Self-Repairing Geothermal Well Cement Composites

T. Pyatina, T. Sugama, and A. Ronne
Brookhaven National Laboratory, Upton NY

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ABSTRACT
Damage of the cement sheath under hostile geothermal environments may compromise well-integrity unless timely repairs are done. Because of the difficulties in locating and accessing damaged areas in subterranean wells self-healing cementitious materials are of particular interest. Self-repairing of Thermal Shock Resistant Cement (TSRC) developed for applications in geothermal wells in steam or carbonate-rich environments at 270°C was evaluated by compressive strength measurements after two crush tests followed by two 5-day healing periods and microstructural analyses of self-repaired samples using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and micro imaging techniques. TSRC performance was compared against that of ordinary Portland cement (OPC)/SiO₂ blend. The strength recoveries were above 80% for all TSRC samples and above 50% for OPC/SiO₂ blend. The recovery rate depended on the age of the samples, healing time, crack size, brittleness of the material and healing environment. Self-healing mechanisms are discussed and ways to further improve self-repairing cement capacities proposed.

1. Introduction
In hostile geothermal environments containing hypersaline brine, CO₂ and H₂S at temperatures >250°C, the well cement sheath between the casing string and rock/clay formation encounters variable mechanical-and chemical stresses that can lead to micro-annuli and cracks, increased cement permeability, cement disbandment from casing and formation, casing corrosion by geothermal fluids migrating through cement and compromised zonal isolation [1-5]. Repairs of well cements are complicated, costly and sometimes impossible since the cement failure locations are challenging to find, to reach and to repair correctly.

Self-healing cements that can recover their original properties without human intervention are of particular interest for subterranean wells. There are several technical strategies for developing the self-healing cements in the building and construction as well as oil or gas fields at temperatures, ranging from 20° to 140°C. Among them, the autogenous- and autonomic-healing technologies may be suitable to geothermal cements facing the high-temperature hydrothermal environments. The former strategy is related to the hydration of residual non-hydrated and partially hydrated cement particles by permeation of water through micro-annuli or cracks, and also the carbonation of hydrated products. The hydration and carbonation reaction products would grow as amorphous and crystalline phases and seal openings and cracks [6,7]. In autonomic healing the recovery process uses materials that are added specifically for the purposes of self-healing, such as the pozzolan-latent cementitious materials [8-11] and expansive additives [12-14]. When these healing aids come in contact with water penetrating through defects, they undergo hydration with- or without swelling and seal the cracks. The other important considerations for self-healing materials is a re-healing capability of previously healed cement after repeated damages, and the time of effectiveness of the healing aids.
In addition to the internal healing processes in cementitious materials, some researchers studied the healing potential of products formed by interactions between failed cements and chemical reactants present in the environments [15-21]. The subterranean geothermal environments offer some special conditions for cement self-healing. Particularly, cements are exposed to fluids that are rich in ions, both cations and anions that may participate in self-healing; there exist elevated temperatures that accelerate most chemical reactions and importantly, cement finds itself in a confined space between casings and formations that helps it to keep some integrity even when damaged.

Earlier studies with construction cements demonstrated that a key factor for a successful self-healing process is the size of the cracks. The cracks that heal in short periods of time under ambient conditions are typically below 60 µm in width [22,23]. For evaluation of self-healing performance designing fractures of controlled size is essential. To achieve controlled micro cracks in cementitious materials various fibers are commonly added to the cement formulations [24-26].

In our previous study of improving the toughness of alkali-activated, high-temperature well cementations materials at 300°C [27,28], the carbon microfiber (CMF) moderately reacting with the cement matrix was identified as the most effective high-temperature reinforcing additive that significantly enhances compressive toughness, provides excellent bridging, controlling crack development and propagation, and suppressing the post-stress cracks’ opening. Class F fly ash (FAF) included into the composition of the Thermal Shock Resistant Cement (TSRC) helped withstanding possible large temperature variations in geothermal wells [29-30]. The chemical composition of TSRC consisted of sodium metasilicate (SMS) as alkali activator, FAF, and calcium aluminate cement (CAC). TSRC demonstrated good thermal- and hydrothermal-stabilities at ≥300°C, and the retention of compressive strength of >6.89 MPa after five superheating-cooling cycles (one cycle: 500°C heat for 24 hrs and 25°C water-quenching). In this blend, the FAF initially acted as a temporary filling and packing responsible for densifying and strengthening the first binding phases of CAC hydrates at an early curing stage. Subsequently, the dissolution of FAF by the alkaline activators, followed by the pozzolanic reactions, led to the formation of a binding phase, an amorphous Na₂O - CaO-Al₂O₃-SiO₂-H₂O gel. The FAF reactions were slow, while the CAC hydration was fast assuring the early strength development. The slow pozzolan reactions of FAF may help the self-healing of the TSRC matrix through reactions of the non-reacted fly ash when cement is damaged.

