Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Lightweight Variable-Density Well Cement with Self-Healing Properties for Applications in Geothermal Wells

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Keywords: Portland cement blend, geothermal cement, zeolite, self-healing, intergrind, pozzolan, acid-resistance, FlexCem®, high-temperature cement

ABSTRACT

FlexCem® Lightweight Variable Density well cement was developed by Trabits Group following completion of a research grant from the Department of Energy Geothermal Technologies Office (GTO). This cement performs well in harsh geothermal conditions with thermal stability at temperatures of up to 300^{0}C with resistance to carbonation. A special cost-effective technology of integrind was developed for its manufacturing as a blend with bimodal particle distribution of API well cement and zeolite micronized to 10 microns during the intergrinding.

The FlexCem® intergrind method has been tested at four U.S. cement plants. Each of these full scale, large tonnage intergrinds were compared for resulting cement chemical properties and cement performance. All four intergrinds were essentially identical in properties and performance proving the method provides a consistent and repeatable cement product. The zeolite used in FlexCem® is Ferrierite which is rare natural crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open, three-dimensional structure. The FlexCem® Ferrierite is mined from the only known minable deposit in the world, located 12 miles north of Lovelock, Nevada.

The specific formulation and choice of zeolite results in a variable density cement with a working range of 1.32 kg/L to 1.71 kg/L (11.0 to 14.3 ppg). The cement retains the original GTO target qualities of thermal stability, resistance to carbonation and additionally exhibits the unique ability to self-repair in a wide range of temperatures. In this work strong-acid high-temperature resistance (pH 0.2, 90^{o}C, 28 days) of FlexCem® is compared against that of common high-temperature formulations of Ordinary Portland Cement. The paper also presents results of moderate- (100^{o}C) and high-temperature (270^{o}C) cement strength recovery after imposed compressive damage and a short 5-day recovery period under the initial curing conditions. Phase analyses using x-ray diffraction, Fourier transform infrared analyses and scanning electron microscopy coupled with energy dispersive x-ray spectroscopy show that zeolite decomposes under hydrothermal alkaline conditions of cement slurries with release of hydrolysates that along with the hydrating cement participate in the formation of new phases contributing to strength recovery.

1. INTRODUCTION

To be economical geothermal wells are constructed in naturally fractured, poorly consolidated or unconsolidated formations (Nelson and Barlet-Gouedard, 2006). Because of that lost circulation during well construction is a common problem that may significantly increase cost of a well. To decrease well-fracturing and lost-circulation problems during cementing jobs lightweight slurries are commonly required. However, often the exact well conditions are not known, and lost-circulation problems may happen at any stage of well-cementing. Ideally, slurry density should be easily and readily adjusted to control the well and simplify logistics so that the same blend can be used both as lead and tail cement eliminating multiple blend requirements at the wllhead. Additionally, although geothermal well- and oil and gas well-construction techniques are very similar, aggressive environments of geothermal brines at high temperatures make it difficult for cements to survive and provide zonal isolation and casing corrosion protection. Geothermal cements must be acid resistant and should have self-healing properties to be able to recover well integrity without human intervention when damaged.

In early 2010, Trabits Group submitted a geothermal cement development research proposal to the U.S. Department of Energy, Geothermal Technologies Office (GTO). The stated goal of the research program was “Development of a zeolite-containing lightweight, high temperature, high pressure geothermal cement which would provide operators with an easy to use, flexible cementing system that saves time and simplifies logistics”. Nine target criteria were established. These were:

- Thermal stability with little strength retrogression to 300° C.
- Tensile strength to withstand temperature and pressure changes.
- Low-density, low-viscosity slurries with low equivalent circulating densities (ECD) without the need for air or nitrogen foaming.
- A single cement blend allowing density adjustments without adversely affecting slurry properties to eliminate the need for separate blends for lead and tail slurries.
- Resistance to carbonation.

- Accurate downhole densities throughout cement placement without significant changes in viscosity.
- Water absorption capacity without retaining free water.
- Good bonding to casing and formation.
- Adequate compressive strength.

During the initial screening, five different types of zeolite, each micronized to 5, 10 and 44µm, were used at three replacements of Class G and Class H cement at 15%, 27.5% and 40%. The initial screening samples totaled 180 individual tests in a heuristic process.

Trabits Group selected one best zeolite/cement blend for detailed testing and development. The zeolite used in this best blend was Ferrierite (FER) which exhibited excellent thermal stability. This best blend was subjected to long-term testing in geothermal brine from the Ormat Brawley field for a 3-month period after which it was tested for compressive strength, modulus of elasticity and permeability. This best blend met all nine target performance criteria.

Throughout the project Trabits Group conducted internal peer review and participated in the annual GTO Peer Review program. The project was completed in 2015 and after considering multi-year Peer Review comments Trabits Group reached the conclusion that commercial development of the technology was warranted.

While the developed cement was successful, the method of making it was not. In the GTO research, jet mill processing was used to micronize test zeolite types. Jet milling, while effective for research sized batches, is not economic for commercial cement manufacture. The research clearly documented that a zeolite particle size of 15 to 20µm was optimal for performance at high temperatures and at low temperatures as well. In addition to the cost of micronizing zeolite there was the cost of dry blending with a finished API cement to make the final composite zeolite-containing cement.

This paper describes optimization of the micronizing and dry blending of Portland-cement clinker – FER blend, organization of a commercial production of the blend, establishing its quality control, field tests and studies of the blend's performance under aggressive geothermal environments of high acidity (pH=0.2, 90°C).

The composition of the blend suggests a possibility of self-healing properties in a range of temperatures. Most cements possess self-healing properties, especially at lower temperatures, because of the slow cement hydration reactions and insufficient water amount, which results in residual non-hydrated particles that can hydrate upon exposure to fluids through cracks in damaged cements allowing some strength recovery. The hydration reaction accelerate exponentially with temperature increase, decreasing amount of non-reacted particles in the cement body, so that the self-healing ability of OPC based composites is relatively low at high temperatures that may be encountered in geothermal wells (Sugama and Pyatina, 2019). On the other hand, the composition of the blend that includes thermally-stable FER suggests that it may possess self-healing properties at high temperatures as well, recovering its strength through slow alkaline reactions of FER. Zeolites belong to natural pozzolans and it is well documented that they contain pozzolanic siliceous or siliceous-aluminous reactants that can be used to partially or totally substitute Ordinary Portland Cement (OPC) (Ahmadi and Shekarchi, 2010; Bilim, 2011; Karakurt and Topçu, 2011; Mertens et al., 2009; Misaelides P, Godelistas A Link F, 2005; Ortega et al., 2000; Uzal et al., 2010; Yilmaz et al., 2007). Zeolites' pozzolanic reactions are initiated by blending with $Ca(OH)_2$-forming alkaline reactants like lime and OPC. Zeolites are crystalline hydrated aluminosilicate minerals with three-dimensional oxygen-linked $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral frameworks containing ion exchangeable counterbalanced cations (Na^+, K^+, and Ca^{2+}) and water molecules situated in their micropores and channels (Misaelides P, Godelistas A Link F, 1997, 1991). Some authors (Misaelides P, Godelistas A Link F, 2003a, 2003b, 2002) also stated that substantial amount of Fe counter-cation is intercalated into the crystalline lattice of zeolite. When zeolite interacts with Ca^{2+} and OH^- liberated from lime and OPC in aqueous media, its aluminosilicate frameworks are disintegrated by the attack of OH^- that leads to alkali dissolution of zeolite and creates $[SiO(OH)_3]^-$ and $[Al(OH)_4]^-$ reactants. Next, these reactants bind with Ca^{2+}, leading to the formation of calcium silicate and calcium aluminosilicate hydrates as cementitious products (Misaelides P, Godelistas A Link F, 2005).

