16}$ (01-075-8689) Anhydrate CaSO_4 (01-072-0916) Gypsum $\text{CaSO}_4(\text{H}_2\text{O})_2$ (01-079-5985) Calcite CaCO_3 (01-080-2791/01-083-0577)	Hematite Fe_2O_3 (04-014-7214) Gehlenite $\text{Al}_2\text{Ca}_2\text{O}_7\text{Si}$ (04-015-7930) Perovskite CaTiO_3 (01-081-0561)
TSRC-2 after exposure, surface Alunite $(\text{K}_{0.805}\text{Na}_{0.132}(\text{H}_2\text{O})_{0.063})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ (01-075-9141/00-001-0879) Boehmite $\text{AlO}(\text{OH})$ (04-010-5683) Bassanite $\text{Ca}_3(\text{SO}_4)_3(\text{H}_2\text{O})_{1.8}$ (04-011-1767/01-072-4535)	Dmisteinbergite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (00-051-0064) Anhydrate CaSO_4 (01-072-0916)	Quartz SiO_2 (04-007-1438/04-011-9932/01-075- 1555) Perovskite CaTiO_3 (00-022-0153) Hematite Fe_2O_3 (00-001-1053)
TSRC-3 before exposure Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (00-012-0301/04-011-2514) Garronite $\text{Na}_8\text{Ca}_{2.82}(\text{Al}_6\text{Si}_{10}\text{O}_{32})(\text{H}_2\text{O})_{12.08}/$ $\text{Na}_{0.1}\text{Ca}_{1.35}\text{Al}_{2.8}\text{Si}_{5.2}\text{O}_{16}(\text{H}_2\text{O})_7$ (01-079-1336/04-0121546) Harmotome $\text{Na}_3\text{Al}_3\text{Si}_5\text{O}_{16}(\text{H}_2\text{O})_{6.5}$ (04-009-5432)	Boehmite AlOOH (00-021-1307) Gobbsinite $\text{Na}_3\text{Al}_3\text{Si}_5\text{O}_{66}(\text{H}_2\text{O})_6$ (00-025-0779) Katoite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$ (04-014-9841) Analcime $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_8$ (04-011-7963) Gismondine (01-076-8378) Calcium carbonate CaCO_3 (04-017-9180/04-002-9082)	Corundum Al_2O_3 (04-013-1687/04-005-4500) Quartz SiO_2 (01-085-0794/01-086-1564) Mullite $(\text{Al}_{2.34}\text{Si}_{0.66})\text{O}_{4.83}$ (01-076-2579)

Table 4. Crystalline phase compositions of cements before and after sulfuric acid exposure; ICDD numbers in parentheses (continued on next page)

Principal phases	Secondary phases	Non-reacted phases
TSRC-3 after exposure, core Katoite silician $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$ (04-014-9841)	Boehmite AlOOH (01-074-2897/01-074-2896) Garronite $\text{NaCa}_{2.5}(\text{Al}_6\text{Si}_{10})\text{O}_{32}(\text{H}_2\text{O})_{14}$ (00-059-0383) Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (04-011-2883) Alunite $\text{KAl}_3(\text{SO}_4)(\text{OH})_6$ (00-047-1884) Katoite $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (04-017-4320) Analcime $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_8$ (04-011-6756) Gismondine (01-076-8378) Calcium carbonate CaCO_3 (04-017-9180/04-002-9082)	Quartz SiO_2 (01-078-1252) Hematite Fe_2O_3 (04-015-9577/01-080-5406) Corundum Al_2O_3 (01-0751862) Mullite $\text{Al}(\text{Al}_{0.69}\text{Si}_{1.22}\text{O}_{4.85})$ (01-089-2644)
TSRC-3 after exposure, surface Boehmite AlOOH (04-010-5683/04016-2858) Bassanite $\text{CaSO}_4(\text{H}_2\text{O})_{0.67}$ (00-036-0617)	Alunite $\text{KAl}_3(\text{SO}_4)(\text{OH})_6$ (04-014-9927) Gorgeyite $\text{K}_2\text{Ca}_5(\text{SO}_4)_6(\text{H}_2\text{O})$ (00-018-0997) Analcime $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_8$ (04-011-6233) Anhydrate CaSO_4 (04-007-4744) Hedenbergite $\text{Na}_{0.45}\text{Ca}_{0.55}\text{FeSi}_2\text{O}_6$ (04-013-1878)	Quartz SiO_2 (04-008-2359) Corundum Al_2O_3 (04-015-8996) Mullite $\text{Al}_2(\text{Al}_{2.8}\text{Si}_{1.2})\text{O}_{9.54}$ (01-084-1205)
TSRC-4 before exposure Analcime $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_8$ (04-011-7963) Garronite $\text{NaCa}_{2.5}(\text{Al}_6\text{Si}_{10})\text{O}_{32}.14\text{H}_2\text{O}$ (00-059-0383)	Phillipsite $\text{K}(\text{K}, \text{Na})_2(\text{Si}, \text{Al})_8\text{O}_{16}.4\text{H}_2\text{O}$ (00-046-1427) Gismondine $\text{Ca}_4(\text{Al}_8\text{Si}_8\text{O}_{32})(\text{H}_2\text{O})_{19}$ (01-076-8378) Katoite $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (04-017-4322) Calcium carbonate CaCO_3 (04-014-1837/01-081-9561)	Quartz SiO_2 (01-085-0865) Gehlenite $\text{Al}_2\text{Ca}_2\text{O}_7\text{Si}$ (04-015-7930) Mullite $\text{Al}(\text{Al}_{0.69}\text{Si}_{1.22}\text{O}_{4.85})$ (01-089-2644) Hematite Fe_2O_3 (00-001-1053) Perovskite CaTiO_3 (00-022-0153)
TSRC-4 after exposure, core Garronite $\text{NaCa}_{2.5}(\text{Al}_6\text{Si}_{10})\text{O}_{32}.14\text{H}_2\text{O}$ (00-059-0383)	Phillipsite $\text{K}(\text{K}, \text{Na})_2(\text{Si}, \text{Al})_8\text{O}_{16}.4\text{H}_2\text{O}$ (00-046-1427) Bassanite $\text{Ca}_{0.98}\text{Na}_{0.03}\text{SO}_4.0.47\text{H}_2\text{O}$ (00-037-0246) Analcime $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_8$ (04-011-7963) Gismondine $\text{Ca}_4(\text{Al}_8\text{Si}_8\text{O}_{32})(\text{H}_2\text{O})_{19}$ (01-076-8378) Gypsum $\text{CaSO}_4.2\text{H}_2\text{O}$ (04-010-9409) Katoite $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (04-017-4322) Calcium carbonate CaCO_3 (04-014-1837/01-081-9561)	Quartz SiO_2 (01-085-0865) Gehlenite $\text{Al}_2\text{Ca}_2\text{O}_7\text{Si}$ (04-015-7930) Perovskite (00-022-0153) Mullite $\text{Al}(\text{Al}_{0.69}\text{Si}_{1.22}\text{O}_{4.85})$ (01-089-2644) Hematite Fe_2O_3 (00-001-1053)
TSRC-4 after exposure, surface Alunite $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ (00-047-1885) Bassanite $\text{Ca}_{0.98}\text{Na}_{0.03}\text{SO}_4.0.47\text{H}_2\text{O}$ (00-037-0246)	Gorgeyite $\text{K}_2\text{Ca}_5(\text{SO}_4)_6(\text{H}_2\text{O})$ (04-012-5273) Analcime $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_8$ (04-011-7963) Anhydrate CaSO_4 (01-074-2421) Phillipsite $\text{K}(\text{K}, \text{Na})_2(\text{Si}, \text{Al})_8\text{O}_{16}.4\text{H}_2\text{O}$ (00-046-1427) Garronite $\text{NaCa}_{2.5}(\text{Al}_6\text{Si}_{10})\text{O}_{32}.14\text{H}_2\text{O}$ (00-059-0383) Gismondine $\text{Ca}_4(\text{Al}_8\text{Si}_8\text{O}_{32})(\text{H}_2\text{O})_{19}$ (01-076-8378)	Quartz SiO_2 (01-075-8320) Gehlenite $\text{Al}_2\text{Ca}_2\text{O}_7\text{Si}$ (04-015-7930) Mullite $\text{Al}(\text{Al}_{0.69}\text{Si}_{1.22}\text{O}_{4.85})$ (01-089-2644) Perovskite CaTiO_3 (00-022-0153) Hematite Fe_2O_3 (00-001-1053)

