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Chapter 13

Cements for High-Temperature Geothermal Wells

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Additional information is available at the end of the chapter

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Abstract

Geothermal environments are among the most difficult conditions for cements to survive. Normally accepted for high-temperature oil wells silica-modified Portland-based cement formulations are not durable in hostile geothermal environments failing to provide good zonal isolation and metal casing corrosion-protection. High-temperature well cement compositions based on calcium-aluminate cements have been designed to seal such wells. Two types of calcium-aluminate cement are of particular interest for geothermal applications. One is–chemical type, calcium-aluminate-phosphate cement (CaP) already used in the field and the other, alkali-activated calcium-aluminate type (thermal shock resistant cement, (TSRC), has been recently developed. The CaP cements were designed as CO_2-resistant cements for use in mildly acidic (pH ~ 5.0) CO_2-rich downhole environments. TSRC was formulated to withstand dry-heat – cold water cycles of more than 500°C. This chapter includes information and discussions of cement forming mechanisms, cements mechanical properties, resistance to mild and strong acids, cement-carbon steel bonding and self-recovery of mechanical strength and fractures closure after imposed damage. Performance of common high-temperature OPC-based composites is discussed for comparison.

Keywords: geothermal cements, chemical cement, calcium-aluminate phosphate cement, alkali activated cement, durability, cement-metal interface, acid resistance, cement corrosion protection, self-healing cement composites, well integrity

1. Introduction

Geothermal resources exist throughout the world. To recover geothermal energy subterranean wells are installed, fluids heated by geothermal formations are produced to the surface, the heat is used to power turbines to generate electrical power and the spent fluid is injected back into the reservoir through injection wells. The formation fluids are often very saline and

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corrosive with high concentrations of toxic metals so most of the time cannot be used outside of the geothermal systems. In regions where there is no fluid at geothermal formations, conditions called "hot dry rock", fluids from the surface are pumped down an injection well, superheat at hot dry rocks and are returned to the surface through production wells. Although the geothermal wells are constructed in the way similar to regular oil and gas wells the conditions to which cement is exposed are often much more severe and some failures of geothermal wells were directly attributed to cement failures [1]. In addition to highly acidic and saline fluids geothermal cements may be exposed to temperatures above 500°C [2] and temperature fluctuations of more than 1100°C [3]. To address such conditions new cement formulations were designed and developed. Because of the most difficult conditions to survive geothermal cements have the most stringent requirements. They are usually designed to have a low water permeability of less than 0.1 mD and compressive strength of at least 7 MPa (API Task Group on Cements for Geothermal Wells, 1985) [4]. The set cement must be stable in saline brines and CO_2-rich environments, resistant to acidic gases and fluids. In addition, geothermal cements must withstand thermal shock conditions where they encounter large temperature variations and provide good corrosion protection of the casing. The majority of geothermal wells are cemented with silica-stabilized Portland cement composites.

Portland cement systems have difficulties with carbonate present in many geothermal wells. Calcium silicate hydrates convert to calcium carbonate and amorphous silica at high carbonate concentrations even at low temperature [5]. Even the systems with low calcium-to-silica ratios traditionally used to withstand carbonate attacks are not stable under geothermal conditions with high CO_2 content [6, 7]. Both high-temperature calcium-silicate hydrates formed at low calcium-to-silica ratios, tobermorite and xonotlite, are sensitive to carbonation. Decrease of silica, proposed as a measure to improve resistance of Portland cement-silica blends to carbonate, produces weaker cement but allows calcium hydroxide formed at low silica content to react with carbonate and form a dense protective layer that slows down cement degradation [8–10]. Various organically-modified Portland-based systems or "synthetic cements" have been proposed for the use in aggressive geothermal environments but their applications are limited by polymers high temperature stabilities [11–13]. To address the difficulties of cementing geothermal wells oil well cements modified with alumina [14] and alternative, calcium-aluminate-cement (CAC) based systems were studied and developed specifically for geothermal well applications [15–19]. Chemical bond calcium phosphate blends (CaP) consisting of calcium-aluminate cement, fly ash, type F and sodium polyphosphate have been successfully used for cementing geothermal wells [20].

Studies on alkali-activated cement composite of calcium aluminate cement and fly ash F (thermal shock resistant cement, (TSRC)) demonstrated excellent performance under various stresses of simulated geothermal environments [21, 22], and outstanding CS bond durability [23]. Further work showed that TSRC has self-healing properties, which is ability to recover its compressive strength and seal the cracks at temperatures up to 300°C [24].

In this chapter the properties of chemical bond calcium phosphate cement and alkali-activated cement composites have been revisited and updated to allow for better understanding of cement behavior under conditions of geothermal wells and in other applications in aggressive environments. Properties of the blend of class G oil well Portland cement modified with silica are presented as a benchmark.

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2. CaP cement and TSRC performance under stresses

2.1. Chemistries and mechanisms of CO_2- and acid-resistance: cement matrix

Both CaP cement and TSRC major components are CAC (Secar #51 and Secar #80 respectively) and fly ash F (FAF). **Table 1** shows oxides composition of these CACs, class G cement and fly ash F. The XRD data identify three crystalline phases in CAC #80, corundum (α-Al_2O_3), calcium monoaluminate ($CaO{\cdot}Al_2O_3$, CA), and calcium dialuminate ($CaO{\cdot}2Al_2O_3$, CA_2) and #51 CAC has CA as its dominant phase, coexisting with gehlenite [$Ca_2Al(Al, Si)_2O_7$] and corundum as the secondary components.