In addition, the use of FAF as an industrial by-product for the cementitious matrix would benefit the environment while offering cost-effective solutions by eliminating the use of Ordinary Portland Cement (OPC), which emits 0.9 metric tons of CO₂ and a great deal of mercury for every ton of OPC manufactured [31-34].

Based upon the information described above, our particular interest is to investigate the ability of the CMF-reinforced TSRCs after repeated crack formation at different ages of the cement, to self-heal and self-re-heal in water and carbonate-rich environments at 270°C [35-37]. For comparison purposes the type II Ordinary Portland Cement (OPC) blended with silica flour was used in this study. The recovery of compressive strength and Young’s modulus was determined after exposure of damaged cements to the two environments for different periods of time and repeated cracking; the micro-image and elemental analyses were conducted to visualize the closing of cracks of different size as well as explore microstructure development at interfacial boundary between crack-plugging reaction products and cement core; and the phases-identification of the newly formed reaction products that plugged the cracks was performed.

2. Materials and Methods

TSRC blend included 56.6% by weight CAC #80, 37.7% FAF and 5.7% SMS. The CAC for TSRC blend was supplied by Kerneos Inc. SMS granular powder supplied by the PQ Corporation under the trade name “Metso Beads 2048,” was used as the alkali activator of FAF in TSRC formulations. The X-ray powder diffraction (XRD) data showed three major crystalline phases in FAF, quartz (SiO₂), mullite (3Al₂O₃·2SiO₂), and hematite (Fe₂O₃). The CAC #80 encompassed crystalline corundum (α-Al₂O₃), monocalcium aluminate (CaO·Al₂O₃, CA), and monocalcium dialuminate (CaO·2Al₂O₃, CA₂). The OPC, type II was dry blended with silica at 70/30 weight ratio and tested for comparison.

To conduct repeated damage tests and follow their healing it was necessary to ensure samples integrity through controlling cracks development and propagation. Carbon micro fibers [38] were added to all the formulations at 10% by total weight of solid blends.

Figure 1 summarizes the experimental protocol. The slurries were mixed by hand at water-to-blend ratio of 0.5 for the TSRC blend and 0.43 for the OPC/SiO₂. After mixing the slurries were poured into 20x40 mm cylindrical molds and left to set at room temperature overnight. The solid samples were demolded and placed under 100% humidity at 85°C for 24 hours imitating placement temperatures in a geothermal well. Set samples were further cured for various periods of time (1, 5 or 10 days) at 270°C in autoclaves representing early curing under static conditions of high-temperature geothermal wells (Figure 1a). The volumetric proportion of cement-to-fluid was 1-to-3.5 and the pressure in the autoclaves was 8.27 MPa. The fluid used as a curing environment was either pure water or 0.05N solution of sodium carbonate. Mechanical properties of the cured samples were tested in crush tests that were stopped at the maximum yield point (Figure 1b). The 5-day curing in steam or carbonate environments followed by mechanical tests were repeated with the damaged samples.
twice to obtain percent of strength recovery after the first and the second crush tests. Each result was averaged over at least three samples.

To visualize the closing of cracks and analyze the microstructures development disk samples with cracks made by Teflon sheets of different thickness were prepared (Figure 1c). Twenty grams of each blend were mixed with water at 0.4 w/blend ratios for OPC/SiO$_2$ and CaP and 0.44 for TSRC. Teflon sheets of 0.13, 0.25 and 0.5 mm were inserted into the slurry (~2 mm deep) and slurries were placed into an oven at 85°C 100% RH. Two days later the solid samples were removed from the cups and placed into an autoclave at 270°C with Teflon sheets in the cracks for overnight curing. The next day the cured samples were removed from the autoclave, the Teflon dividers pulled out of the samples. The samples were ground with an abrasive paper to get smooth surfaces. This was done for the following reasons – firstly, the µEDX studies require smooth samples for proper focus. Secondly, the grinding removed the top layer that could be different from the bulk of the samples due to the segregation during the two-day static curing.