Table 4. Continued

Principal phases	Secondary phases	Non-reacted phases
CPC before exposure Dmisteinbergite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (00-051-0064)	Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (00-041-1486) Calcium hydrogen phosphate CaHPO_4 (01-075-1520) Analcime $\text{NaSi}_2\text{AlO}_6\text{H}_2\text{O}$ (00-019-1180) Carbonated hydroxylapatite $(\text{Ca}_{3.13}\text{Na}_{0.53})(\text{Ca}_{4.66}\text{Na}_{0.79})(\text{PO}_4)_{4.3}(\text{CO}_3)_{1.7}(\text{OH})_{0.74}(\text{H}_2\text{O})_{1.3}$ (01-073-7334) Katoite silician $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ (00-038-0368) Portlandite $\text{Ca}(\text{OH})_2$ (00-050-0008) Calcium carbonate CaCO_3 (04-014-1601) Hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ (04-016-1709) Boehmite AlOOH (01-074-2896)	Perovskite CaTiO_3 (00-022-0153) Gehlenite $\text{Al}_2\text{Ca}_2\text{O}_7\text{Si}$ (04-013-2147) Quartz SiO_2 (01-085-0457) Hematite Fe_2O_3 (04-003-1445) Mullite $\text{Al}(\text{Al}_{0.69}\text{Si}_{1.22}\text{O}_{4.85})$ (01-089-2644)
CPC after exposure, core Dmisteinbergite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (04-011-6236) Hydroxylapatite $\text{Ca}_{4.758}(\text{H}_{0.21}(\text{PO}_4))(\text{OH})_{0.726}$ (01-07409764)	Carbonated hydroxylapatite $(\text{Ca}_{3.13}\text{Na}_{0.53})(\text{Ca}_{4.66}\text{Na}_{0.79})(\text{PO}_4)_{4.3}(\text{CO}_3)_{1.7}(\text{OH})_{0.74}(\text{H}_2\text{O})_{1.3}$ (01-073-7334) Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (04-012-1276) Phillipsite $\text{K}_{2.5}\text{NaSi}_{11.3}\text{Al}_{4.7}\text{O}_{32} \cdot 13\text{H}_2\text{O}$ (00-051-1497) Katoite $\text{Ca}_{2.93}\text{Al}_{1.97}(\text{Si}_{0.64}\text{O})(\text{OH})_{9.44}$ (01-077-1713) Calcium hydrogen phosphate CaHPO_4 (01-075-1520) Calcium carbonate CaCO_3 (04-014-1601) Hydroxylapatite sulfonated $\text{Ca}_{4.95}(\text{P O}_4)_{2.9}(\text{SO}_4)_{0.1}(\text{OH})$ (04-013-7494)	Quartz SiO_2 (04-018-0234) Gehlenite $\text{Al}_2\text{Ca}_2\text{O}_7\text{Si}$ (04-015-7931) Hematite Fe_2O_3 (01-089-0597) Mullite $\text{Al}(\text{Al}_{0.69}\text{Si}_{1.22}\text{O}_{4.85})$ (01-089-2644)
CPC after exposure, surface Gypsum $\text{CaSO}_4(\text{H}_2\text{O})_2$ (04-009-1810/00-033-0311/04-015-4421)	Boehmite AlOOH (04-016-2858/01-073-9093) Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (04-012-1276) Dmisteinbergite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (04-011-6236)	Gehlenite $\text{Al}_2\text{Ca}_2\text{O}_7\text{Si}$ (04-015-7930) Quartz SiO_2 (01-085-0798/04-007-1438/ 04-007-1808) Perovskite CaTiO_3 (01-073-9783) Mullite $\text{Al}(\text{Al}_{0.69}\text{Si}_{1.22}\text{O}_{4.85})$ (01-089-2644) Corundum Al_2O_3 (04-007-9625)
Class G/silica before exposure Tobermorite 9A $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ (04-012-1761) Calcium carbonate CaCO_3 (04-006-6528/04-011-5985/01-075-9987)	Portlandite $\text{Ca}(\text{OH})_2$ (00-050-0008)	Quartz SiO_2 (04-006-1757) Brownmillerite $\text{Ca}_2\text{Fe}_{1.63}\text{Al}_{0.37}\text{O}_5$ (04-015-8017)
Class G/silica after exposure, core Tobermorite 9A $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ (04-012-1761) Gypsum $\text{CaSO}_4(\text{H}_2\text{O})_2$ (00-033-0311)	Iron oxide hydroxide FeOOH (04-015-8205) Calcium carbonate CaCO_3 (01-081-2502)	Quartz SiO_2 (04-015-7167) Brownmillerite $\text{Ca}_2\text{Fe}_{1.63}\text{Al}_{0.37}\text{O}_5/\text{Ca}_2\text{FeAlO}_5$ (04-015-8017/04-011-5939)
Class G/silica after exposure, surface Gypsum $\text{CaSO}_4(\text{H}_2\text{O})_2$ (00-033-0311)		Quartz SiO_2 (04-015-7167) Brownmillerite $\text{Ca}_2\text{Fe}_{1.63}\text{Al}_{0.37}\text{O}_5$ (04-015-8017/04-011-5939)