CaP is formed by chemical reactions between #51 CAC, FAF, and sodium hexametaphosphate [SHMP: $(NaPO_3)_6$]. These reactions take place in two stages – firstly, a fast chemical reaction between sodium polyphosphate and calcium ions released from calcium aluminate cement takes place with formation of calcium hydrogen phosphate. It further reacts with calcium aluminate cement forming hydroxyapatite. Aluminum released by CAC forms aluminum oxide hydroxide, boehmite. Secondly, the fly ash reacts with sodium ions from sodium polyphosphate at high temperatures with formation of analcime. The reactions may be summarized by the following equation:

$$\begin{aligned} &CaO \cdot Al_2O_3(CaO \cdot 2Al_2O_3) + Al_2O_3 \cdot 2SiO_2\,(SiO_2) + [NaPO_3]_n \rightarrow \\ &Ca_5\,(PO_4)_3(OH) + Na_8Al_8Si_{16}O_{48}(H_2O)_8 + AlOOH \end{aligned}$$

Carbonation of CaP cement matrix proceeds with formation of very stable carbonated apatite from apatite and cancrinite from analcime. The analcime → cancrinite transition results in increased matrix porosity and some loss of the strength, which however stabilizes after longer curing times [16].

$$Ca_5\,(PO_4)_3(OH) + H_2CO_3 \rightarrow Ca_5\,(PO_4)_3 \cdot CO_3 + H_2O$$

$$Na_8Al_8Si_{16}O_{48}(H_2O)_8 + H_2CO_3 \rightarrow Na_8[(AlSi)_{12}O_{24}CO_3] \cdot 3H_2O$$

Since CaP cement generally develops high initial compressive strength of more than 35 MPa, the reduced strength of about 20 MPa after the carbonation is still more than sufficient for all the cement functions in a well.

Component	Oxide composition, wt%							
	Al_2O_3	CaO	SiO_2	Fe_2O_3	Na_2O	K_2O	TiO_2	SO_3
Class G cement	2.9	66.0	18.0	3.8	0.3	1.3		5.4
CAC, #80	75.2	24.7	—	0.1	—	—	—	
CAC, #51	45.1	49.7	—	2.8	—	—	2.4	
FAF	35	2.7	50.0	7.1	0.30	3.1	1.6	

Table 1. Oxide compositions of cement blends' starting materials.

TSRC is formed by reactions of CAC#80, FAF and sodium meta-silicate. In the case of TSRC reactions are more concomitant than in the case of CaP cement. CAC and SMS-activated FAF react with formation of aluminum oxide hydroxide from Al of CAC, calcium-aluminum-silicates from ions released by all cement components and zeolites from FAF and SMS reactions. The reaction with formation of calcium-aluminum-silicate, high-temperature zeolites, analcime and hydroxysodalite, at 300°C can be written as follows:

$$CaO \cdot Al_2O_3\,(CaO \cdot 2Al_2O_3) + Al_2O_3 \cdot 2SiO_2\,(SiO_2) + Na_2O \cdot nSiO_2 \rightarrow$$
$$CaAl_2Si_2O_8 + Na_8Al_8Si_{16}O_{48}\,(H_2O)_8 + Na_4Al_3Si_3O_{12}(OH) + AlOOH$$

Katoite and katoite silician, hydrogrossular and other zeolites (thomsonite, garronite, Lind A) form at lower curing temperatures.

Wet carbonation of TSRC matrix proceeds with formation of carbonated zeolite, cancrinite as in the case of CaP cement:

$$Na_8Al_8Si_{16}O_{48}\,(H_2O)_8 + H_2CO_3 \;\rightarrow\; Na_8\left[(AlSi)_{12}O_{24}CO_3\right] \cdot 3H_2O$$

Since CaP and TSRC are both blends of CAC and FAF many of their hydration products are similar. Specifically, the hydration products of the common phases (CAC and FAF), such as boehmite, calcium-aluminate, katoite, calcium-aluminum silicates dmisteinbergite/anorthite, and analcime are present in both cements. Some other products are specific for the reactant (sodium polyphosphate)/activator (sodium meta-silicate) used in the blends. They are apatite (a product of CAC and polyphosphate reaction) in CaP cement blend, silicon-rich phases such as katoite silician and more zeolites because of the faster alkali activation of FAF by sodium-meta-silicate in TSRC. These zeolites are more silica-rich than for CaP cement. They include Lind A, thomsonite and sodalite depending on hydration temperature. As a result of similar mineralogical composition, the responses of these two cements to many stress environments are also similar.

Specifically, in carbonate-rich environment one of the main carbonation products is stable CO_3-contaning mineral cancrinite [16, 24]. CaP also forms carbonated apatite. In the case of sulfuric acid attack calcium reacts with sulfates forming anhydrate in both cements and the remaining alkali aluminum-silicates provides structural stability of the acid-treated matrix [22].

A noticeable difference in the phase composition development of the two cements is fast formation of $CaHPO_4(H_2O)_x$, chemical reaction product in CaP at 90–101°C and no visible reaction of FAF for the first 25 days under these conditions. In fact FAF has a low reactivity at low pH (~6.6) of CaP cement. On the other hand TSRC hydration products include crystalline zeolite (zeolite A, gismondine) already after 22 days at 85°C due to the fly ash F activation by sodium meta-silicate present in the composition of that cement [25]. Due to the dissolution of sodium meta-silicate with release of sodium ions TSRC slurry is highly alkaline (pH~13). While fast chemical reactions of CaP cement allow fast early strength development, faster FAF reactions in TSRC may be important in acidic environments where low permeability is required to limit acid penetration into the cement matrix causing its deterioration. In the case of CaP cement such penetration may take place along the non-reacted FAF particles at early hydration times.

