**ABSTRACT**

We studied the effectiveness of sodium silicate-activated Class F fly ash in improving the thermal shock resistance of Secar #80 refractory cement. We performed a multiple heating-water cooling quenching cycle test to evaluate cement thermal shock resistance. In one cycle, the 200°C-autoclaved cement was heated at 500°C for 24 hours, and then the heated cement was rapidly immersed in water at 25°C. This cycle was repeated five times. The phase composition of the autoclaved #80/Class F fly ash blend cements comprised four crystalline hydration products, boehmite, katoite, hydrogrossular, and hydroxysodalite, responsible for strengthening cement. After a 5-cycle heat-water quenching test, three crystalline phase transformations in this autoclaved cement were observed: boehmite → γ-Al₂O₃, katoite → calcite, and hydroxysodalite → carbonated sodalite. Among these phase transformations, the hydroxysodalite → carbonated sodalite not only played a pivotal role in densifying cementitious structure and sustaining the original compressive strength developed after autoclaving, but also offered an improved resistance of #80 cement to thermal shock. In contrast, the autoclaved Class G well cement with and without Class F fly ash and silica flour failed this cycle test, generating multiple cracks in the cement. The major reason for such impairment was the hydration of lime derived from the dehydroxylation of portlandite formed in autoclaved cement, causing the cement’s volume expansion.

**1. Introduction**

The major thrust in assembling and constructing Enhanced Geothermal Systems (EGSs) is the creation of a hydrothermal reservoir in hot dry rock stratum ≥200°C, located at ~ 3-10 km below the ground surface. In this operation, water at a low temperature is pumped down an injection well to stimulate the hot rock stratum. This hydraulic stimulation in terms of hydro-shearing initiates the opening of existing fractures. Also, multi-injection wells are required to create a desirable reservoir of a permeable fracture flow network. After forming the reservoir, a production well is installed within the fracture’s network.

During the water stimulation cycles, considerable attention is paid to a significant temperature differential between the bottom of the well and the stimulation water from the injection well. Because of this differential the cement sheath surrounding the down-hole casing may encounter a sudden drop in its temperature of ≥180°C. Such a large thermal gradient due to the cooling effect of the injection water can give an undesirable thermal stress to the cement sheath, causing its potential failure which may lead to a catastrophic loss of the well. To mitigate such temperature differential-caused stresses, the cement placed in EGS is required to possess the resistance to thermal cycle fatigue and thermal shock.

As is well documented, (1-3) when the Ordinal Portland Cement (OPC) is exposed to heating environment at temperatures ≥300°C, the dehydroxylation of portlandite [Ca(OH)₂] formed in hydrated cements lead to its conversion into lime (CaO). One inevitable concern about the formation of lime is its hydration due to the penetration of water through the set cement. Such in-situ portlandite → lime → hydration phase transformation under the combination of dry and wet conditions is detrimental to the cement’s integrity; namely this hydration generates the expansion-caused cracks in the cement body. This undesirable thermal property of OPC containing a certain amount of portlandite can be improved by incorporating quartz (silica flour) into OPC.(4-8) The quartz reacts with portlandite to form additional calcium silicate hydrates, reducing the amount of portlandite. However, it is very difficult to eliminate all portlandite from OPC-based cement systems.

Thus, to develop thermally and hydrothermally stable cement, we focused on formulating the cementitious materials possessing two specific characteristics: One characteristic is absence of portlandite formation in hydraulic cement exposed to hydrothermal environments; the other is good refractory properties in thermal environments. There are two candidates for designing an ideal cement encompassing these properties: One candidate is a geopolymer, which can be prepared by interactions between Na- or K-based
alkaline activators and aluminum silicate-based reactants, such as metakaoline and Class F fly ash, and this assembled structure comprises both the amorphous phase and semi-crystalline zeolitic phases related to hydroxyl sodalite, Na-P1 type, and chabazite. (9) The ceramic-like aluminosilicate network structure in geopolymer is responsible for exerting an excellent thermal stability. (10-12) However, our study on the compressive strength of the sodium silicate-activated granulated blast-furnace slag/Class F fly ash blend cement systems after autoclaving at 200°C reveals that the contribution of geopolymer derived from Class F fly ash to developing the compressive strength of this blended cement is minor, (13) although the conversion rate of Class F fly ash into geopolymer depends on the content of sodium silicate. The major contributor to strength development is the hydrothermal reaction products of slag, suggesting that if the Class F fly ash is employed as a resource in the geopolymer synthesis, the incorporation of additional cementitious material into the geopolymer binder may be required to ensure that the cured cement adequately develops a desirable strength under hydrothermal conditions. For the additional cementitious binder, our particular interest is the use of calcium aluminum refractory cement consisting of three major chemical constituents, calcium monoaluminate, calcium dialuminate, and α-aluminum oxide because of its great thermal resistance. (14-16)