Table 4. Continued

2θ: degrees						Identified phase (see Table 4 for ICDD numbers)
Control		Acid treated, core		Acid treated, surface		
TSRC-1	TSRC-2	TSRC-1	TSRC-2	TSRC-1	TSRC-2	
—	—	12.05	12.07	—	—	Dminsteinbergite
—	—	12.47	—	12.47	—	Garronite
14.58	14.44	14.56	14.46	14.55	14.59	Boehmite
—	—	—	14.75	—	14.75	Bassanite
—	—	—	—	15.41	15.54	Alunite
—	—	—	15.86	—	—	Analcime
—	—	16.48	16.3	16.35	16.35	Mullite
17.62	17.46	—	17.56	—	—	Katoite
—	—	18.02	—	17.88	17.98	Garronite/alunite
—	—	—	18.34	—	—	Analcime
—	—	20.10	20.08/20.11	—	20.08	Dminsteinbergite/gypsum
20.14	20.18	20.18	20.1	20.1	20.16	Quartz
20.38	20.20	—	20.20	—	—	Katoite
—	—	21.5	—	21.5	—	Garronite
—	—	22.02	—	22.02	—	Garronite
—	—	23.48	23.38	23.4	23.50	Dminsteinbergite
—	—	24.18	24.12	24.0	24.1/24.16	Dminsteinbergite/hematite
—	—	—	25.50	—	25.42	Anhydrate
25.74	—	25.74	—	25.56	25.48	Corundum/alunite
—	—	—	25.86	—	25.76–26.0	Bassanite
—	—	26.08	26.05	—	—	Analcime
26.32	26.22	26.32	26.2	26.19/26.32	25.9–26.3	Quartz/mullite
—	—	26.62	—	26.62	26.6	Quartz
26.98	26.86	26.98	26.99	—	—	Katoite
—	—	27.8	—	—	—	Garronite
28.16	28.18	28.12	28.1	28.18	28.18	Quartz
28.29	28.23	28.29	28.14	28.29	28.22	Garronite/boehmite
28.86	28.76	—	28.9/28.84	—	—	Katoite/gypsum/quartz
29.5	29.4	29.5	29.34	—	—	Calcium carbonate
—	—	—	29.48	—	29.8–30.2	Bassanite
—	—	—	—	29.90	30.1	Alunite
—	—	—	30.64/30.3	—	30.36	Analcime/hematite
—	—	—	31.34	—	31.36	Anhydrate
—	—	—	—	31.36	31.37	Alunite
—	31.40	—	31.40	—	31.4	Gehlenite
—	—	31.63	31.58	—	31.62	Dminsteinbergite
—	—	—	31.7	—	31.8	Bassanite
32.38	32.24	—	32.39	—	—	Katoite
33.28	33.12	33.26	33.14	33.08/33.28	33.12/33.3	Perovskite/iron oxide/mullite
—	—	33.60	—	33.60	—	Garronite
—	—	35.16	35.14	—	35.20	Dminsteinbergite
35.22	35.4	35.22	35.2	35.22	36.2	Corundum/mullite
36.1	36.1	35.78	35.9/35.68	—	35.9–35.8	Dminsteinbergite/hematite
37.06	36.88	—	37.08	—	—	Katoite
37.9	—	37.7	—	37.7	—	Corundum

Table 5. Identified XRD reflections in TSRC-1 and TSRC-2 blends
(continued on next page)

2θ: degrees						Identified phase (see Table 4 for ICDD numbers)
Control		Acid treated, core		Acid treated, surface		
TSRC-1	TSRC-2	TSRC-1	TSRC-2	TSRC-1	TSRC-2	
38.42	38.3	38.42	38.33	38.42	38.36	Boehmite
39.5	39.36	39.4	39.4	39.73	39.4–39.8/39.6	Alunite/calcium carbonate
—	—	—	39.58	—	39.7	Bassanite
—	—	39.82	39.88	40.0	39.72	Dminsteinbergite
39.85	39.72	—	39.95	—	—	Katoite
41.0	41.15	40.8/40.87	40.8/40.9	40.75	40.75/40.8	Iron oxide/calcium carbonate/ mullite/anhydrate
—	—	42.10	42.00	—	42.1	Dminsteinbergite
—	—	42.71	42.63	—	42.75	Dminsteinbergite
—	—	—	42.95	—	42.3–42.8	Bassanite
43.47	—	43.31	—	43.31	—	Corundum
45.11	45.01	—	45.22	—	—	Katoite
—	47.59	—	47.51/47.24–47.55	—	47.3–47.4	Perovskite/calcium carbonate
—	—	—	—	47.65	47.80	Alunite
48.99	48.87	—	48.89	—	48.9–49.2	Boehmite
49.47	49.21	49.27–49.40	49.33	49.27	49.2–49.3	Dminsteinbergite/quartz/boehmite

Table 5. Continued

advanced argillic alterations after extreme base leaching and sulfate fixation by minerals upon encountering groundwater with a high sulfuric acid concentration (Kiyosaki *et al.*, 2003; Steiner, 1968; Wohletz and Grant, 1992). Alunite has a low dissolution rate over a wide temperature range (Miller *et al.*, 2016; Stoffregen *et al.*, 1994).

For all other samples, calcium sulfates such as bassanite crystallised along with alunite in the surface layers. In the FAF-rich mixes (TSRC-3 and TSRC-4), calcium-potassium sulfate, gorceyite, was identified. Boehmite survived in the surfaces of all the TSRC samples along with non-reacted phases such as mullite, corundum, quartz, hematite, gehlenite and perovskite. Some anorthite, dmisteinbergite and zeolites remained as minor phases along with iron silicate, hedenbergite (TSRC-3).