Compared with the properties of OPC-based cements, such pozzolan cements have the following advantages: Improved resistance to sulfate-caused erosion, minimized water permeability, and elimination of the calcium silicate-related swelling hydrogel brought about by interfacial reactions between $Ca(OH)_2$ and amorphous or poorly crystallized silica phases in aggregates, thereby mitigating an undesirable expansion-caused failure of concrete. On the other hand, there are two major drawbacks: One is slow development of early strength; the other - increased water demand for accomplishing adequate slump of fresh concrete. In dealing with these drawbacks, over more than three decades, several different processing techniques involving ultra-fine pulverization (Alexander, 1960; Misaelides P, Godelistas A Link F, 1994), thermal-, hydrothermal-, and acid-treatments (Collepardi et al., 1976; Costa and Massazza, 1977; Hemings et al., 1988; Misaelides P, Godelistas A Link F, 2016), and chemical method (Misaelides P, Godelistas A Link F, 1993) have been employed to enhance the reactivity of pozzolans. The efficacy of these treatments in enhancing pozzolanic reactivity of clinoptilolite was due to the extraction of Al from clinoptilolite (dealumination) caused by the breakage of aluminosilicate structure, thereby resulting in a loss of crystallinity and conversion of crystal into amorphous phases. Correspondingly, Si/Al ratio of clinoptilolite significantly increases after the treatments (Ates and Hardacre, 2012; Cakicioglu-Ozkan and Ulku, 2005; Elaiopoulos et al., 2010; Misaelides et al., 1966; Zhang et al., 2002). Nevertheless, among these processing techniques, Shi et al. described that the most effective one was the chemical method using Na_2SO_4 and $CaCl_2$ activators (Shi and Day, 2001). For high-temperature geothermal wells slow reactions of zeolite in composition of a blend with OPC is an advantage, since it may help self-healing of damaged composites at later curing times.

The paper discusses self-healing properties of the blend in a temperature range between 100 and 300°C after repeated mechanical damage.

2. INTERGROUND PROCESS AND CEMENT DESIGN

Alternatives were investigated to reduce the high cost of micronizing and dry blending. The most economic option identified was to intergrind cement clinker and zeolite which can be done at the cement plant or at a standalone grinding facility. Intergrinding zeolite and cement clinker provides a bimodal particle size distribution given that zeolite is a "softer" material than clinker with the zeolite preferentially grinding finer. This preference for zeolite grinding finer results in the zeolite being "micronized" as the cement product is made.

The advantages of Intergrinding include: economic gain of replacing a higher cost clinker with a lower cost zeolite, improved strength of the zeolite intergrind product, lower permeability and resistance to carbonation, lowering the resulting interground cement environmental cost associated with greenhouse gases.

First intergrind cements were designed with API class cements, zeolite, strength retrogression prevention additives and retarders for high-temperature applications. After successful laboratory tests a 1,000-ton intergrind run was performed at a Western U.S. cement plant to test the basic parameters of milling rate, particle size distribution, resulting Blaine and final cement chemistry. For this first intergrind a Class G clinker and the zeolite Clinoptilolite were used in a design ratio of 55% clinker, 40% zeolite and 5% gypsum. The manufactured cement had an Optimum Density of 12.73 ppg, which was good, and had required strength at 24 hours but lacked the target of high early strength.

For the second trial zeolite FER replaced clinoptilolite and Type I/II clinker replaced Class G one to meet material's criteria. Additionally, cement-to-zeolite ration was changed. These changes allowed meeting performance criteria set for the inerground cement.

In keeping with the Concept Goal of "multiple applications from a single intergrind" Trabits Group applied for and was issued a Trademark for "FlexCem" by the U.S. Patent and Trademark Office. Now with a method, formulation and a product name the cement was ready for commercial production.

What FlexCem® is:

FlexCem® LVD is a lightweight variable-density well cement with a density range of 11.5 to 14.3 ppg. It is manufactured using patented technology in which cement clinker and proprietary zeolite are interground in specific ratios to maximize set-cement properties. FlexCem® LVD can be used in all types of cement applications, as a lead or tail slurry, and it is compatible with most currently-used cement additives.

The first commercial production was conducted at a cement plant in South Dakota and targeted the Bakken field in North Dakota. FlexCem® was used as lead cement for intermediate completions in the Bakken. Table 1 shows Bakken well conditions and slurry design. A total of fifteen wells were cemented with no problems and good results reported by the service company.

Table 1: Bakken well conditions and FleCem® slurry design.

Date	10/21/2017
Fluid Type	Lead
Job Type	Intermediate
TMD	11211 ft
TVD	10904 ft
BHCT	220°F
BHST	245 °F
Temperature Gradient	1.51 °F/100ft
Surface Temperature	80 °F
Density	11.50 lb/gal
Yield	2.42 ft^3/sk
Water Requirement	14.20 gal/sk
Sack Weight	85.00 lbs
Fluid SG	1.38
Service District	Dickinson

Although successful in the Bakken, commercial production of FlexCem® was moved to a cement plant in Oklahoma and a cement plant in Texas. The market in the Bakken is limited while markets in what is referred to as “MidCon” and the Permian Basin are much larger. In these markets FlexCem® is being used as a lightweight lead cement at 11.0 ppg and 11.5 ppg for most applications.

Cement plants take great care to ensure that cements manufactured are the same from one batch to another and meet specific quality parameters. Quality is also paramount in the manufacture of FlexCem® with a few added conditions. For example, in the finish mill cement plants use grinding aids to improve mill efficiency. Because certain grinding aids interfere with additives FlexCem® is interground without the use of grinding aids. The intergrind also has to be repeatable, not just from one batch to another in the same plant, but also repeatable at other plants. The logic here is geographic flexibility and taking advantage of the readily available Type I/II clinker which is made at most cement plants.

The following two Tables illustrate Repeatability of the same intergrind design at four different cement plants.

Table 2: Chemistry comparison for cements from four different cement plants.

	Plant A	Plant B	Plant C	Plant D
SiO2	35.42	36.51	36.16	34.34
Al2O3	6.25	6.50	6.56	6.09
Fe2O3	3.33	2.53	2.47	2.76
CaO	44.87	44.26	48.55	46.68
MgO	1.92	1.59	1.26	1.07
SO3	2.81	3.04	2.94	2.71
Na2O	0.43	0.69	0.58	0.58
K2O	1.90	1.71	1.35	1.60
Free CaO	0.630			
LOI	3.97	3.93		4.2
Alk. Eqv.	1.67	1.81	1.46	1.63
S. G. (C188)	2.715	2.740		2.763
Blaine	7420	7598	7140	7270

In Table 2 above, the chemistry is about the same, but Blaine is lower for Plants C and D. As shown in Table 3 below the effect of lower Blaine can be seen in final cement performance where lower 24-hour compressive strength appears to directly correlate with lower Blaine.