The phase compositions of the cements depend on temperature, curing time and curing regime (how fast the final temperature is reached). If the cement sets and rests for some time at lower temperature (e.g. pumping temperature of below 100°C) before the high final temperature is reached, the low-temperature stable phases may still be present after high-temperature curing. For example, Linde A zeolite that forms in TSRC cured for 3 days at 85°C persists after 7-day curing at 200°C but disappears if the sample is cured at 300°C [25]. Another important factor of the curing regime is whether CAC and FAF react consecutively or simultaneously. At lower temperatures the hydration starts with more reactive CAC especially in the case of CaP cement that does not have alkali activator for FAF. As a result calcium aluminate hydrates (katoite) and chemical reaction products (calcium-hydrogen phosphate and apatite) form when the temperature increase is slow. If the temperature rises fast enough for both CAC and FAF to react simultaneously or close in time mixed products containing starting materials from both CAC and FAF form (dmisteinbergite) along with the reaction products of CAC (apatite), and FAF (analcime) reacting separately. **Table 2** summarizes possible crystalline phase compositions of CaP and TSRC at different temperatures after short curing times (<5 d). It can be seen that in the case of CAP cement zeolite analcime becomes one of the major phases only at high temperature of 300°C.

2.2. Thermal shock and corrosion protection: cement-carbon steel interface

Portland cement modified with crystalline silica for high-temperature cementing applications in underground wells generally demonstrates a poor bonding to CS casings. The annuluses formed along the cement-casing interface because of the poor cement bonding may cause fluids and gas migration, contamination of underground formations, severe casing corrosion, and, in the worst case scenario, catastrophic well collapse events. To overcome the problem slurries are modified with organic additives such as latex-based bonding aids/gas migration

Temp.	Major phases		Minor phases	
	CaP	TSRC	CaP	TSRC
~100°C	Hydroxyapatite	Gibbsite, Linde A	Boehmite, calcium hydrogen phosphate	Katoite, gismondine
~200°C	Hydroxyapatite	Katoite, thomsonite, gismondine;	Katoite, boehmite; calcium hydrogen phosphate; P-type zeolite; analcime	Sodalite/hydroxysodalite, dmisteinbergite, boehmite; analcime
~300°C	Dmisteinbergite hydroxyapatite, analcime	Dmisteinbergite, analcime, hydroxysodalite, boehmite	Anorthite, calcium hydrogen phosphate, Boehmite	Boehmite, gismondine, muscovite, margarite

Table 2. Short-term crystalline-phase compositions of TSRC and CaP cement at different temperatures.

prevention products. Although costly, such additives noticeably improve bonding strength of cement but also impose temperature limitations. The products does not survive temperatures above ~200°C on one hand and slow down cement hydration and, as a result, compressive strength development at ~60–85°C. Set retardation of latex-modified slurries at temperatures above ~120°C for placement in the wells may be also problematic.

Calcium-aluminate-cement containing blends have stronger CS bond and bond durability under various stress environments [23]. Further work showed that TSRC is able to recover its compressive strength and seal the cracks after imposed damage at temperatures up to 300°C [24]. It was demonstrated that the strength recovery of TSRC could be further enhanced to above 100% by addition of micro glass fibers (MGF, see below). Performance of MGF-modified TSRC, CaP and G/SiO_2 blend sheath samples with CS in thermal shock tests was evaluated. In these tests all the blends were modified with 5% by weight carbon micro fibers (for more information see [23, 26]) and with 5% micro glass fibers (Fiber Glast Development Corporation, part #38; 16 × 230 micron diameter × length) to improve their "self-healing" performance. Thermal-shock tests were performed on samples of carbon steel tube surrounded by cement sheath. After a day of curing in water at 300°C the samples were dry heated to 350°C for 24 hours and then cold water of about 20°C passed through the tube. The dry heat-cold water cycles were repeated up to 7 times. The thermal shock tests reduced the bond strength of all tested composites consistent with earlier reports [23, 26]. After 7 cycles the TSRC and CaP samples developed very thin cracks ("hair cracks"). The G/SiO_2 formulation developed noticeable wide crack that was getting wider during the heating period and narrower during the cooling (**Figure 1**). As expected both calcium-aluminate cement-based blends showed a stronger initial bonding and significantly better thermal shock resistance than class G blend. Furthermore, TSRC, developed to withstand large temperature variations, outperformed CaP in both the initial shear bond strength and the strength remaining after the tests. The composition difference that allows the better performance of TSRC at the interface with CS and in thermal shock tests is higher alkalinity of the slurries due to the presence of sodium-meta-silicate and as a result faster activation of fly ash F than in CaP cement blends. It was reported that the presence and reactions of FAF mostly contribute to the thermal shock resistance of blend cements [27].