The CPC sample partially lost calcium aluminium silicates and calcium phosphates from the cores of the exposed samples and their peaks almost disappeared in the acid-treated surfaces. An intermediate phase of apatite degradation, sulfonated hydroxylapatite (ICDD 04-013-7494), was identified in the core (split peaks at 2 θ of 25.9, 29.16, 32.0, 40.16), while the major crystalline phases at the acid-attacked surfaces were non-reacted gehlenite and gypsum.

The class G/silica control sample showed peaks of non-reacted quartz, tobermorite 9A, portlandite or calcium carbonates and brownmillerite. After acid exposure, the crystalline composition

of the sample surfaces mostly included gypsum along with non-reacted phases (quartz and brownmillerite). The cores of the samples had some tobermorite and calcium carbonate along with crystalline gypsum.

In summary, the XRD studies demonstrated the susceptibility of calcium-based crystalline phases to low-pH sulfuric acid attack. They transferred mostly into amorphous phases or crystalline calcium sulfates. These acid-sensitive phases included anorthite and dmisteinbergite, katoites, calcium phosphates, portlandite, tobermorite and calcium carbonates. All zeolites formed in FAF-containing blends were also susceptible to acid attack. The TSRC blends formed potassium aluminium sulfate, alunite, which persisted under the experimental conditions.

Analyses of degraded samples – μ EDX oxide composition

Table 8 shows the oxide compositions of the blends averaged over 3 by 4 mm areas of ground samples. After the acid treatment, the silicon content of all the TSRC samples and the CPC increased at the surface. Calcium strongly decreased, especially for TSRC-1, which did not form any calcium sulfates, while the decline in aluminium content was less significant than that of calcium. Relating these data to the XRD results suggests that decomposition of calcium-(aluminium)-silicate hydrates leads to calcium dissolution and partial precipitation of its sulfate salts when they reach their saturation level, polymerisation of remaining –Si–O– under acidic

2θ: degrees						Identified phase (See Table 4 for ICDD numbers)
Control		Acid treated, core		Acid treated, surface		
TSRC-3	TSRC-4	TSRC-3	TSRC-4	TSRC-3	TSRC-4	
12·27	12·27	12·21	12·21	—	12·2	Gismondine
12·47	12·48	12·43	12·47	—	12·4	Garronite/harmotome/gobbinsite/ phillipsite
14·49	—	14·42	—	14·49	—	Boehmite
—	—	14·73	14·84	14·73	14·71	Bassanite
15·83	15·83	15·93	15·74	15·89	15·79	Analcime/gorgeyite
16·43	16·48	16·32	16·38	16·42	16·38	Mullite/phillipsite
17·84	17·7/17·9	17·82	17·8	17·92	17·84	Phillipsite/garronite/harmotome/ gobbinsite/katoite/alunite
18·04	18·04	18·06	18·06	—	—	Gismondine
18·20	18·30	18·34	18·26	18·32	18·28	Analcime
—	—	—	20·74	20·74	20·78	Bassanite
20·88/20·94	20·94	20·86/20·92	20·84	20·86	20·86	Quartz/gismondine
21·64	21·68	21·58	21·54	21·64	21·74	Garronite/harmotome/gobbinsite/ phillipsite
25·6	—	25·6	—	25·46	25·38	Alunite/anhydrate/corundum
—	—	25·54	25·68	25·68	25·68	Bassanite
25·9/26·2	25·99	26·16	25·94	25·9/26·0	25·97	Mullite/analcm/calcium carbonate
26·68	26·7	26·62	26·6	26·64	26·68	Quartz/gobbinsite/gismondine
27·8	27·8	27·8	27·7	—	27·8	Garronite
27·86– 28·12	28·00	28·04	28·04	27·98	28·06	Anorthite/phillipsite/gismondine
28·3	28·36	28·16	28·22	28·12/28·22/28·24	28·2	Garronite/gobbinsite/harmotome/ boehmite/gorgeyite
29·42/29·44	29·4	29·5	29·4–29·8	29·42/29·73	29·4–29·8	Gobbinsite/katoite/katoite silician bassanite/calcium carbonate/ gorgeyite/hedenbergite
—	—	—	—	29·94	29·9	Alunite
30·54	30·60	30·46	30·5	30·62	—	Analcime
30·96	31·04	30·96	30·92	30·99	30·92	Mullite
—	31·32	—	31·26	—	31·28	Gehlenite
—	—	31·86	31·94	31·88/31·92	31·82	Gorgeyite/bassanite
32·86	32·70	32·6	32·68	—	—	Gobbinsite/phillipsite/gismondine/ perovskite/katoite/katoite silician/ calcium carbonate
33·24/33·3	33·3	33·2/33·3	33·2/33·3	33·2	33·1	Mullite/hematite/phillipsite
33·4–33·52	33·4	33·5	33·4	—	33·5	Garronite/harmotome/gobbinsite
35·20	—	35·04	—	35·14	—	Hedenbergite/corundum
35·27	35·22	35·3	35·23	35·26	35·18	Mullite
35·58	—	35·5	—	—	—	Gobbinsite
35·74	35·87	35·67	35·68	35·76	35·68	Hematite/analcm
36·6–37·1	36·9	37·01	36·94	37·0	36·91	Gobbinsite/mullite
37·8	—	37·84	—	37·76	—	Corundum/gobbinsite/calcium carbonate

Table 6. Identified XRD reflections in TSRC-3 and TSRC-4 blends
(continued on next page)