Based on this information we evaluated the thermal shock resistance of the blended cements consisting of the refractory cement and sodium silicate-activated Class F fly ash, prepared in the hydrothermal environment. For comparison purposes, Class G well cements, unmodified and modified with quartz and Class F fly ash, also were evaluated as the control. The evaluated factors included the phase identification and transformation, dehydration and dehydroxylation. The data on phase transformation are correlated directly with the changes in density and compressive strength after thermal shock resistance testing. To conduct an accelerated thermal shock resistance test and to impose considerable thermal stress, we adapted multiple heat-water quenching cycle fatigue test under the extremely large temperature differential between the heating at 500°C and water quenching at 25°C.

2. Experimental Procedure

2.1 Materials

Class F fly ash was obtained from Boral Material Technologies, Inc., and its chemical composition detected by micro energy-dispersive X-ray spectrometer (µEDX) was as follows; 49.3% SiO2, 36.1% Al2O3, 5.9% Fe2O3, 2.3% K2O, 2.1% MgO, 1.9% CaO, 1.1% TiO2, and 1.5% Na2O. A sodium silicate granular powder under the trade name “Metos Bead 2048,” supplied by the PQ Corporation was used as the alkali activator of Class F fly ash. Its chemical composition was 50.5 mol. wt% Na2O and 46.6 mol. wt% SiO2. Secar #80, supplied by Kerneos Inc. was used as calcium aluminoferrite refractory cement. The X-ray powder diffraction (XRD) data showed that the crystalline compounds of Class F fly ash consisted mainly of three major phases, quartz (SiO2), mullite (3Al2O3·2SiO2), and hematite (Fe2O3), while #80 included three crystalline phases, corundum (α-Al2O3), calcium monoaluminate (CaO·Al2O3, CA), and calcium dialuminate (CaO·2Al2O3). The formulas of the dry #80 and Class F fly ash blend cements had #80/Class F fly ash fly ash ratios of 100/0, 80/20, 60/40, and 40/60 percent by weight. For Class F fly ash-blended #80 cements, sodium silicate powder of 6.2% by the total weight of the blend was added to prepare the one dry mix cement component. No sodium silicate was incorporated into bulk #80 cement denoted as 100/0 #80/Class F fly ash ratio. The non-blended and blended cement slurries were prepared by adding an appropriate amount of water to the dry mix cement component. The proportion of water to dry cement (water/cement ratio) ranged from 0.42 to 0.47. After the cement slurries were thoroughly hand mixed in a bowl for 1 min, slurry samples were cast in cylindrical molds (20 mm diam. and 40 mm long), and allowed to harden for 3 days at room temperature. The hardened cements then were exposed in an autoclave at 200°C for 24 hours. We adapted three formulas for Class G well cements as the control. One formula was bulk Class G cement without any additives; the second formula was composed of 65 wt% Class G cement and 35 wt% quartz; and the third consisted of 65 wt% Class G cement and 35 wt% Class F fly ash. The slurries of these cements were prepared based upon the water/cement ratios ranging from 0.41 to 0.43. These slurries then were hardened in the same fashion as that described above.

To obtain information on the thermal shock resistance, a multiple heating-water cooling quenching cycle test was conducted. Namely, in the one cycle, the 200°C-autoclaved cements were placed in an air oven at 500°C for 24 hours, and then heated cements were rapidly immersed in water at 25°C. This 500°C heating → water quenching cycle was repeated five times.

2.2 Measurements

The changes in density and compressive strength of the autoclaved cements after one, three, and five heat-water quenching cycles were measured by helium pycnometry and Forney F-25-Ex Compressive Testing. X-ray powder diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) were used to identify the crystalline phase composition formed in the autoclaved cements and to define the phase transformations after cycle testing. To support information on the phase transformation due to the annealing at 500°C, the dehydration and dehydroxylation behaviors of hydration reaction products formed in the autoclaved cements were investigated using Thermo-Gravimetric Analysis (TGA) at the heating rate of 20°C/min in a N2 flow.