High pH of TSRC slurries also helps corrosion protection of the CS. **Figure 2** shows CS corrosion rates, cement layer thickness and appearance of CS plates after the corrosion tests for CaP, TSRC and G/SiO_2 blends. The samples cured at 300°C for 1 d before the lap-shear bond strength tests (two CS plates bound by a thin layer of set cement are pulled apart) were exposed for 5 more days to the curing environment. Then electrochemical measurements were taken on three different locations for each sample to obtain corrosion rate. In addition, cement layer thickness was measured. During the lap-shear bond strength tests the samples underwent different failure mechanisms. In the case of class G/SiO_2 blend the bond between the cement layer and CS broke leaving CS plate for the most part free of cement and exposed to corrosion (adhesive failure). For TSRC the break happened inside the cement layer (cohesive failure) with some cement left on the CS plate providing its corrosion protection. CaP cement underwent mixed failure mechanism with partial cement coverage left on the plate after the bond tests.

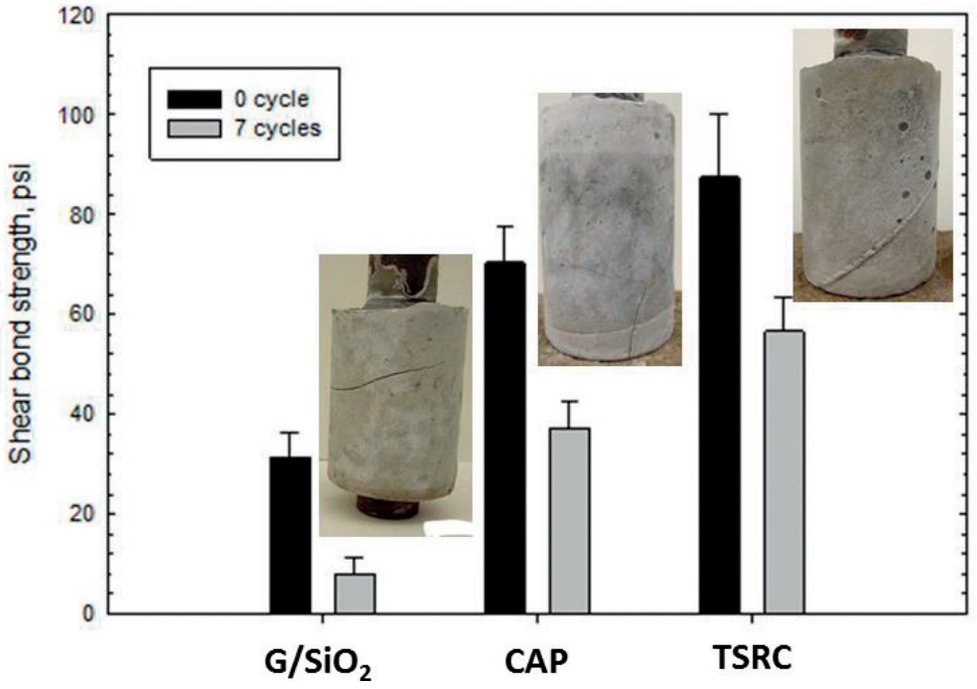


Figure 1. Shear bond strength and appearance of cement-CS sheath samples hydrothermally cured at 300°C and subjected to 7 cycles of thermal shock tests.

The appearances of the samples show clear signs of corrosion of class G/SiO_2 covered CS plate and some corrosion spots on the plate with CaP cement. TSRC samples do not have signs of corrosion. This observation is confirmed by corrosion rate and cement thickness data – showing the lowest corrosion rate and the thickest cement layer for the plate with TSRC. Class G cement blend provides the least corrosion protection of carbon steel. **Figure 3** gives microphotographs and elemental composition of TSRC and G/SiO_2 cement covering carbon steel plates. The measurements of iron from the underlying plates are consistent with the cement layer thickness data – the level of iron from CS measured at the G/SiO_2 blend is 5 times higher than that at TSRC suggesting thinner more porous cement layer for the Portland cement-based blend than for alkali activate FAF/CAC cement.

An important observation is high levels of Al in the interface layers. Class G cement is relatively poor in aluminum, so the amorphous, aluminum-rich layer protecting carbon steel is thin. On top of it calcium-silicate hydrate, xonotlite, with short parallel needles is sparingly spread. In general, the samples with needle-shaped xonotlite crystals exhibit higher permeabilities [7]. TSRC on the other hand forms thick aluminum-rich amorphous layer covered with intertwined rods of zeolite crystals (the bottom part of the microphotograph) acting as a self-reinforcing material.

In summary, calcium-aluminate cement blends with fly ash F significantly outperformed high temperature class G/SiO_2 Portland cement-based blend in bond strength with CS and its resistance to large temperature variations under the thermal shock conditions. Dense and thick aluminum-rich amorphous TSRC layer formed on the surface of CS plate and highly alkaline environment of its slurry provided excellent corrosion protection of CS. Randomly