Polished samples were placed into autoclaves with water or with 0.05N Na$_2$CO$_3$ solution for 5 days at 270°C. After the 5-day curing samples were placed into a vacuum oven at 60°C for a day before running the µEDX tests. The samples prepared for the microscope analyses contained CMF and were mixed at the same water-to-blend ratios as the cylindrical samples described above. They were not ground or dried before the tests.

3. Results and Discussion

3.1 Mechanical Properties and Visualization of the Healing of Damaged Samples

Mechanical properties measurements indicated that both compressive strength and Young’s modulus increase at longer curing times (Figure 2). This fact suggests that when damaged at early curing ages cements may recover some of their mechanical strength through continuous hydration of non-hydrated particles and, in the case of TSRC, through the slow pozzolanic reactions of FAF. In addition, the crystallization of amorphous hydrates will proceed as cements will age resulting in higher Young’s modulus. The experimental results showed similar compressive strengths and modulus values in steam and carbonate environments. They were predictably higher for the OPC/SiO$_2$ blend than for TSRC that builds up the strength at later times.

Figures 3 and 4 summarize the results of the recovery of mechanical properties after the first and the second crush tests followed by five-day healing periods. The TSRC formulations demonstrated significant compressive strength recoveries, which were slightly better in carbonate than steam environments (89 vs. 84% when averaged over all tests); the averaged recoveries of OPC/SiO$_2$ compressive strength were 54% in steam and 67% in carbonate. Notably, for TSRC the recoveries in carbonate after the first crush slightly increased with the increasing initial curing time of the samples: 1-day cured recovery < 5-day cured <10-day cured; while for water-curing the compressive strength recovery varied in the order: 10-day cured < 1-day cured < 5-day cured. Recoveries decreased with the increased initial curing time of the TSRC samples after the second crush for both environments: 10-day

Figure 1. Experimental protocol for evaluations of the strength recovery of damaged samples (a). The crush tests were conducted up to the maximum yield point (b). A disk sample with three sizes of cracks made by Teflon sheets of different thickness for visual observations of cracks filling during the self-healing process (c).

Figure 2. Compressive strength and Young’s modulus after different curing times in carbonate (a,b) or water (c,d) environments for TSRC and OPC/SiO$_2$ blends.
cured < 5-day cured < 1-day cured. These data suggest that the healing capacity diminished with the aging of the samples. Additional modifications of the original formulations may be necessary to increase the autonomic self-healing capacity of the TSRC.

The OPC/SiO₂ blend healing rate declined with aging in the steam environment after both the first and the second crush tests and underwent the maximum for the 5-day cured sample in the carbonate environment. Similarly to TSRC formulations modification to enhance self-repairing properties by adding healing aids may be necessary. The photographs in Figure 5 show the appearance of the samples after the second crush and a 5-day healing. There is a noticeable difference between TSRC and OPC/SiO₂ blends: the cracks in the TSRC sample are narrow and spread through the cement body in various directions, while the OPC/SiO₂ sample shows a single wide and long crack. Accordingly, the healing of small widely distributed cracks of TSRC samples is more efficient than healing of wide cracks of the OPC/SiO₂ blend. The crack formation and distribution depends on the fibers interactions with the cement matrix. The moderate interactions between TSRC and the CMF were shown to control crack formation and propagation resulting in tougher cement samples [38].

The fiber-cement interactions take place through calcium and aluminum bonding to the fibers as can be seen from the enriched Ca and Al content of the material covering the fibers and decreased content of these elements in the print of the fiber pulled of the matrix (Figure 5e). Preservation of the samples’ integrity allows for quicker repairs through formation of reaction products in small openings of damaged TSRC (Figure 5a).