Table 3: Blaine effect on 24-hour compressive strength development

	Plant A 13 lb/gal	Plant B 13 lb/gal	Plant C 13 lb/gal	Plant D 13 lb/gal
Initial Viscosity	9	17	31	3
Time to 30 Bc	66	79	0	87
Time to 70 Bc	94	95	91	106
Time to 100 Bc	104	105	104	116
Free Fluid (ml)	0	0	0	0
S.G.	2.71	2.76	2.85	2.85
24 HR	1720	1997	1209	1529
Viscometer Readings				
300	76	88	83	87
200	68	81	77	81
100	58	76	68	72
6	29	23	25	26
3	19	18	17	20

2. SELF-HEAING PROPERTIES AND ACID RESISTANCE

2.1 Experimental procedure

The FlexCem was prepared from OPC clinker (Type I/II) – FER – Gypsum blend (65/30/5 weight % respectively) by grinding together unground clinker and the natural zeolite to a final composite with a mean particle size of 24 µm. OPC Type I/II modified with 30% by weight of cement silica was used as a reference in strength recovery tests. Portland cement, class G was used to prepare blends with clinoptilolite zeolite (CLIN). The elemental analyses of CLIN showed 68% Si, 11% Al, 8% K, 6.3% Fe and 4.7% Ca in its composition (all in atomic percent). The x-ray diffractometric characterization (XRD) demonstrated that its major crystalline component was Clinoptilolite-Ca ($Ca_{3.16}Si_{36}O_{72}(H_2O)_{21.8}$; ICDD: 01-070-1859) with some Krotite ($CaAl_2O_4$; ICDD: 00-023-1036), Quartz (SiO_2; ICDD: 01-075-8320) and Goethite ($FeO(OH)$; ICDD: 04-015-8198).

Carbon micro fibers (CMF) 7-9 µm in diameter and 100-200 µm in length were added to ensure controlled crack formation. Silica flour was added at 14.5 wt% of the entire blend to some of the FlexCem samples (Table 4). A solution of sodium carbonate at 0.05M was used to simulate conditions of alkali carbonation in geothermal wells.

The slurries were mixed at a water-to-blend mass ratio of 0.54, poured into 20x40 mm cylindrical molds and left to set for 24 hours at room temperature and then under 100% humidity at 85°C for 24 more hours imitating placement temperatures in a geothermal well. Set samples were further cured for 24 hours at 270°C (300°C for class G/CLIN blends) in autoclaves filled with water or sodium carbonate solution representing early curing under static conditions of high-temperature geothermal wells. The volumetric proportion of cement-to-solution was 1-to-3.5 and the pressure in the autoclave was 8.27 MPa.

Table 4: Composition of FlexCem and class G formulations in weight %

	FlexCem	FlexCem/SiO_2	G/CLIN	Type I/II/SiO_2
FlexCem	94.3	66	-	-
Silica	-	28.3	-	28.3
Cement	-	-	34.2	66
Clinoptilolite	-	-	22.9	-
Carbon	5.7	5.7	5.7	5.7

After curing samples were crushed to their yield point used to calculate the compressive strength and Young's modulus of the control and then autoclaved for 5 more days at 270°C in carbonate or water environments. The crush tests and the 5-day autoclaving were repeated, to simulate repeated damage, followed by the final compressive strength measurements. Additionally, the crack filling was examined on the samples with cracks of 0.25 mm wide and ~2 mm deep made with Teflon tabs inserted into the slurries before their curing for 24 hours at 270°C as described above. After the initial curing the Teflon tabs were removed, and crack sealing examined after 5 and 10 days of autoclaving in carbonate or water at 270°C.

After the final compressive strength measurements, the samples were ground into a very fine powder and dried at 90°C for 24 hours before XRD characterization. The samples were examined using a 40 kV, 40 mA copper anode X-ray tube. The results were analyzed using PDF-4/Minerals 2015 database of International Center for Diffraction Data. The morphologies of the selected formulations were explored on typical spots of freshly fractured and chromium-coated samples with JEOL 7600F scanning electron microscope.

Three cured samples of each type were weighed, measured and placed into solutions of sulfuric acid at 90°C, pH 0.2 for 28 days. Although the reactions' kinetic depends on the temperature the technical limitations did not allow conducting acid experiments at geothermal temperatures of 300°C. The volume of the acid solutions was twice the volume of the samples and the solutions were replaced with fresh ones every 3 days to maintain <15% increase in pH during the treatment. After the acid exposure the specimens were rinsed with water, weighed, measured and tested for compressive strength.

2.2 Results and discussion

2.2.1 Mechanical properties and microscope study of fracture filling

Figure 1 shows compressive strength of tested formulations after repeated damage in water or carbonate. Zeolite-modified cements had a lower initial compressive strength than OPC with silica flour. All the formulations recovered some compressive strength both after the fist and the second crush tests and additional 5-day curing at 270-300°C so that their final strength was more than 1000 psi except for OPC/CLIN one cured in water (760 psi). Surprisingly, the strength of FlexCem cured in water increased after the two crush tests and repeated healing of 5 days and increased after the first crush test before decreasing after the second crush test when healed in carbonate. The strength of OPC/SiO_2 and OPC/CLIN in water decreased consecutively in two crush tests with two healing periods. The strength of OPC/CLIN formulation cured in carbonate stayed around 2000 psi throughout the testing. FlexCem demonstrated very high recoveries of >160% (1st break) and >130% (2nd break); its recovery in carbonate was 170% (1st break) but only 70% after the 2nd break. OPC/SiO_2 recoveries stayed constant between ~60 and 65% in two damage tests and two healing periods (Figure 1). The recoveries of OPC/CLIN were around 100% after both crush tests when cured in carbonate but only 80/56% after the first and the second crush tests followed by healing in water. Low strength recoveries were generally associated with the formation of large, long cracks. Young's modulus mirrored the compressive strength behavior with especially conspicuous increase in it for FlexCem cured in water (Figures 2). To further improve FlexCem performance in carbonate environment it was modified with silica flour (Table 1, Figure 3). Silica addition increased the initial compressive strength both in water and carbonate to more than 3000 psi. It also allowed to keep strong strength recoveries in carbonate after the second damage and 5 curing (111%). However, silica-modified FlexCem recoveries in water decreased to the level of OPC/SiO_2 formulation (59 and 56% after the first and the second crush tests respectively).

Since the major role of a cement sheath in a subterranean well is zonal isolation, healed cement should possess low permeability along with recovered strength. The efficiency of crack filling for FlexCem samples was studied by taking images and reconstructing the 3D structure of pre-cracked (0.25 mm width) samples after 5 or 10 d of curing in water or carbonate (Figure 4). The crack filling was noticeably better in samples cured in the carbonate environment than those cured in water. For the sample modified with silica, the crack was completely sealed after 5 d. The crack in the unmodified samples was partially filled after 10 d in carbonate solution, but additional curing time would complete the crack plugging. The water-healed samples had some minor solid depositions in the fractures, but they were insufficient to seal the large cracks.