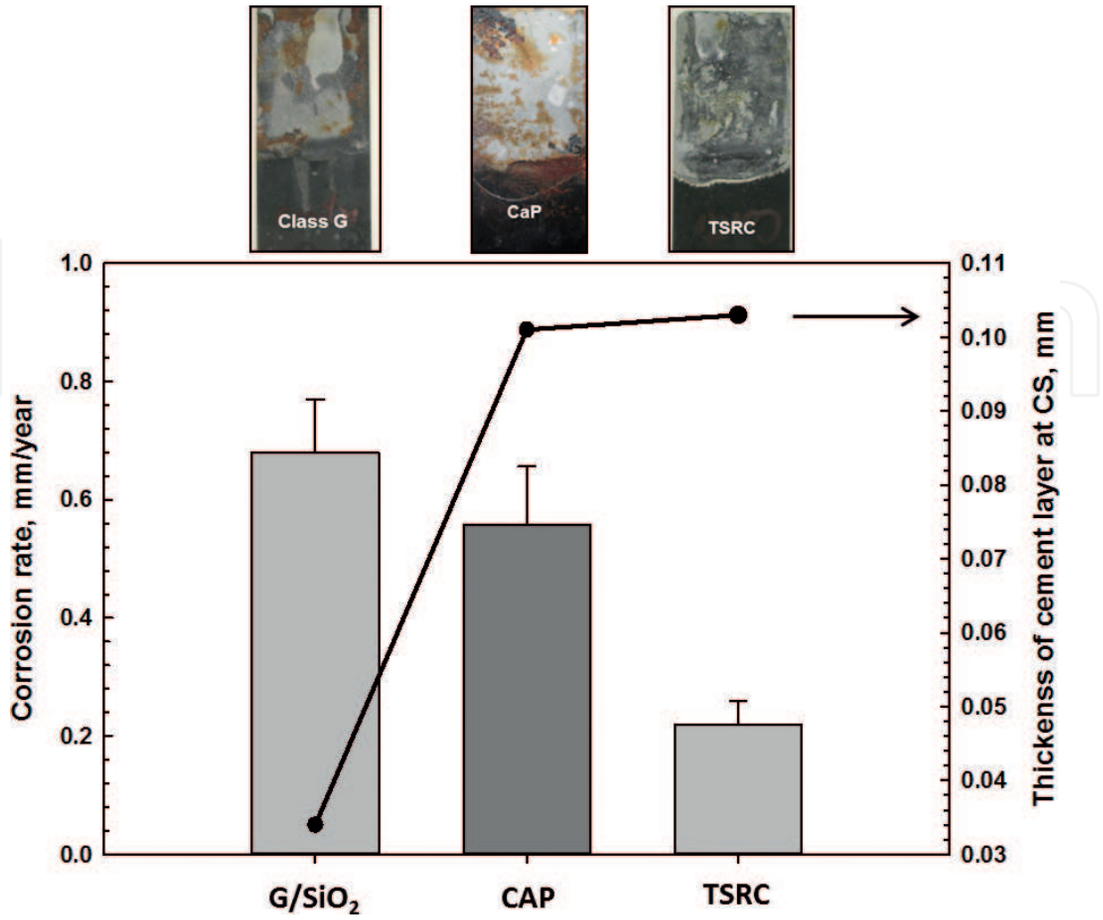
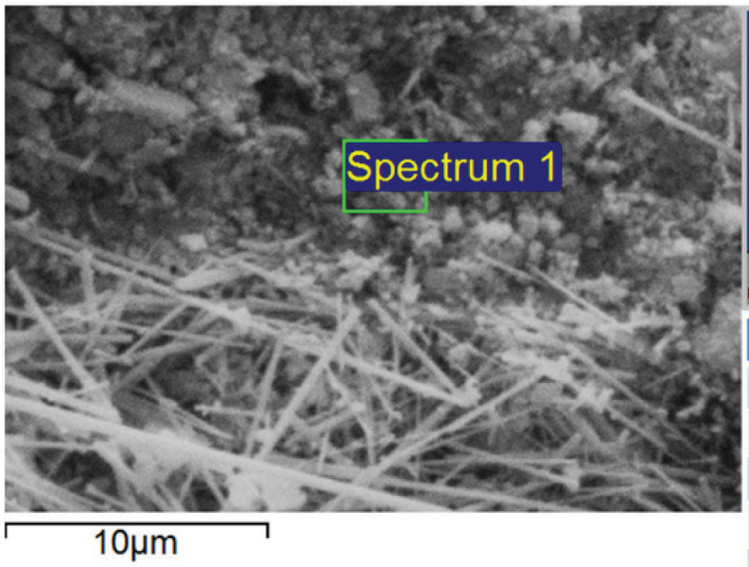


Figure 2. Corrosion rate, cement layer thickness and appearance of carbon steel samples with cement layer after hydrothermal curing for total 6 d at 300°C.

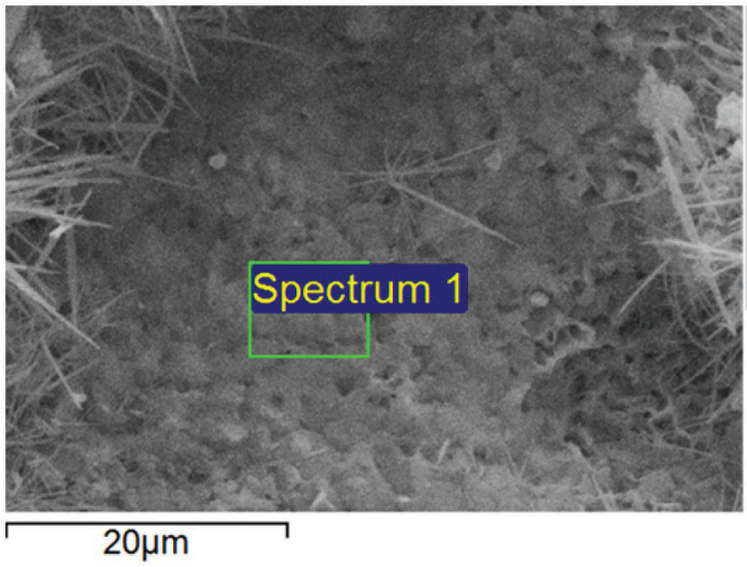
oriented zeolite crystals with rode-morphology provided self-reinforced cement on top of the amorphous phase in contact with the CS plate. As expected, Portland cement-based blends underwent adhesive failure in lap shear bond tests. With little cement left on CS the corrosion protection was poor. The spots of CS covered with remaining G/SiO_2 blend had thin amorphous layer covered with needle-like xonotlite crystals that are known to exhibit high permeability.