2θ: degrees						Identified phase (See Table 4 for ICDD numbers)
Control		Acid treated, core		Acid treated, surface		
TSRC-3	TSRC-4	TSRC-3	TSRC-4	TSRC-3	TSRC-4	
38.3	38.43	38.40	38.43	38.3	38.3	Boehmite/gobbsinite/calcium carbonate
39.34	39.22	39.36	39.3	39.24	39.11	Mullite
39.46	—	39.5	39.4	39.4	39.4	Quartz
—	—	39.64	39.6	39.66	39.6	Bassanite
—	—	—	—	39.76	39.70	Alunite
40.57	40.55	40.58	40.41	—	—	Katoite/katoite silician/analcime
40.85	40.89	40.83	40.81	40.77	40.77	Mullite/gobbsinite
40.98	40.8	40.8	40.8	40.81/40.97	40.8	Bassanite/hematite
42.51	42.61	42.21/42.45	42.0–42.7	42.23/42.49/42.67	42.0–42.7	Hedenbergite/diopside/bassanite/ mullite/gobbsinite
43.35	—	43.37	—	43.33	—	Corundum
45.91–46.3	45.97	45.89–45.91	45.81	45.75	45.77	Katoite/katoite silician/gobbsinite/ garronite/calcium carbonate
—	47.72	47.59	47.6	47.65/47.91	47.75	Bassanite/alunite/gorgeyite/perovskite
48.9–49.5	—	48.93	—	48.79	—	Anhydrate/boehmite/gobbsinite
49.3	—	49.29	49.27	48.81–49.49/49.51	49.23/49.4	Bassanite/boehmite/gorgeyite
50.11	50.11/50.27	50.07	50.1	50.09–50.27	50.07	Gismondine/quartz/bassanite

Table 6. Continued

Table 6. Continued

conditions into an amorphous gel that stays on the surface, and the formation of amorphous or crystalline (alunite) phases involving aluminium. Correspondently, the formulations with higher calcium contents (class G/silica, TSRC-2, TSRC-4 and CPC) have increased precipitation of calcium sulfates, forming a surface layer that controls sulfur concentrations and limits its further permeation (4.3%, 2.7%, 2.3% and 0% core sulfur in the class G/silica, TSRC-2, TSRC-4 and CPC blends respectively). With the exception of the class G/silica blend, this layer was not sufficient to prevent weight and diameter losses of the samples (Table 3).

In aluminium-rich TSRC-1, the surface sulfur-poor solution concentration is probably controlled by alunite and sulfur-reacting aluminium-rich amorphous phases, resulting in its absence in the sample's core. Relatively high sulfur permeation into the core of FAF- and aluminium-rich TSRC-3 could be a result of low calcium content, and the presence of non-reacted FAF that would increase permeability and acid sensitivity of both FAF-rich samples (TSRC-3 and TSRC-4). In these formulations, the sulfur surface content is lower than in the CAC-rich counterparts (TSRC-1 and TSRC-2), suggesting partial removal of sulfates. This is in agreement with the smaller corrosion depth, higher weight loss and more significant diameter decrease in comparison with TSRC-1 and 2 (Table 3).

The EDX measurements confirm the elimination of calcium phosphates from the CPC under acid attack (73% and 83% of phosphorous is lost from the surface and the core, respectively).

Analyses of degraded samples – differential thermal gravimetric (DTG) analyses

Figure 5 shows DTG analyses of the cement blends. For the TSRC samples, the weight losses below about 250°C are associated with calcium-sodium-aluminium-silicate hydrates (mostly probably amorphous from fly ash F and CAC) (Foldvari, 2011; Winnefeld *et al.*, 2010) and zeolite-related weight losses (peaks at ~60–90°C, ~150–230°C). The weight loss at ~280°C is due to the decomposition of katoite with a possible contribution of zeolites (~270–360°C) and that at ~500°C from boehmite with a possible contribution of analcime (Harada *et al.*, 1972). The losses above ~600°C are from carbonates from the blend components or formed during mixing of the slurries and the weight losses at temperatures above about 800°C were attributed to non-reacted fly ash (Pyatina and Sugama, 2016). The flu ash volume fraction increased after the erosion of calcium-containing phases, as did the high-temperature weight loss peak on the thermograms of acid-treated samples.

The control sample of TSRC-1 had a narrow DTG peak at ~81°C, likely due to the decomposition of hydroxysodalite. In

2θ: degrees						Identified phase (see Table 4 for ICDD numbers)
Control		Acid treated, core		Acid treated, surface		
CPC	G/silica	CPC	G/silica	CPC	G/silica	
—	—	—	—	11·66	11·61	Gypsum
11·96	—	11·98	—	—	—	Dmisteinbergite
—	12·19	—	12·34	—	—	Brownmillerite
14·52	—	14·64	—	14·52	—	Boehmite
16·22	—	—	—	16·3	—	Mullite
17·54	—	—	—	—	—	Katoite silician
—	—	—	17·78	—	—	Iron oxide hydroxide
—	18·04	—	—	—	—	Tobermorite 9A
20·00	—	20·24	—	20·06	—	Dmisteinbergite
—	20·88	—	21·06/21·12	20·78	20·68	Gypsum/quartz/iron oxide hydroxide
—	23·12	—	23·12	—	—	Brownmillerite
23·38	—	23·62	—	23·37	23·38	Dmisteinbergite/quartz/gypsum
24·1	—	24·32	—	24·18	—	Dmisteinbergite/hematite
—	24·94/24·96	—	25·16	—	—	Tobermorite 9A/calcium carbonate
25·92/26·6	—	26·14	—	26·02	—	Mullite/hydroxylapatite/analcime/carbonated hydroxylapatite/hydroxylapatite sulfonated
—	26·34	—	—	—	—	Portlandite
26·6/26·82	26·66	—	26·84	26·64	26·64	Anorthite/calcium hydrogen phosphate/quartz
—	26·92–27·22	—	27·16–27·6	—	—	Calcium carbonate
27·88/28·1	—	28·34	—	28·16/28·14	—	Anorthite/boehmite
28·93	—	28·9	—	—	—	Hydroxylapatite/katoite silician/portlandite
29·2	29·16	29·16	29·24	29·11/29·12	28·12/29·11	Hydroxylapatite sulfonated/gypsum/calcium carbonate
29·22	29·44	29·6	29·56	—	—	Boehmite/tobermorite 9A/calcium carbonate/quartz
30·18	—	—	—	—	—	Anorthite/calcium hydrogen phosphate
—	—	—	—	31·12	31·18	Gypsum
31·28	—	31·36	—	—	—	Gehlenite
31·5	—	31·47	—	31·59	—	Dmisteinbergite
31·6	—	31·76	—	—	—	Hydroxylapatite/dmisteinbergite
31·94	31·9	—	—	—	—	Carbonated hydroxylapatite/portlandite
32·18	—	32·02	—	—	32·1	Hydroxylapatite/carbonated hydroxylapatite/hydroxylapatite sulfonated/gypsum
—	32·2/32·36	—	32·44	—	32·15	Tobermorite 9A/brownmillerite
32·48/32·8	32·64	32·46	—	—	—	Calcium hydrogen phosphate/katoite silician/portlandite