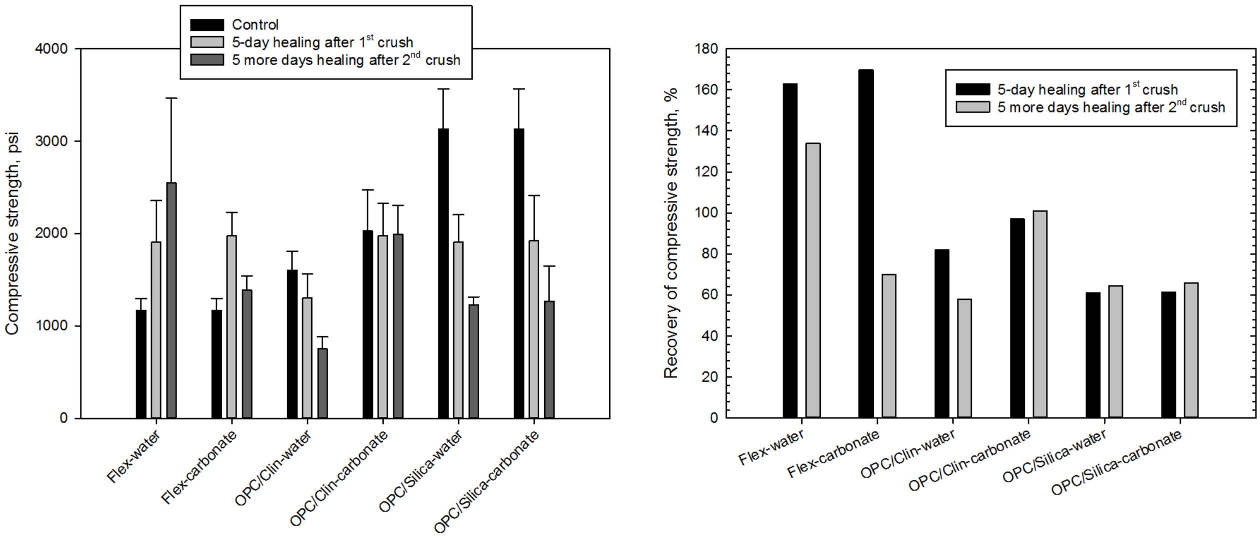

Figure 1: Compressive strength and percent its recovery in water or carbonate at 270-300°C after repeated damage.

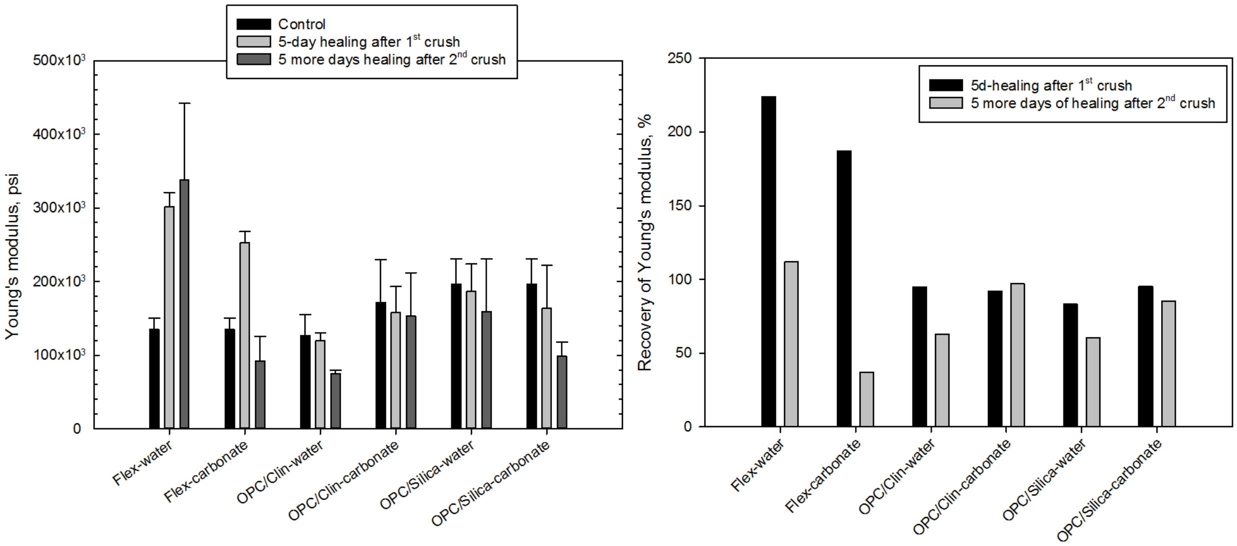

Figure 2: Young's modulus and its recovery in water or carbonate at 270°C after repeated damage.

The results clearly showed that the strength recovery and crack filling in the tested samples differed. Crack filling was unambiguously better in samples cured in carbonate than those in the water. The FlexCem sample modified with silica showed the best combination of strength recovery and fracture sealing when cured in the alkali carbonate environment.

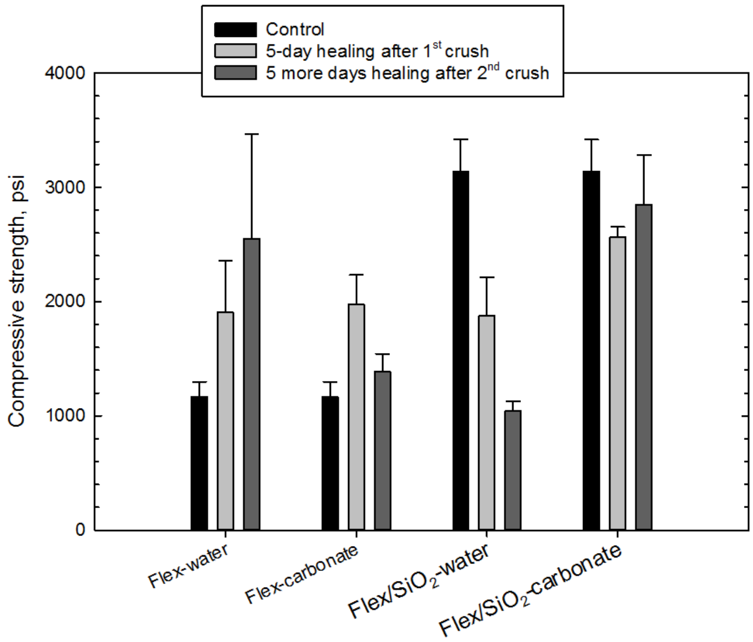

Figure 3: Comparison of compressive strength recovery for modified and non-modified FlexCem in water or carbonate at 270°C after repeated damage.