2.3. Strength recovery after compressive damage

Although strong, cements are brittle and, as a result, are likely to be damaged under various stresses of geothermal wells. To locate and repair such damage in underground constructions is very difficult and costly. That is why cements self-healing properties are of particular interest for underground applications. The subterranean geothermal environments offer some special conditions for cement self-healing. Particularly, cements are exposed to fluids necessary for reaction of latent components of cementitious blends and these fluids are rich in ions, both cations and anions that may participate in formation of new phases contributing to healing of damaged cements. Dissolution of slow-reacting volcanic ash components in interstitial water with release of hydroxyl ions and solution enrichment in Na, K, Ca, and Si was shown to result



Element	Atomic %
Na	3.6
Fe	3.6
Ca	4.2
Si	11
Al	19



Element	Atomic %
K	2.5
Fe	18
Ca	1.3
Si	15
Al	5.3

Figure 3. Microphotographs and elemental compositions of TSRC (top) and G/SiO_2 layers on carbon steel plates after 6 d hydrothermal curing at 300°C.

in long-term crystallization of zeolite, Al-tobermorite, and stratlingite reinforcing Roman marine concretes [28]. Such authigenic mineral cycling when new minerals form through in-situ precipitation and recrystallization may regenerate geothermal cements with FAF pozzolanic component in their composition. High temperatures help to accelerate the process.

Table 3 shows strength recoveries of the three blends after repeated damage and two 5-day healing periods. Detailed information on experimental set up can be found elsewhere [24]. The brine composition is given in [29]. In these tests 1-day cured samples were compressively damaged or broken (the compression tests were stopped at the maximum yield point) and then exposed to the curing conditions for 5 more days. The compressive strength was retested

Cement system	Curing environment (300°C)		
	Water	Alkali carbonate 0.05 M $NaCO_3$	Hypersaline brine
Class G/SiO_2	C	B	B
TSRC	A	A	A
CaP cement	C	C	A

Table 3. Cement strength recoveries after repeated compressive damage and two 5 d healing periods. Average recovery rates after 1st and 2nd compressive breaks for 1 d 300°C- cured samples: A 80–99%; B 60–79%; C < 60%.

after the 5-day healing period. The damage-healing cycle was repeated and the compression strength recovery data averaged.

The data show that at short curing times TSRC may successfully recover its strength after repeated damage in different environments. The recoveries of class G and CaP cement blends are not as good with the exception of CaP cement in hypersaline brine.

As mentioned above one possible mechanism of strength recovery are FAF reactions contributing to the "healing" process of damaged cements. However, although both CaP cement and TSRC contain FAF strength recoveries of CaP cement are inferior to those of TSRC and in the environment of alkali carbonate even to class G blend. One of the reasons for poor strength recoveries is the brittleness and the strong bond nature (chemical bond) of the CaP blend. Fast early compressive strength development through chemical reactions of sodium phosphate with calcium aluminate makes this cement strong but brittle. So the Young's modulus of the control CaP blend after 1 d curing at 300°C is 1896 MPa, while for TSRC it is 971 MPa. As a result wide cracks and fractures form under the compressive damage, making the repairs problematic. Another possible cause of lower healing performance of CaP cement could be its lower alkalinity in comparison with TSRC and G/SiO_2 blends. Under conditions of low alkalinity dissolution of fly ash and crystallization of healing phases requires longer times or may not happen at all.

Addition of slowly-reacting components, such as MGF, to the blends helps to improve strength recoveries (**Table 4**). MGF react under alkaline conditions contributing sodium, aluminum, and silicon to the pore water of the blends. These ions favor formation of zeolites that at later times may alter to other more stable zeolites or feldspar minerals [30].

In case of MGF additions strength recoveries are improved to above 100% (higher strength of damaged samples after the healing than the original strength) for TSRC and to 80–99% for class G/SiO_2 blend. In addition to the exceptional strength recoveries of TSRC samples optimal selection of pozzolanic materials allows binding cement pieces completely broken off the samples. The bond strength of such re-adhered pieces can be evaluated from the stress–strain curves of compressive strength tests. An example of such curve for a TSRC sample broken into two pieces and then cured at 300°C for 5 days in alkali carbonate environment is shown in **Figure 4**. On the curve the yield point (YP) compressive strength is 17.3 MPa. However, the initial failure (IF) of the sample where the re-adhered piece breaks off can be seen as a left shoulder with the failure point at 10.8 MPa. Such points of IF allow evaluation of the

Cement system	Curing environment (300°C)		
	Water	Alkali carbonate 0.05 M $NaCO_3$	Hypersaline brine
Class G/SiO_2	A	A	A
TSRC	A+	A+	A+
CaP cement	C	B	A

Table 4. Cement strength recoveries for blends reinforced with MGF after repeated compressive damage and two 5 d healing periods. Average recovery rates after 1st and 2nd compressive breaks for 1 d 300°C-cured samples: A+ > 100%; A 80–99%; B 60–79%; C < 60%.