3. Results and Discussion

3.1 Thermal Shock Resistance Test

The #80 cement, its blends with Fly Ash Class F as well as Class G well cement with and without quartz or Class F fly ash as the control were tested.

3.1.1 Density and Compressive Strength

We compared changes in density of the 200°C-autoclaved cement specimens made with bulk Class G cement, 65/35 Class G/Class F fly ash and /quartz ratio, bulk #80, and 80/20, 60/40, and 40/60 #80/Class F fly ash ratios, as a function of the number of 500°C heat-25°C water quenching cycles. The density of bulk Class G well cement specimens sharply dropped to 1.88 g/cm3 from 2.54 g/cm3 after only one cycle. Such a drastic reduction of density engendered an undesirable alteration of cement including volumetric expansion that resulted in numerous cracks and
impaired the integrity of the cement. The resistance of Class G cement was markedly improved by incorporating Class F fly ash or quartz into it. In fact, when 35 wt% Class G cement was replaced with Class F fly ash, corresponding to 65/35 Class G/Class F fly ash ratio, the sample’s original density decreased only by 8 % to 2.18 g/cm³ after one cycle, and by 12.2 % after 5 more cycles. A similar tendency for density to fall with the number of cycles was observed for the 35 wt% quartz-blended Class G cement. The density of 2.81 g/cm³ of non-cycled cement reduced by 18.9 % to 1.89 g/cm³ after 5 cycles. We observed the generation of cracks after 3 cycles for the Class G cement modified with either fly ash F or quartz, and concluded that the ability of Class G cement to resist the thermal shock stress was poor.

In contrast, the bulk #80 cement denoted as 100/0 ratio demonstrated that its original density slightly increased after 3 cycles and somewhat declined beyond that. A similar trend was observed with the 80/20 #80/Class F fly ash ratio. A further replacement of the total #80 cement with Class F fly ash to 40 and 60 wt% resulted in density increase after one cycle, and leveling off further on. The thermal shock resistance of #80-based cements appears to be greater than that of the Class G-based cements, and it may be further improved by the addition of Class F fly ash.

Figure 1 plots the changes in compressive strength as a function of the number of heat-water quenching cycles for the same cement specimens as those used in the density testing. In the Class G cement series, the 200°C-autoclaved bulk Class G cement had a compressive strength of 3175 psi. Its strength fell by 31 % to about 2200 psi after one cycle. No further testing was performed for this specimen because of its severe disintegration. The compressive strength of autoclaved Class G cement with 35 wt.% cement replaced with quartz or Class F fly ash, improved 2.0- or 1.5-fold respectively. However, the annealing at 500°C, followed by water quenching, was detrimental to these Class G cement blends, causing a considerable reduction in strength after 3 cycles down to 3800 psi from its original strength of 6190 psi for quartz and to 1980 psi from 4610 psi for the blend with Class F fly ash. After 5 cycles, we observed severe damage of these specimens, making it difficult for us to conduct their strength testing.

In the #80-based cement series, among the autoclaved specimens, the bulk #80 cement displayed the highest compressive strength of 6475 psi. The strength declined as the amount of Class F fly ash in the blend increased. In fact, the 40/60 #80/Class F fly ash ratio cement had a compressive strength of 2700 psi, which is 2.4-fold lower than that of 100/0 ratio. The results from the cycle test revealed that the strength of the cements made with 100/0 and 80/20 ratios decreased with the number of cycles. After 5 cycles, the 4325 psi and 3260 psi compressive strengths for 100/0 and 80/20 ratios, decreased by 33 % and 37 % respectively. For comparison, the compressive strength of 60/40 and 40/60 ratio cements did not change significantly after 5 cycles. In particular, the compressive strength of the 60/40 ratio blend was somewhat higher after 5 cycles than after 3 cycles. As a result, the sodium silicate-activated Class F fly ash blended #80 cements appeared to have potential as alternative thermal shock-resistance cements.

3.1.2 XRD and FT-IR Analyses

To better understand why sodium silicate-activated 60/40 and 40/60 #80/Class F fly ash ratio cements sustained their compressive strength without any generation of cracks during the 5 cycles of water quenching tests, we analyzed these cements by XRD and FT-IR before and after 5 cycles.