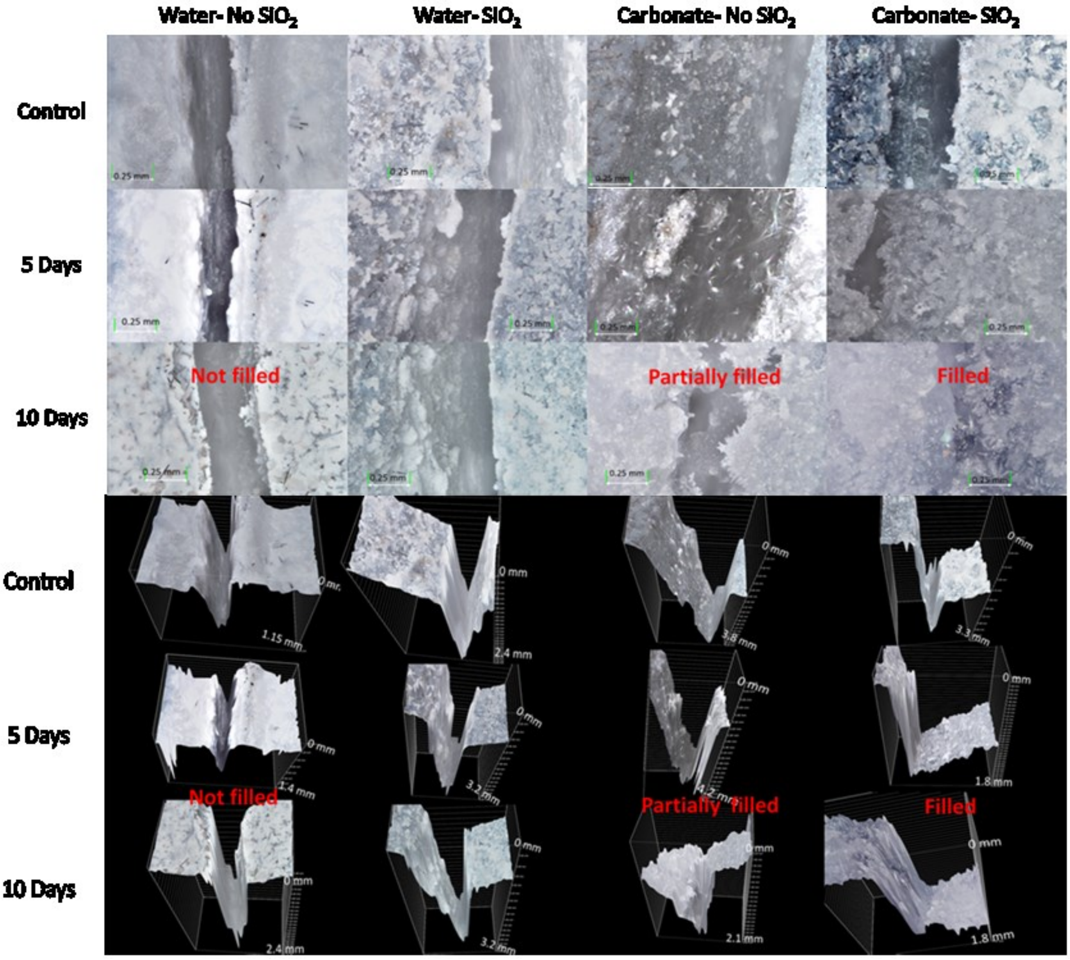

Figure 4: Crack filling of FlexCem and FlexCem/Silica in water or carbonate environment at 270°C.

2.2.2 Samples analyses – crystalline phases

Figure 5 compares patterns of cores of the 10-day cured samples after water or carbonate solution curing (top) and surfaces for carbonate-cured specimens (bottom).

Both control and 10-day cured samples showed some non-reacted clinker peaks (C_3S, ICDD: 04-014-9801 and C_2S, ICDD: 00-033-0302) and peaks of crystalline silica for silica-modified samples. The intensities of the residual clinker peaks were higher for the samples without silica and those cured in water compared against those cured in alkali carbonate (peaks intensities at ~2θ° 29.4; 32.2 and 32.6) indicating acceleration of clinker hydration by carbonate in the presence of silica. FER peaks disappeared after a day of curing in all the specimens suggesting fast alkaline decomposition of the zeolite.

After 10 days of curing the major types of crystalline reaction products included calcium-silicates and aluminum-modified calcium-silicate hydrates (xonotlite, tobermorite and tobermorite aluminium, pseudowollastonite, kilchoanite); carbonated calcium-silicate hydrates (scawtite and spurrite); magnesium (calcium, iron) silicates; magnesium and calcium carbonates; high-temperature stable zeolites such as mordenite, analcime, thomsonite Ca; calcium sulfates such as bassanite and anhydrate. Crystalline silica was dominant in the surfaces of specimens cured in alkali carbonate even for the non-modified samples.

Crystalline compositions of silica-modified and non-modified samples noticeably varied. Calcium-silicates with the Ca:Si ratio between 0.7 and 1, such as tobermorite and predominantly xonotlite, formed as the major crystalline products in both environments for samples modified with silica. Tobermorite persisted up to 10 days of curing and its calcium-to-silica content decreased as the curing time in carbonate solution increased suggesting calcium removal through carbonation. Aluminum, likely from decomposed FER was included into tobermorite detected in control samples in carbonate environment. In addition to aluminum, zeolite decomposition supplied silicon and magnesium for further reactions.

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

In the case of non-modified samples kilchoanite and dicalcium silicate were the major calcium-silicate hydrates with Ca:Si ratios of 1.5 and 2 respectively formed after a day at 270°C (control). Hydrothermal formation of dicalcium silicates and transformation to kilchoanite at temperatures above 220°C were reported earlier (Mitsuda et al., 1985). Kilchoanite persisted in water cured samples after 10 days, coexisting with xonotlite that became the major calcium silicate phase both in water and alkali carbonate.

Carbonated calcium-silicate hydrates were the main hydration products in the absence of silica in both water and especially in alkali carbonate solution. They formed in the control samples and the intensity of their peaks steadily increased at longer curing times of 5 and then 10 days. These were scawtite and spurrite. The hydrothermal formation of carbonated calcium-silicates from dicalcium silicate and silica was reported earlier (Kalousek and Nelson, 1978). Scawtite persists under high-temperature hydrothermal conditions; it was present in natural rocks exposed to carbonates forming a stable layer during carbonation of calcium silicate hydrate-bearing rocks from Northern Ireland (Milodowski *et al*. 2011). It was also reported to be commonly encountered in high-temperature wells where aqueous solutions of carbon dioxide entering pores of hydrating cement form scawtite and release silica that may partially seal fractures (Bensted, 1988).

Decomposed FER was the main source of magnesium while clinker provided calcium for calcium magnesium silicates crystalized after the first day of curing (akermanite, diopside, and enstatite). At longer curing times in the alkali carbonate solution intensities of their peaks strongly decreased even in cores of the samples, likely because of the calcium removal through carbonation. The dolomite crystallized as one of the principle phases in non-modified samples through the calcium hydroxide attack of FER but its peaks weakened strikingly already after 5 days of curing and were completely replaced by talc in the surfaces after 10 days through skarnification reactions with silica accompanied by calcium carbonate formation, which was a major crystalline phase in the surface of non-modified samples. Talc is a soft, clay-type mineral, and is unlikely to play any significant role in the strength recovery; however, it may aid sealing small crevices.

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

High temperature-stable zeolites formed mostly in the surface layer of carbonate-cured specimens after 10 days of curing. In the presence of silica very silica-rich zeolite, mordenite, was predominant (Si/Al = 7) and for the sample without silica peaks of thomsonite Ca with lower silica content were detected (Si/Al = 1). Notably, there were no zeolites among the principle core products in any of the specimens. Zeolites could be crystalizing from the silica-aluminate amorphous phase after the decomposition of FER and magnesium reactions with calcium, silica and carbonate or crystalize from solution with high dissolved sodium, aluminum and silicon contents at the solid's surfaces. In both cases sodium and carbonate ions of the solution would play a major role in zeolites crystallization explaining their presence in the surface samples.

Some iron-containing hydrates formed with the iron associated with FER and likely added to the strength recoveries. After 10 days of curing they included andradite aluminian (both water and carbonate curing environments) and magnesium iron silicate in the surface of modified samples cured in alkaline carbonate solution.