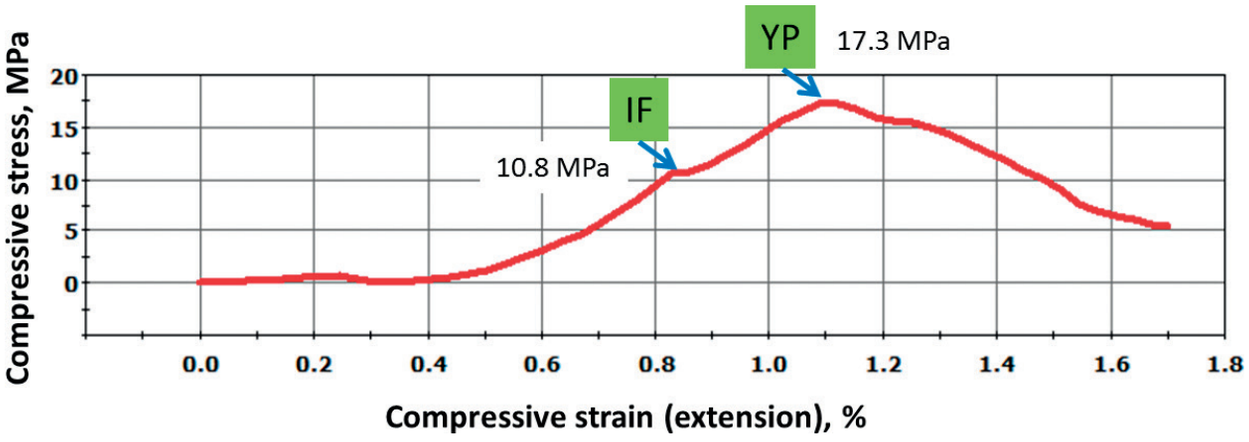


Figure 4. Strain–stress compressive curve for TSRC sample broken into two pieces and re-bound in alkali carbonate (0.05 M $NaCO_3$) at 300°C for 5 days; points of breaking off the re-adhered piece (initial failure, IF) and the yield point (YP) of the sample are shown.

recovered bond strength between broken off cement pieces and cement matrix. In the TSRC example the recovered strength (10.8 MPa) was above that required by the API task group on cements for geothermal wells (7 MPa).

The recoveries do not improve as much for CaP blend as for TSRC. This is likely due to significantly lower alkalinity of that slurry (pH~6.6), which does not allow fast MGF reactions and, on the other hand, fast chemical reactions resulting in stable products with little phase transitions that could help strength recoveries. As mentioned above another reason for lower strength recoveries in the case of CaP cement is its brittle nature that causes formation of large, smooth, difficult-to-repair cracks under compressive stresses.

3. Conclusions

Two types of calcium-aluminate cement – fly ash F blends, chemical (CaP) and alkali activated (TSRC), noticeably outperform common high-temperature well-cement blends of Portland cement and silica. The factors that contribute to their good performance under conditions of thermal shock, CO_2-rich- and strong-acid environments are as follows.

Good acid and thermal shock resistance of fly ash F reaction products, formation of stable carbonation phases, including carbonated apatite from apatite in CaP cement and cancrinite from zeolites in both CaP cement and TSRC.

The differences in the performance of these blends come from the minor components, sodium polyphosphate (CaP) and sodium-meta-silicate activator (TSRC). In CaP cement fast chemical reactions of sodium polyphosphate produce calcium phosphate-containing phases at early curing times, contributing to the early strength development and CO_2-resistance through formation of stable carbonated apatite phase. The reactions of fly ash F are delayed in CaP cement because of low ash reactivity at low pH of the interstitial water of this cement. This, along with the brittle cement nature limits early strength recoveries after cement damage. The low pH is also unfavorable for corrosion protection of carbon steel.

On the other hand, in TSRC samples sodium meta-silicate creates highly alkaline slurries that promote fly ash F reactions at earlier curing times than in the case of CaP. Fly ash F reaction products contribute to strong acid-, thermal shock resistance and high pH favorably changes the environment for corrosion protection of carbon steel. Excellent strength recoveries for damaged or broken TSRC samples are possible thanks to the cement's ductile nature and highly alkaline pH of its interstitial solution promoting fly ash F reactions with formation of new healing phases. However, the relatively high (>100°C) temperatures are necessary for fast early strength development of TSRC, while chemical reactions with the formation of phosphate in CaP cement allow fast early strength development over a wide temperature range.

This different natures of the two discussed calcium-aluminate cements may provide important advantages when specific properties are required under aggressive environments – whether it is fast early compressive strength development or formation of tough composites with regenerative potential.

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References

[1] Nelson E, Barlet-Gouedard V. Thermal cements. In: Nelson E, Guillot D, editors. Well Cementing. 2nd ed. Sugar Land, Texas, USA: Schlumberger; 2006. pp. 319-341

[2] Uchida T, Akaku K, Yanagisawa N, Kamenosono H, Sasaki M, Miyazaki S, Doi N. Deep geothermal resources survey project in the Kakkonda geothermal field. Journal of Energy Recourses. 1998;**20**:215-222

[3] Bensted J. Current calcium aluminate cement applications in well plugging. In: Fentiman C, Mangabhai R, Scrivener K, editors. Calcium Aluminate Cements. Proceedings of the Centenary Conference. HIS: bre press; 2008. p. 345-356

[4] API Task Group on Cements for Geothermal Wells. API Work group reports field tests of geothermal cements. Oil and Gas Journal. 1985;**83**:93-97

[5] Taylor H. The Chemistry of Cements. London, England: Academic Press Press Inc. Ltd.; 1964