Table 7. Identified XRD reflections in CPC and class G/silica blends
(continued on next page)

2θ: degrees						Identified phase (see Table 4 for ICDD numbers)
Control		Acid treated, core		Acid treated, surface		
CPC	G/silica	CPC	G/silica	CPC	G/silica	
33·16	32·68–33·0	33·21	33–33·6/33·18	33·23	—	Carbonated hydroxylapatite/ perovskite/hematite/calcium carbonate/iron oxide hydroxide
—	—	33·42	33·4	33·41	33·34	Gypsum
—	33·58	—	33·70	—	—	Tobermorite 9A
—	33·88/34·1	—	33·7/34·1	—	33·52	Brownmillerite
35·06	—	35·28	—	35·20	—	Mullite/dmisteinbergite
35·6/35·7	—	35·86	—	35·74	—	Katoite silician/calcium carbonate/ hematite
—	—	—	—	—	35·96/36·7/37·3	Gypsum
35·9/38·3	36·06	37·34/38·43	36·8	38·36	—	Boehmite/quartz/calcium carbonate/iron oxide hydroxide
39·23	39·23	—	—	—	—	Portlandite
39·6	—	39·76	—	39·8	—	Dmisteinbergite
39·68	—	39·98/40·16	—	—	—	Hydroxylapatite/hydroxylapatite sulfonated
40·83	—	40·93	—	40·74	40·73	Mullite/gypsum
41·95	—	42·21	—	42·3	—	Dmisteinbergite/calcium carbonate
42·59	—	42·81	—	42·53	—	Mullite/dmisteinbergite
—	—	—	—	43·3–43·6	43·39–43·57	Gypsum
—	43·25/43·9	—	44·3	—	44·23	Calcium carbonate/gypsum
—	44·05	—	44·0	—	—	Tobermorite 9A
45·15	—	45·15	—	—	—	Katoite silician
—	—	—	45·7	—	45·47	Gypsum
—	46·99	—	46·99	—	—	Portlandite
—	47·45	—	47·4	—	47·5	Brownmillerite/iron oxide hydroxide
47·55	47·7	47·77	—	47·79	—	Calcium hydrogen phosphate/ perovskite/calcium carbonate
47·83	—	—	—	47·79	47·83	Dmisteinbergite/gypsum
47·87	—	48·07/48·21	—	48·37	48·37	Hydroxylapatite/gypsum
48·49/48·91	48·7	48·9	—	48·9	—	Boehmite/quartz/calcium carbonate
49·03	—	49·05	—	—	—	Calcium hydrogen phosphate
49·27	—	—	—	—	—	Hydroxylapatite/carbonated Hydroxylapatite
49·39/49·51	—	49·53	—	49·4	—	Dmisteinbergite/hydroxylapatite/ calcium carbonate/hematite
—	49·95/50·15	—	49·93/50·35	50·27	50·23	Tobermorite 9A/Gypsum/quartz/ calcium carbonate/ brownmillerite

Table 7. Continued

agreement with the XRD data, this peak was absent from the TSRC-2 thermogram. Both TSRC-1 and TSRC-2 showed DTG peaks at ~236°C from various zeolites. The katoite peak

was more significant for TSRC-2 than for TSRC-1, while boehmite peaks at ~500°C were similar for both formulations, corresponding to 2·2–2·3% of weight loss. The peaks between

	Control	Core	Surface	Control	Core	Surface
	TSRC-1			TSRC-2		
Aluminium oxide	48	49	48	35	32	21
Silicon dioxide	25	24	28	23	24	36
Calcium oxide	19	21	1.5	32	33	11
Iron oxide	4.3	4.8	4.9	6.1	6.0	7.6
Potassium oxide	2.0	1.0	3.3	1.3	—	2.7
Titanium dioxide	0.80	—	1.0	2.3	2.7	3.2
Sulfur trioxide	—	—	14	—	2.7	18
	TSRC-3			TSRC-4		
Aluminium oxide	41	41	38	29	30	18
Silicon dioxide	35	31	35	35	32	48
Calcium oxide	13	12	6.4	24	25	13
Iron oxide	6.6	6.2	5.5	7.4	8.1	6.5
Potassium oxide	2.7	2.3	2.6	3.0	2.5	1.9
Titanium dioxide	1.3	1.1	1.0	2.1	2.5	2.8
Sulfur trioxide	—	7.0	11	—	2.3	13
	CPC			Class G/silica		
Aluminium oxide	29	35	27	2.9	—	—
Silicon dioxide	18	21	31	29	30	15
Calcium oxide	29	32	17	59	60	38
Phosphorus pentoxide	15	2.6	4.0	—	—	—
Iron oxide	5.1	5.5	6.3	5.5	5.7	1.2
Potassium oxide	1.9	0.8	—	0.9	—	—
Titanium dioxide	2.0	2.2	2.7	0.2	0.3	—
Sulfur trioxide	—	—	12	2.8	4.3	46

Table 8. Oxide composition (in weight %) of samples after 18 d exposure to sulfuric acid at 90°C (pH 2.5 for 6 d followed by pH 0.5 for 12 d)

675°C and 680°C were from carbonates and represented less than 2% of the total weight loss.

The most noticeable new peaks after acid exposure were in the 710–730°C range from potassium aluminium sulfate, alunite (Foldvari, 2011), representing 4.1% and 5.8% weight losses for TSRC-1 and TSRC-2, respectively. In addition, there was a small peak at ~412°C on the thermogram of TSRC-2, possibly related to calcium hydroxide (Nuruddeen, 2014). In agreement with the XRD results, the DTG peaks of zeolites and katoite clearly decreased for both TSRC-1 and TSRC-2 (~30% reduction) while sulfate weight losses appeared (small weight loss in TSRC-1 samples at ~115°C and at 120°C for TSRC-2).

The increase of FAF in TSRC-3 and TSRC-4 increased losses below 250°C, associated with zeolites and calcium(sodium)-aluminium-silicate (C,N-A-S) hydrates (8.4% and 8% for TSRC-3 and TSRC-4 compared with ~5.7% and 5.2% for TSRC-1 and TSRC-2), and decreased the katoite weight loss at ~280°C, which became only a shoulder on the peaks of zeolites decompositions. Boehmite decomposition at (~500°C and 508°C for TSRC-3 and TSRC-4, respectively) was more clearly resolved for TSRC-3 containing more aluminium than for TSRC-4, where no clear peak of boehmite decomposition could be registered.