In summary, the XRD analyses showed high-temperature alkaline FER decomposition after the first day of curing, persistence of non-reacted clinker and silica phases for 10 days and faster clinker loss for silica-modified samples in alkali carbonate. Calcium from clinker and magnesium from FER combined into calcium magnesium silicates or dolomite. These products were not stable in carbonate solution transforming to calcium-free magnesium silicates and talc at longer curing times. The major identified crystalline phases contributing to the strength recovery were calcium silicates (xonotlite, tobermorite, kilchoanite, pseudowollastonite), magnesium silicate (orthoenstatite), calcium iron aluminate (andradite). The phases participating in sealing the cracks were mostly forming in carbonate environment and included crystalline silica, talc and high-temperature stable zeolites (mordenite, analcime, thomsonite Ca). Carbonated calcium silicates, scawtite and spurrite formed in non-modified samples as principle phases in carbonate and to a lesser extent in water. They increased samples' brittleness and compromised second-time recoveries in the first case and likely contributed to the strength when present in small amounts in water-cured samples. Sodium carbonate environment played an important role in conditioning the reaction/hydration products stable after 10-day curing through interactions with calcium and magnesium cations and contribution of sodium and carbonate/bicarbonate ions for formation of new phases.

For the CLIN-modified sample of class G Portland cement there was a noticeable increase in crystalline silica (strong peak at 26.6, peaks at 28.4 and 50.1), silica-rich phases, and formation of feldspar minerals (anorthite). Xonotlite was still the major crystalline phase, however, tobermorite, stabilized by Si from CLIN was clearly more prominent than in the control sample (riversideite-9A; ICDD: 00-029-0329, clinotobermorite; ICDD: 01-074-2596). The peak at 2 Theta 7.83 may belong to aluminum-substituted tobermorite. The andradite peak detected in water-cured FlexCem sample was missing in G/CLIN samples, where iron was mostly coming from the cement itself since the iron content of CLIN is relatively low.

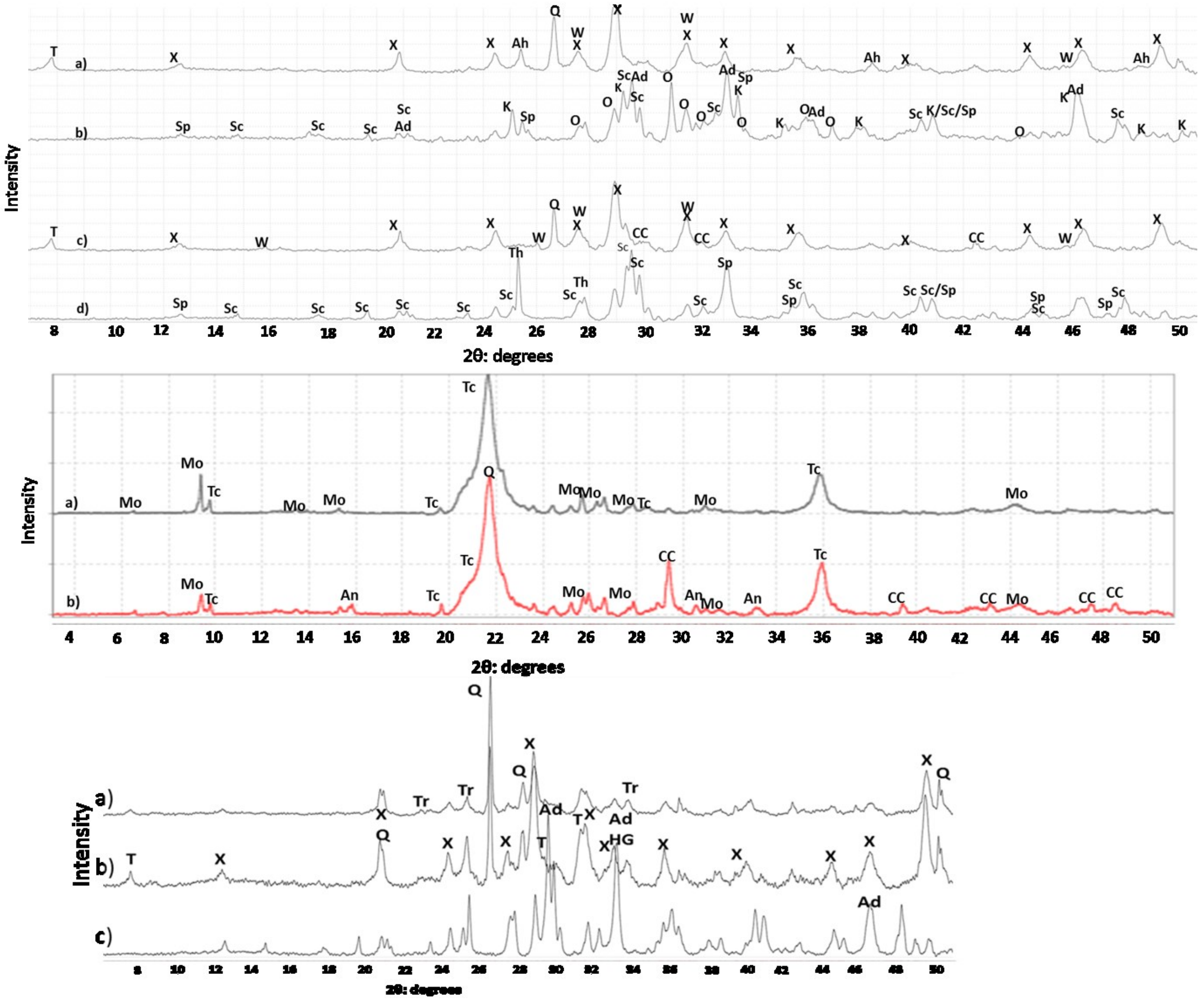

Figure 5: XRD patterns of FlexCem (top two) and G/CLIN (bottom) after curing for 10 days at 270°C. XRD patterns of clinker/FER blends after 10 days at 270° for (top): (a) silica-modified and (b) non-modified samples cured in water and for (c) silica-modified and (d) non-modified samples cured in alkali carbonate; middle: surface of silica-modified (a) and non-modified (b) samples cured in alkali carbonate; bottom: G/CLIN comparison with FlexCem (a) G/CLIN surface cured in water and (b) G/CLIN matrix cured in water and (c) FlexCem cured in water Peaks labels: T=tobermorite; X=xonotlite; O=orthoenstatite; K=kilchoanite; Sc=scawtite; Sp=spurrite; Th =thomsonite; Ad=andradite aluminian; Ah= anhydrate; Q=quartz; CC=calcium carbonates; An=analcime; Mo=mordenite; Tc=talc; Tr=truscotite; HG=hydrogrossular.

2.2.3 Samples analyses – morphologies and elemental compositions

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

Morphologies of G/CLIN samples, like FlexCem, were mostly amorphous, Si, Al-rich because of the decomposition of CLIN at elevated temperature (point 16). The short-interweaved needle crystals had a composition of truscotite (point 17) and longer needle crystals that of aluminum-substituted tobermorite (point 18) (Chaou et al., 2017).