[6] Hedenquest J, Stewart M. Natural CO_2-rich steam-heated water in the Broadlands-Okaaki geothermal system, New Zealand: their chemistry distribution and corrosive nature. In: GRC Transactions. 1985 Davis, CA

[7] Grabowski E, Gillot JE. Effect of replacement of silica flour with silica fume on engineering properties of oil well cements at normal and elevated temperatures and pressures. Cement and Concrete Research. 1989;**19**:333-344

[8] Milestone N, Sugama T, Kukacka L, Carciello N. Carbonation of geothermal grouts — Part 3: CO_2 attack on grouts containing bentonite. Cement and Concrete Research. 1987;**17**:295-306

[9] Milestone N, Sugama T, Kukacka L, Carciello N. Carbonation of geothermal grouts — Part 2: CO_2 attack at 250°C. Cement and Concrete Research. 1987;**17**:37-46

[10] Milestone N, Sugama T, Kukacka L, Carciello N. Carbonation of geothermal grouts — Part 1: CO_2 attack at 150°C. Cement and Concrete Research. 1986;**16**:941-950

[11] Zeldin A, Kukacka L. Polymer Cement Geothermal Well Completion Materials. Brookhaven National Laboratory report BNL 51287. Upton, NY: Brookhaven National Laboratory; 1980

[12] Pettit R. Completion of hot dry rock geothermal well systems. Paper SPE 8267 SPE Annual Technical Conference and Exhibition, 23-26 September, Las Vegas, NV, USA; 1979

[13] Degouy D, Martin M. Characterization of the evolution of cementing materials after aging under severe bottomhole conditions. Paper SPE 20904 SPE European Petroleum Conference, 22-24 October, The Hague, The Netherlands; 1990

[14] Meller N, Kyrtsis K, Hall C. The minerology of the CaO-Al_2O_3-SiO_2-H_2O (CASH) hydroceramic system from 200 to 350°C. Cement and Concrete Research. 2009;**39**:45-53

[15] Roy D, White C, Langton E, Grutzeck M. New high temperature cementing materials for geothermal wells: stability and properties. Brookhaven National Laboratory report BNL 51249. 1980; Brookhaven National Laboratory, Upton, NY, USA

[16] Sugama T, Weber L, Brothers L. Sodium-polyphosphate-modified fly ash/calcium aluminate blend cement: durability in wet harsh geothermal environments. Materials Letters. 2000;**44**:45-53

[17] Sugama T, Brothers L, Weber L. Calcium aluminate cements in fly ash/calcium aluminate blend phosphate cement systems: Their role in inhibiting carbonation and acid corrosion at a low hydrothermal temperature of 90°C. Journal of Materials Science. 2002;**37**:3163-3173

[18] Sugama T, Brothers L, Van de Putte T. Air-foamed calcium aluminate phosphate cement for geothermal wells. Cement and Concrete Composites. 2005;**27**:758-768

[19] Sugama T, Weber L, Brothers L. Resistance of sodium polyphosphate-modified fly ash/calcium aluminate blend cements to hot H_2SO_4 solution. Cement and Concrete Research. 1999;**29**:1969-1976

[20] Brookhaven National Laboratory. Brookhaven Lab., Halliburton Company, and Unocal Corporation Win R&D 100 Award for High-Performance Cement. Press release 00-56. 2000

[21] Sugama T, Gill S, Muraca A, Pyatina T. Corrosion-resistant foamed cement for carbon steels in enhanced geothermal systems. In: GRC Transactions, vol. 37, 29 September-2 October 2013; Las Vegas, NV

[22] Pyatina T, Sugama T. Acid resistance of calcium-aluminate cement- fly ash F blends. Advances in Cement Research. 2016;**28**:433-457

[23] Sugama T, Pyatina T. Bond durability of carbon-microfiber-reinforced alkali-activated high-temperature cement adhering to carbon Steel. Engineering. 2017;**9**:142-170

[24] Pyatina T, Sugama T, Ronne A. Self-repairing geothermal well cement composites. In: GRC Transactions, vol. 40, 23-26 October 2016, Sacramento, CA, USA

[25] Pyatina T, Sugama T, Moon J, James S. Effect of tartaric acid on hydration of a sodium-metasiliscate-activated blend of calcium aluminate cement and fly ash F. Materials. 2017;**10**:342-362

[26] Pyatina T, Sugama T. Use of carbon microfibers for reinforcement of calcium aluminate-class F fly ash cement activated with sodium meta-silicate at up to 300°C In: GRC Transactions, vol. 39, 20-23 September 2015, Reno, NV, USA

[27] Gill S, Pyatina T, Sugama T. Thermal shock resistant cement. In: GRC Transactions, vol. 36, 30 September-3 October 2012, Reno, NV, USA

[28] Jackson M, Mulcahy S, Chen H, Li Y, Li Q, CaPpelletti P, Wenk H. Phillipsite and Al-tobermorite mineral cements produced through low-temperature water-rock reactions in Roman marine concrete. American Mineralogist. 2017;**102**:1435-1450

[29] Sugama T, Pyatina T, Redline E, McElhanon J, Blankenship D. Degradation of different elastomeric polymers in simulated geothermal environments at 300°C. Polymers Degradation and Stability. 2015;**120**:328-339

[30] Hay R, Sheppard RA. Occurence of zeolites in sedimentary rocks: an overview. Reviews in Mineralogy and Geochemistry. 2001;**45**:217-234

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