Boehmite losses increased by ~20% at the acid-attacked surfaces of TSRC-3 and the new peaks at ~410(404)°C and 684 (689)°C for TSRC-3(TSRC-4) could be attributed to calcium

Figure 5. DTG analyses of cement blends. The lower curves are the control samples and the upper curves are for surfaces of the samples exposed to sulfuric acid

hydroxide and alunite, respectively. The broad band between $\sim 350^{\circ}\text{C}$ and 500°C on the thermogram of TSRC-4 was possibly associated with overlapping calcium hydroxide and analcime decompositions. Confirming the XRD data, katoite disappeared from the surface and the weight losses associated with zeolites and amorphous C,N-A-S hydrates decreased conspicuously after the acid exposure (by $\sim 36\%$ and 27% for TSRC-3 and TSRC-4, respectively). The decomposition of sulfates indicated by the XRD patterns, possibly due to their low crystallinity, happened at lower than expected temperatures, giving shoulders on the peak at $\sim 81^{\circ}\text{C}$ (TSRC-3) and $\sim 103^{\circ}\text{C}$ (TSRC-4).

The control CPC sample showed weight losses of amorphous hydrates and zeolites (DTG peaks at $\sim 66^{\circ}\text{C}$ and 90°C), further losses associated with zeolites at $\sim 185^{\circ}\text{C}$ and 245°C , followed by weight loss of katoite and analcime at $\sim 294^{\circ}\text{C}$ ($\sim 2\%$). This was followed by weight loss of portlandite decomposition with a possible analcime contribution at $\sim 449^{\circ}\text{C}$ (Harada *et al.*, 1972), boehmite decomposition at 541°C and carbonate and non-reacted FAF decompositions at $>600^{\circ}\text{C}$. After the acid exposure, the gypsum decomposition at $\sim 116^{\circ}\text{C}$ ($\sim 5\%$) completely dominated the small weight losses of residual zeolites ($\sim 235^{\circ}\text{C}$) and calcium hydroxide ($\sim 412^{\circ}\text{C}$).

Figure 6. FTIR spectra of TSRC-1 and TSRC-3 blends before and after sulfuric acid exposure

The class G/silica blend weight losses after curing occurred below $\sim 100^{\circ}\text{C}$ for calcium-silicate hydrates, at $\sim 136^{\circ}\text{C}$ for gypsum, in a broad band between $\sim 250^{\circ}\text{C}$ and 350°C for tobermorite and in a much shorter temperature range ($\sim 435^{\circ}\text{C}$) for portlandite; the weight loss above $\sim 850^{\circ}\text{C}$ was not identified. In agreement with XRD and EDX measurements, the acid-exposed surface showed just one dominant weight loss at $\sim 97^{\circ}\text{C}$, associated with gypsum.

Analyses of degraded samples – ATR-FTIR measurements

The results of the ATR-FTIR measurements were in agreement with the XRD data. They confirmed three major chemical compounds in TSRC-1 – carbonates at 1482 cm^{-1} and 868 cm^{-1} ,

silica gel at 1228 cm^{-1} and C,N-A-S hydrates at 986 cm^{-1} and 903 cm^{-1} . The spectrum of the core sample was similar to the control, while the chemical composition of the surface layer mostly consisted of some major sulfate phase, and minor C,N-A-S hydrates along with silica gel. An increased fly ash content (TSRC-3) (Figure 6) engendered a shift of the most prominent M–O (M: silicon or aluminium) asymmetric ($V_{\text{as M-O}}$) band of C,N-A-S hydrates to a higher frequency, from 903 cm^{-1} for TSRC-1 to 989 cm^{-1} for TSRC-3, and the absence of a silica-gel-related band around 1220 cm^{-1} . The major bands of the TSRC-3 components were at 1034 cm^{-1} from $V_{\text{as M-O}}$ stretching in $\text{Al}_2\text{O}_3\text{--SiO}_2$ in FAF and at 770 cm^{-1} for aluminium-oxygen in the ‘condensed’ aluminate (AlO_4) tetrahedra network

Figure 7. FTIR spectra of TSRC-2 and TSRC-4 blends before and after sulfuric acid exposure)

of the monocalcium aluminate phase of CAC (not shown) (Husung and Doremus, 1990; Roy, 1987). Thus, the shift of the TSRC-3 band to higher frequency points to a larger proportion of FAF reaction products with lower calcium content. FTIR analyses of the acid-exposed TSRC-3 confirmed the presence of sulfate in the core, with shoulder and weak bands at 1159, 1074 and 660 cm^{-1} . As expected, the surface layer of this cement was dominated by sulfates, while the presence of C,N-A-S hydrates was very low, if any.

The spectra of blends TSRC-2 and TSRC-4 (Figure 7) were very similar to those of TSRC-1 and 3, respectively.

The spectrum of the control CPC (Figure 8) included bands of groups containing phosphorous, aluminosilicates and silica gel. They were P–O asymmetric ($V_{\text{as P-O}}$) stretching vibration bands at 1066 and 1031 cm^{-1} and P–O symmetric ($V_{\text{s P-O}}$) stretching at 905 cm^{-1} of phosphates (PO_4^{3-}) in calcium phosphates (Kolmas *et al.*, 2015; Low *et al.*, 2011; Nasiri-Tabrizi and Fahami, 2013; Taddei *et al.*, 2014). The band at 905 cm^{-1} was also attributable to the asymmetric ($V_{\text{as M-O}}$) stretching mode (M: silicon or aluminium) in the Si–O–Si and Si–O–Al in C, N-A-S reaction products and that at 676 cm^{-1} was interpreted as the M–O symmetric ($V_{\text{s M-O}}$) stretching mode (Clayden *et al.*, 1999; Criado *et al.*, 2007; Husung and Doremus, 1990;

Figure 8. FTIR spectra of CPC and class G/silica blends before and after sulfuric acid exposure

Roy, 1987; Sugama *et al.*, 2000) and a band of silica gel at 1220 cm^{-1} (Almeida and Pantano, 1990; Donatello *et al.*, 2013; Fidalogo and Ilharco, 2001; Innocenzi, 2003; Tanner *et al.*, 2000). The spectrum of the sample core after acid exposure resembled the unexposed sample. The surface of the CPC was primarily composed of sulfates; the presence of weak bands at 1220 cm^{-1} and 905 cm^{-1} suggested some silica gel, C,N-A-S and possibly some calcium phosphate coexisting with sulfates.