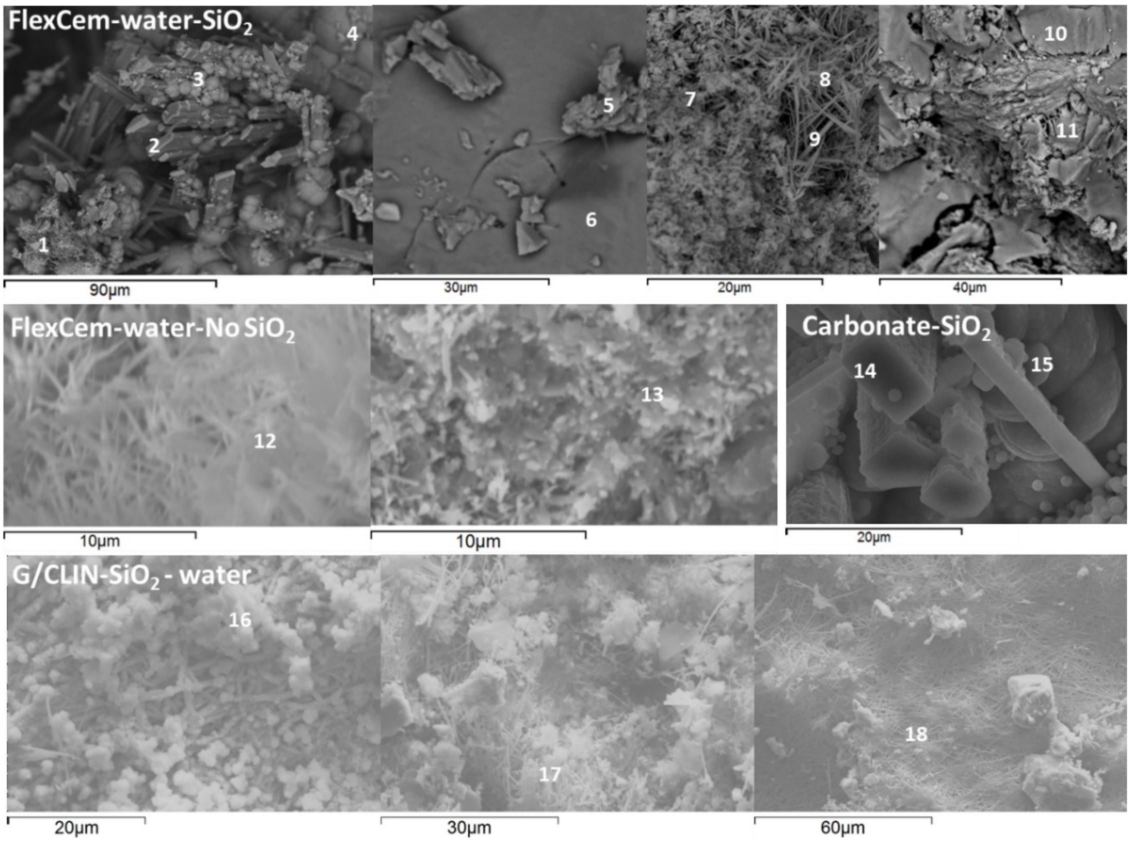

Figure 6: Scanning electron micrographs of typical cement microstructures of FlexCem and G/CLIN samples cured for 10 d at 270°C.

Table 5: Elemental composition of the points shown in Figure 6.

Point	C	Na	Mg	Al	Si	Ca	Fe	Possible phase
1	12	-	0.19	0.63	10	14	0.24	Kilchoanite
2	2.9	-	0.13	0.52	14	23	0.26	Amorphous matrix
3	5.4	0.39	0.42	4.6	14	14	0.81	Xonotlite; non-reacted ferrierite
4	-	1.6	-	1.6	31	-	-	Mordenite; SiO_2
5	-	0.72	-	0.39	33	-	-	SiO_2
6	-	0.56	-	0.32	33	-	-	SiO_2
7	-	3.9	-	3.2	28	-	-	Mordenite
8	-	0.23	-	0.3	33	-	-	Amorphous matrix
9	11	-	-	1.1	13	13	0.31	Xonotlite, Scawtite

10	8.3	0.31	0.64	1.2	15	13	0.3	Ferrierite, Xonotlite
11	8.8	0.43	-	1.0	14	13	0.23	Amorphous matrix
12	19	-	-	0.73	14	-	-	Amorphous silica-rich matrix
13	5.2	-	-	-	28	-	-	Silica
14	9.9	0.47	-	0.22	23	-	-	Silica
15	-	1.8	-	1.8	31	-	-	Mordenite, Silica
16	-	0.6 (5.7)	-	8.6	15	0.6	12	Silicon-aluminum rich amorphous phase
17	-	1.0 (2.1)	0.2	5.7	18	9.3	4.4	Truscotite
18	-	0.44 (1.3)	-	3.6	19	15	1.5	Tobermorite-aluminum

2.2.4 Self-healing properties at 100°C

Since many geothermal and oil and gas wells are at lower than 300°C temperatures it was of interest to evaluate self-healing performance of FlexCem at 100°C. Since the major factor of successful healing observed at 300°C was alkali decomposition of FER at this high temperature it was questionable whether the FER will be effective at lower temperature of 100°C.

Figure 7 shows compressive strengths before and after 5-day healing for 300°C cured and healed sample and 8 or 16 days of healing for 100°C cured and healed samples. The original compressive strength of the samples cured for a day at 100°C was noticeably, nearly 3-times, higher than for the samples cured at 300°C. This is likely the result of different nature of hydrates at these two temperatures. Lower-temperature stable amorphous and crystalline hydrates, generally, have a higher silica-to-calcium ratio than high-temperature hydrates (e.g. tobermorite vs. xonotlite) involve more water in their structure and form a denser, more compact matrix that results in higher compressive strength. High-strength samples are usually less flexible and fail forming brittle difficult to repair fractures under stresses. However, after 8 and 16 days of healing the 100°C-cured and healed samples recovered their strength. Although the strength recovery was lower than that at 300°C because of the very high initial strength of the samples it was still above 100%, specifically 120% after 8 days of healing and 122% after 16 days of healing. Based on these data it is likely that the healing was completed in a short time and additional curing did not significantly change the composition of the samples so that the strength recoveries remained similar after 8 and 16 days (Figure 8).

Previous work on high-temperature performance of OPC/SiO_2 blend demonstrated significantly lower strength recoveries (60% after the first break in water at 300°C). Several factors may contribute to the good self-recovery of the FlexCem. At a moderate temperature of 100°C cement hydration could be only partial after a day of the initial curing. So continuous cement hydration was likely a strong contributor to the good recovery rate. Another factor that differ FlexCem from the regular OPC formulations is the presence of FER, that decomposes under alkali environment of hydrating cement, contributing ions for formation of new phases. Although FER decomposition at 100°C should be slower than at 300°C it still may contribute to the formation of new phases and improve recovery

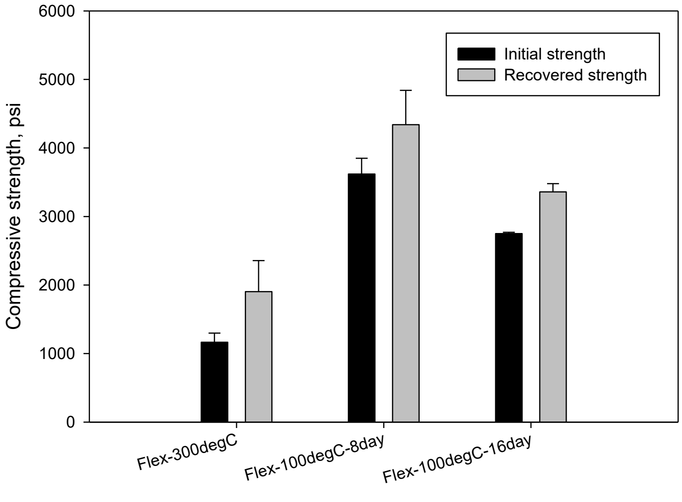

Figure 7: Comparison of compressive strength before and after healing periods of 5 days (300°C), 8 days (100°C or 16 days (100°C) for 1-day FlexCem samples cured at 300°C or 100°C respectively.