The XRD patterns of unmodified Class G cement after autoclaving at 200°C included three crystalline hydrothermal reaction products, portlandite [Ca(OH)₂] as the major phase, and α-dicalcium silicate hydrate (α-2CaO·SiO₂·H₂O, α-C₂S·H₂O) as well as calcium silicate hydrate (l) (CaO·SiO₂·H₂O, CSH) as minor phases. For Class F fly ash-modified Class G cement, the X-ray pattern was quite different; in particular, two new major hydrothermal reaction products, 1.1 nm tobermorite, [Ca₆(OH)₂Si₄O₁₀·4H₂O] and hydrogrossular [Ca₃Al₂Si₂O₇·(OH)₄], were formed, while the portlandite became the minor crystalline phase. Also, the CSH (l) phase was present as one of the major crystalline compounds. Since Class F fly ash consisted of three crystalline phases, quartz (SiO₂), mullite (3Al₂O₃·2SiO₂), and hematite (Fe₂O₃), it is possible to rationalize that the hydrogrossular was formed by hydrothermal reactions between Class G cement and mullite in Class F fly ash. Concurrently, the reactions between Class G cement and quartz in Class F fly ash led to the creation of 1.1 nm tobermorite and well-formed CSH (l) phases. A similar X-ray pattern, with the exception of the absence of hydrogrossular, was observed for the quartz-modified Class G cement; namely, tobermorite and CSH (l) were the major hydrothermal reaction products.

These crystalline reaction products were responsible for strengthening the 200°C-autoclaved cements before cycle-fatigue testing.

As described earlier in this paper, when these autoclaved cements were annealed at 500°C, followed by water-quenching, all Class G cement-based specimens generated cracks and fissures in the cement bodies, although the extent of the cement failure depended on the silica- and silicate-based additives. The XRD result from unmodified Class G cement after 1 cycle showed the presence of calcite (CaCO₃) and lime (CaO), while the intensity of all portlandite-related d-spacing lines strikingly declined, suggesting that the dehydroxylation and carbonation of portlandite...
led to its conversion into the lime and calcite. This result agreed with the previously published results. (1-3) The formation of lime was detrimental to the integrity of cement because of its hydration and recrystallization to reform portlandite in the water-quenching period, causing an undesirable volumetric expansion of cement. Thus, in the heat-quenching cycles, the portlandite was first converted into lime during annealing at 500°C, and then the hydration of lime after being immersed in water led to the formation of crystalline portlandite. Repeated in-situ reversible phase transformation, Ca(OH)₂ ↔ CaO, created the volumetric expansion and -shrinkage of cement, and then promoted the disintegration of cement by generating cracks and fissures.

In contrast, no calcite or lime phases were found for both Class G/Class F ash-modified Class G and /quartz blend cements after 3 cycles. The XRD pattern of Class G/Class F fly ash cement show a marked reduction of tobermorite- and CSH (l)-related line intensities, elimination of hydrogrossular-related d-spacing, and presence of some portlandite. Although a relative amount of tobermorite and CSH (l) phases was reduced by annealing-caused dehydration, we still believed that the crack’s generation of Class F fly ash-modified Class G cement was due preliminary to a reversible portlandite↔lime phase transformation during heat-water quenching testing. A similar X-ray pattern also was observed from Class G/Class F fly ash-modified Class G cement after 200°C autoclaving. The autoclaved bulk #80 cement marked as 100/0 ratio was brought about by portlandite presence in cement.

Figure 2A compares XRD patterns for 100/0 (a), 80/20 (b), 60/40 (c), and 40/60 (d) #80/Class F fly ash cements after 200°C autoclaving. The autoclaved bulk #80 cement marked as 100/0 ratio was composed of three crystalline phases, boehmite (γ-AlOOH) and Si-free katoite [Ca₃Al₂(OH)₁₂] belonging to the hydrogarnet family as the major hydrothermal reaction products coexisting with corundum (α-Al₂O₃) as the non-reacted original ingredient present in #80 cement. Replacing 20% of the #80 cement with Class F fly ash denoted as 80/20 #80/Class F fly ash led to an additional reaction product in the autoclaved sample, hydroxy-sodalite [Na₃Al₅Si₃O₁₄(OH)₆] in the family of zeolite, known as hydroceramic (17,18), while the detected quartz came from the Class F fly ash. The hydrolysis of sodium silicate activator in water generated two major reactants, sodium hydroxide and silicic acid. The hydrothermal reactions between sodium hydroxide and mullite (3Al₂O₃.2SiO₂) in Class F fly ash led to the formation of hydroxy-sodalite. Increasing Class F fly ash content up to 40 wt%, resulted in the formation of another new product, an intermediate hydrogrossular [Ca₃Al₂Si₂O₈(OH)₈]. Also, this X-ray pattern revealed that the intensity of d-spacing lines related to boehmite and katoite phases declined considerably with the increase of Class F fly ash content. With 40/60 #80/Class F fly ash ratio (d), two reaction products, hydroxy-sodalite and intermediate hydrogrossular, became the major phases; meanwhile it was very difficult to detect the boehmite- and katoite-associated d-spacing lines.