Furthermore, to visualize the healing of the cracks microscopic images of samples with model cracks of different sizes were analyzed. Figure 6a shows images of a 0.25 mm crack in TSRC samples healed in sodium carbonate solution for different periods of time. As the exposure time increases the crack shrinks in depth and width. The images show that it was completely closed after 5 days of healing. Wider cracks of 0.5 mm were still partially open after 5 days, while narrow cracks of 0.13 mm were healed after a 1-day exposure. Likewise, the OPC/SiO₂ samples with controlled cracks needed longer curing times for healing wider cracks (Figure 6b).

In summary, TSRC samples demonstrated significant strength recoveries in both steam and carbonate environments (84 and 89% respectively) after two crushes and two 5-day healing periods. The recoveries depended on the environment and the initial curing time of the samples (samples age). OPC/SiO₂ blends strength recoveries were inferior to those of TSRC (54% in steam and 67% in carbonate).
3.2 XRD, TGA, SEM and Elemental Composition Studies

The samples exposed to carbonate solutions showed a clear difference in the composition of the surface, its adjacent layers and the cores, while samples healed in steam environments were mostly uniform. The EDX measurements of oxides revealed loss of about 70% of calcium and buildup of silica (~100% increase in concentration) in the top layers of TSRC samples in the carbonate environment suggesting calcium removal with carbonate anions and release of silica. Also, the silica could precipitate from the curing solution during the cooling of the autoclave before samples removal. Because of the low silica solubility in carbonate such precipitation could be expected to be more important in the carbonate environment.

The results of semiquantitative XRD analyses of TSRC and OPC/SiO$_2$ samples after healing in carbonate or steam environments are summarized in Table 1. In agreement with previous studies [39] the major phase of the control TSRC samples was a feldspar mineral, dmisteinbergite (ICDD: 04-011-5220). In addition carbonated feldspathoid mineral cancrinite (ICDD: 01-080-6031) formed in the core of the sample already after the first 5-day curing in the sodium carbonate solution. Longer exposure to carbonate solution removed calcium from dmisteinbergite leading to the decline of this mineral’s peaks, while the carbonated phase, cancrinite, persisted. Noticeably, calcium carbonate content was low in all the samples, indicating that at this high carbonate ion concentration calcium dissolved as

![Figure 5. Samples of TSRC and OPC/SiO$_2$ blends after the second crush test followed by 5 days of self-healing in steam (a,c) or carbonate (b,d) environments; the microphotograph showing CF interactions with the TSRC matrix (e).](image)

![Figure 6. Visualization of healing – a) closure of a 0.25 mm crack in TSRC healed in sodium carbonate; b) closure of cracks in OPC/SiO$_2$ blend after 5 days in sodium carbonate at 270°C.](image)
calcium bicarbonate. The top surface layer composition (5-day curing, carbonate, surface) included two crystalline components – silica and zeolite analcime, which likely precipitated from the solution rich in sodium, aluminum and calcium after dissolution of calcium and release of other cations. The SEM study confirmed presence of big analcime crystals on the surface of the sample (Figure 7a). As for silica, sodium silicate condensation reactions with formation of Si-O-Si bonds at high temperatures and low silica solubility in carbonate solution could favor precipitation with further crystallization of silica, along with the crystallization of amorphous silica left after calcium bicarbonate dissolution. The SEM analyses demonstrated that significant part of the sample matrix was amorphous sodium-aluminum silicate (Figure 7b).

After a total healing of 20 days in steam the crystalline composition of TSRC included dmisteinbergite coexisting with smaller amounts of analcime, silica and boehmite in agreement with the earlier study [39]. The TGA analyses confirmed presence of boehmite, analcime, and calcite as well as cancrinite in carbonate environment (Table 1).

Similar to TSRC, EDX measurements showed that 87% of calcium was lost from the top layer of OPC/SiO2 blends exposed to the carbonate solution and the silica content increased by 200%. The crystalline composition of the OPC/SiO2 samples consisted for the most part of xonotlite (ICDD: 00-023-0125/04-017-1287) and scawtite (ICDD: 00-031-0261 and 04-011-1632) and some amounts of other calcium silicate hydrates (such as riversideite – 9A, ICDD: 00-029-0329 and truscottite, ICDD: 00-029-0382). Scawtite forms from xonotlite when the latter is exposed to carbonate-containing solutions [44]. At low quantities scawtite is desirable since it may fill the cracks and fractures itself or as a result of silica release from xonotlite upon transformation to scawtite (Ca/Si ~1.2 in scawtite vs. ~1 in xonotlite). However, at large quantities, scawtite makes cement brittle forming large, difficult-to-heal cracks under stress. Scawtite was present both in steam- and carbonate-cured samples. In the case of steam-exposed samples scawtite could form from the carbonates present in the “as received” OPC and in steam. According to TGA measurements scawtite quantities were about 1.7 times lower in steam samples than in those cured in carbonate.