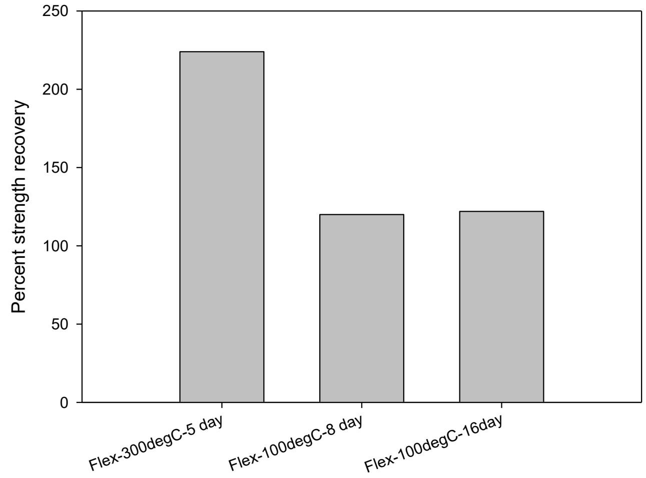

Figure 8: Strength recoveries for FlexCem samples after compressive damage and 5 days (300°C), 8 days (100°C) or 16 days (100°C) of healing under the original curing conditions.

2.2.5 Acid resistance and acid strength recoveries

Geothermal wells are often highly acidic through H_2S dissolution with formation of sulfuric acid. Cements modified with pozzolanic materials are generally more acid resistance due to the lower calcium, particularly sensitive to acid attack, and higher aluminum and silicon contents. The data of OPC/SiO_2 and FlexCem exposure to sulfuric acid of pH 0.2 for 28 days at 90°C summarized in Table 6 clearly support this demonstrating a superior performance of FlexCem. The appearance of the samples after the first 14 days of acid exposure and after a crush test and 14 more days of acid exposure is given in Figure 9.

After the first 14 days of exposure to a strong acid FlexCem lost only 9% of its strength compared against 37% loss for the OPC/SiO_2 blend and 7% of Young's modulus vs. 31% for OPC/SiO_2. There was also significantly smaller increase in samples diameter and weight indicative of scale deposition from acid reactions with cement (2.4% diameter and 12% weight increase for FlexCem vs. 10 and 17% increases for OPC/SiO_2 respectively). Acidification of cements accelerated after the compressive damage to the point that OPC/SiO_2 samples could not be tested anymore (see Figure 9b). FlexCem survived additional 14 days of strong-acid exposure with a residual compressive strength of 960 psi. In summary, clinker modification with FER improved its resistance to strong acid at elevated temperature.

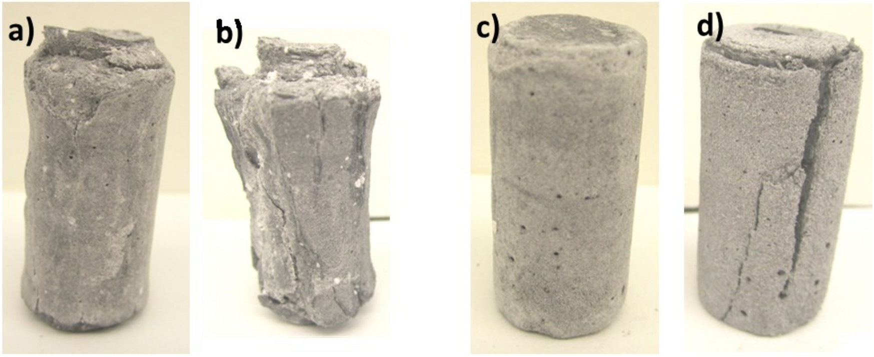

Figure 9: Sulfuric acid-treated samples (pH 0.2, 90°C): a) OPC/SiO_2 after 14 days in the acid; b) OPC/SiO_2 after 14 days in the acid, break and 14 more days in the acid; c) FlexCem after 14 days in the acid; d) FlexCem after 14 days in the acid, break and 14 more days in the acid.

Table 6: Changes in mechanical properties, weight, and diameter after exposure for 14 and 28 days in 90°C-pH 0.2-H_2SO_4 and after compressive strength test and 14 more days in the same acid for OPC/SiO_2 and FlexCem

Formulation Conditions	Compressive strength, psi	Youngs' modulus, psi	Changes in diameter, %	Changes in weight, %
OPC/SiO_2				

Control	3140±640	220700±83300	N/A	N/A
After 14 days in acid	2130±560 (-37%)	152000±39000 (-31%)	+10	+17
After break and 14 more days in acid	N/A	N/A	N/A	+7.2
FlexCem				
Control	2670±60	232000±31450	N/A	N/A
After 14 days in acid	2440±250 (-9%)	216000±4900 (-7%)	+2.4	+12
After break and 14 more days in acid	960±160 (-60%)	95800±6100 (-56%)	N/A	+1.4

3. Conclusions

Research to develop an improved cement for geothermal wells evolved into a lightweight, variable density cement that is useful for oil and gas completions particularly where fragile formations or hydrostatic conditions require a low density cement. Formulation of the new cement does not exclude geothermal application but rather enhances such use by providing self-healing to ensure cement competence and acid resistance to geothermal environments.

The work completed by the Brookhaven study demonstrated that tested zeolites (ferrierite and clinoptilolite) decompose in blends with Portland cement or clinker at elevated temperatures contributing reactants, such as silicon, aluminum, iron, magnesium (FER) for formation of new phases at high temperatures (270-300°C). Under the tests conditions the decomposition-reaction of zeolites starts later than cement hydration resulting in lower initial compressive strength than in non-modified cement; however, the strength builds up at longer curing. Additionally, decomposition of tested zeolites, resulting in increased concentrations of silicon and aluminum in interstitial water, stabilized tobermorite at temperatures where it is usually converted to xonotlite with accompanying strength loss. Tobermorite stabilization was favorable for samples mechanical properties and acid resistance. In addition to silicon and aluminum ferrierite contributed iron and magnesium that formed such cement strengthening phases as andradite, magnesium silicates (in the matrix) and talc (at the surface).

FlexCem demonstrated self-healing ability not only at high 300°C hydrothermal temperature but also at moderate, 100°C temperature, recovering 120% of its strength after a short 8-day curing. This strength recovery was likely due to the continuous hydration of the cement at lower temperatures. In self-healing evaluations FlexCem showed an ability of strength recovery over a wide range of temperatures due to the combined effect of continuous cement hydration at lower temperatures and zeolite alkaline decomposition and reactions at higher temperatures.

FlexCem clearly outperformed OPC blend with silica in acid-resistance tests surviving 28 days at pH 0.2 and 90°C. This excellent performance of FlexCem may be explained by the decreased calcium content and pozzolanic reactions of ferrierite.

4. Acknowledgements

This publication was based on the work supported by the Geothermal Technologies Office in the US Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE), under the auspieces of the US DOE, Washington, DC, under contract No. DE-AC02-98CH 10886. Research was carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the US Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704.

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