The spectrum of the control class G/silica blend (Figure 8) included two bands at 1478 cm^{-1} and 1411 cm^{-1} from the C–O asymmetric ($V_{\text{as C-O}}$) stretching vibration in carbonate

(CO_3^{2-}) and the band at 873 cm^{-1} from O–C–O out-of-plane bending ($\delta_{\text{O-C-O}}$) in carbonate (Gunasekaran *et al.*, 2006; Xyla and Koutsoukos, 1989; Ylmen and Jaglid, 2013), the calcium-silicate-hydrate-related Si–O asymmetric stretching ($V_{\text{as Si-O}}$) in the silicate (SiO_4^{4-}) wide band at 965 cm^{-1} (Mollah *et al.*, 2000; Taddei *et al.*, 2014) and the three quartz-related bands at 1080 , 799 and 693 cm^{-1} (Guan *et al.*, 2014; Ramasamy and Suresh, 2009; Saikia *et al.*, 2008). The spectrum from the core of the acid-exposed sample was similar to that of the control. In agreement with XRD and TGA analyses, the surface sample revealed replacement of the most of the carbonate- and silicate-associated bands by the three sulfate ones (SO_4^{2-}), at 1144 , 1088 and 660 cm^{-1} , in gypsum (Al-Hosney and

Figure 9. SEM images of typical cement microstructures and their elemental compositions after sulfuric acid exposure

Grassian, 2005; García-Lodeiro *et al.*, 2011; Ylmen *et al.*, 2009).

Analyses of degraded samples – morphologies of TSRC-1 and TSRC-2

The microphotograph of the acid-treated TSRC-1 sample shows a rough, partially eroded surface (Figure 9(a)) rich in aluminium and sulfur with small inclusions of alunite (site 1) (Stoffregen *et al.*, 1994) and sites with the elemental composition of mullite (site 2). A typical atomic composition of the mostly amorphous surface is similar to the alunite elemental composition (site 3), in agreement with other data. The core of the sample is dense (Figure 9(b), site 1), amorphous for the most part, with some aluminium-silicate crystals (sites 2 and 3) and prints of displaced FAF particles. It becomes more porous and less compact closer to the surface. The insert on the microphotograph shows some sulfur-containing crystals with a strong aluminium signal (site 4). This could be an intermediate product of cement-sulfuric acid interactions that later decomposes with the loss of calcium to sulfate. Similarly, the microphotograph of sample TSRC-2 shows an eroded rough surface (Figure 9(c)). The bassanite crystals are either embedded into the sample's matrix (site 1) or grow in the open shells of the partially reacted FAF particles (site 2). For the most part, the surface is composed of silica-aluminate gel (site 3) with some sites that have a typical composition of dmisteinbergite crystals (site 4). The core structure of the sample is porous, mostly amorphous with inclusions of some katoite crystals (site 1) and partially reacted FAF particles (site 3). The SEM data confirmed that the surfaces of samples TSRC-1 and TSRC-2 were attacked by the sulfuric acid, resulting in the formation of amorphous and crystalline sulfate-containing products, some surface erosion and increased porosity.

Conclusions

Blends of thermal shock resistant cement (TSRC) composed of calcium aluminate cement (CAC) and class F fly ash (FAF) activated with sodium metasilicate were hydrated for 24 h at 300°C and tested for their resistance to sulfuric acid solutions at 90°C for 18 d. Four blends were prepared with CAC of varied calcium and aluminium contents and different CAC to fly ash ratios. Their short-term resistance to acid attack was compared to that of a Portland cement class G/silica blend and to a calcium phosphate cement (CPC) made of CAC, FAF and sodium hexametaphosphate.

The following general conclusions can be drawn from the study.

- (a) After 18 d of sulfuric acid exposure at 90°C, all the TSRC formulations lost weight and decreased in diameter while keeping or increasing their compressive strength and forming only a thin rim layer. The changes were the smallest for the aluminium-rich blend (TSRC-1) and the most significant for the silicon- and calcium-rich blend

(TSRC-4). Of all the tested formulations, the CPC lost most weight, diameter and some compressive strength. In contrast, the class G/silica blend increased both in mass and diameter due to the formation of a thick gypsum layer partially eroded from the core of the sample.

- (b) The attack of sulfuric acid on TSRC samples starts with calcium-sulfate reactions and calcium removal from the samples' surfaces. All calcium-containing hydrates were susceptible to the sulfuric acid attack. These hydrates included feldspar family minerals such as anorthite and dmisteinbergite and various zeolites formed in pozzolanic reactions of the fly ash. Aluminium formed potassium-aluminium hydrate, alunite, which persisted under the experimental conditions. The aluminium-containing CAC hydration product, boehmite, better resisted acid attack than did aluminium-containing phases formed from FAF (zeolites). XRD and μ EDX data confirmed boehmite's survival in the surface layers of aluminium-rich blends and the lesser surface loss of aluminium compared with the blends rich in fly ash.
- (c) In the CPC, the hydration products containing calcium phosphate were susceptible to attack by the sulfuric acid. The phases containing phosphates, such as apatites and calcium phosphate, reacted with the sulfuric acid, resulting in the formation of gypsum that helped to prevent sulfur penetrating into the core of the samples. However, it could not stop mass, diameter and compressive strength losses. In agreement with numerous previous studies, the class G/silica blend hydrates reacted with the sulfate ions, with the formation of a thick gypsum layer. Concentrations of both calcium and silicon strongly decreased in the surface layer of this sample and its integrity was compromised due to the partial erosion of calcium sulfate and low cohesion of the remaining silica gel.
- (d) Based on sulfur penetration into the core of the samples, changes in sample appearance, size and compressive strength, the resistance of the tested blends to short-term exposure to pH 0.5 sulfuric acid at 90°C could be ranked as follows: TSRCs rich in aluminium and CAC (TSRC-1 and TSRC-2) > TSRCs rich in fly ash (TSRC-3 and TSRC-4) > CPC > class G/silica blend. Long-term exposure tests would be necessary to confirm the long-term stability of the alunite phase formed in aluminium-rich formulations as a result of sulfuric acid attack. The CAC-FAF blends with high cement content (60% by weight) were the most resistant under the experimental conditions and would thus be the preferred choice for the acidic environments of geothermal wells.

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