TGA measurements also demonstrated that carbonate-exposed OPC/SiO2 samples had almost twice as much calcium carbonate in the cores as in the surfaces (1.6 vs. 3.1 wt.%). This was partially due to the significant silica precipitation and partially due to the dissolution of calcium as calcium bicarbonate. The presence of small amounts of sodium-aluminum-silicate zeolite, analcime, among calcium silicate hydrates, was confirmed by SEM-EDX observations (Figure 7c). Analcime could form from the aluminum released from calcium aluminate after the dissolution of calcium as bicarbonate. Peaks of a high-temperature calcium silicate hydrate, truscottite, were also present in the XRD patterns. Crystallization of this low-calcium hydrate (Ca:Si ~ 0.6) was probably favored by the decreased calcium content due to the calcium bicarbonate dissolution in carbonate environment. Finally, some non-reacted C2S was still present after 20 days of curing at 270°C.

Based on the experimental results the following interactions may be proposed for TSRC and OPC/SiO2 blends in carbonate environments (Figure 8). Calcium-containing phases of feldspar minerals and amorphous calcium-alkali-silica aluminates react with carbonate ions from the solution forming calcium carbonate that dissolves as bicarbonate at high carbonate concentrations. Calcium removal releases condensed and partially protonated silicate clusters, aluminum hydroxide and sodium ions. New zeolite phase, analcime, forms from the dissolved ions, silica precipitates as amorphous and crystalline phases, calcium-poor amorphous hydrates and

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[^1] Truscottite was not weighted
crystalline cancrinite with low calcium content partially replace the feldspar minerals and calcium-rich amorphous hydrates. Cancrinite may undergo further transformation from calcium-containing to alkali-based crystals.

In the case of OPC/SiO₂ blend interactions of both crystalline and amorphous calcium silicate hydrates with carbonate ions result in xonotlite transformation to calcium carbonate and scawtite; at high carbonate concentrations calcium carbonate dissolves as bicarbonate, while silica released from xonotlite precipitates as amorphous or crystalline phase. This silica participates in cracks closure likely contributing to the healing of damaged samples. Small amounts of precipitated calcium carbonate and scawtite may also assist to the strength recovery.

4. Conclusions

Two cement formulations with 10 weight percent carbon microfibers for controlled development of cracks, TSRC and OPC/SiO₂ blend were tested for self-healing at 270°C in steam and sodium carbonate solution after two series of crush tests followed by two 5-day recovery periods. The TSRC samples demonstrated significant strength recoveries in both steam and carbonate environments (84 and 89% respectively). OPC/SiO₂ blends strength recoveries were lower (54% in steam and 67% in carbonate). For TSRC samples the healing was a result of latent pozzolanic reactions of fly ash F, cracks sealing by precipitation of silica and analcime after calcium dissolution in carbonate environment, formation of new cancrinite phase as a result of reactions between the hydration products and carbonate ions. In the case of OPC/SiO₂ blend the following factors contributed to the strength recovery: hydration of slow-reacting phases, such as C₃S, matrix carbonation with formation calcium carbonate and scawtite resulting in release and condensation of silica.

The factors that affected the self-healing included aging of the samples, with more non-reacted and slowly-reacting phases present at earlier curing times, cement brittleness that controls crack development and propagation, size of the cracks, and the nature of the environment. Moderate interactions between the carbon fibers and TSRC matrix allowed preserving samples integrity and increased samples toughness that led to better recovery rates.

![Figure 7. Microphotographs and EDX measurements of TSRC (a,b) and OPC/SiO₂ (c) samples after total 20 days of healing in sodium carbonate solution.](image)

![Figure 8. Schematics of TSRC and OPC/SiO₂ blend interactions in sodium carbonate solutions.](image)
Further enhancement of the healing properties may be possible by slowing down cement hydration through the use of slowly-reacting components in cement formulations and introduction of self-healing enhancing additives that may form new stable phases with the ions from the environments.

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