To support information on the phase composition of the #80/Class F blended and non-blended cements described above, FT-IR analyses were carried out for the same cement as those used in the XRD study, over the range of 4000-650 cm⁻¹ (Figure 3A). The FT-IR spectrum of the autoclaved bulk #80 cement (a) encompassed the seven absorption bands at 3659, 3302, 3087, 1498, 1411, 1068, and 729 cm⁻¹. All bands, except for 3659, 1498 and 1411 cm⁻¹, were ascribed to boehmite- and katoite-related groups; (19, 20) namely, the bands at 3302 and 3087 cm⁻¹ are due to the O-H stretching vibrations, at 1068 cm⁻¹ correspond to Al-O-H bending mode, and at 729 cm⁻¹ are associated with the Al-O stretching mode. The band at 3659 cm⁻¹ is a OH valence-stretching vibration of non-bonded hydroxyl group in water, and two other bands at 1498 and 1422 cm⁻¹ are attributable to the stretching vibration of CO₃ in carbonated compounds. With 80/20 #80/Class F fly ash ratio (b), two new additional absorption bands at 1161 and 967 cm⁻¹ appeared in the spectrum of bulk #80 cement. The possible contributor to the former new band is the Si-O asymmetric stretching mode in Si-O-Si or -Al linkages, (21) and the latter new band is from oxygen non-bonding Si-O-Si’ stretching mode in Na⁺-O-Si- linkage in hydroxy-sodalite. (22-24) If this interpretation is correct, increasing the amount of Class F fly ash to 40 (c) and 60 wt% (d) was responsible for intensifying the absorbance at 967 cm⁻¹ band, showing that these cements included more hydroxy-sodalite. Meanwhile, the absorbance of boehmite- and katoite-related bands was considerably reduced, reflecting a minimal amount of these phases.

Relating this information on mineral phases to the compressive strength of 200°C- autoclaved cements discussed earlier, the two phases, katoite and boehmite, formed in hydrated #80 cement, were responsible for developing the highest compressive strength in #80/Class F fly ash blend cement series. Since incorporating Class F fly ash into the #80 cement resulted in the decreased compressive strength, the other phases, such as hydroxy-sodalite and intermediate hydrogrossular, derived from Class F fly ash, did not contribute significantly to improving any compressive strength in the hydrothermal environment.
Figure 2B depicts the X-ray patterns of 100/0 (a), 80/20 (b), 60/40 (c), and 40/60 (d) #80/Class F fly ash cements after 5 cycles. For 100/0 ratio, two new crystalline compounds emerged, \( \gamma\text{-Al}_2\text{O}_3 \) and calcite (\( \text{CaCO}_3 \)), while all other hydration products identified in autoclaved cements, such as boehmite and katoite, disappeared. \( \gamma\text{-Al}_2\text{O}_3 \) phase was formed by the dehydration of boehmite, (25-26) and the calcite might have derived through a dehydration-carbonation process of katoite at 500°C, while a strong line intensity of corundum-related \( d \)-spacing still remained unchanged. Relating this information to the changes in compressive strength, it can be seen that the two different phase transformations, boehmite \( \rightarrow \gamma\text{-Al}_2\text{O}_3 \) and katoite \( \rightarrow \) calcite, engendered the reduction of compressive strength of the cycled cements. In other words, the performance of \( \gamma\text{-Al}_2\text{O}_3 \) and calcite phases as cementitious binder in sustaining compressive strength was relatively poor. With 80/20 #80/Class F fly ash cement, the XRD result showed sodium carbonate sodalite (\( \text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3 \)) phase formed through the carbonation of sodalite coexisting with calcite and \( \gamma\text{-Al}_2\text{O}_3 \). The carbonation of hydroxysodalite expressed as \( \text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{OH} \) \( \rightarrow \text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3 \) phase transformation led to intercalating \( \text{CO}_3 \) into sodalite structure by replacing the OH group in sodalite with \( \text{CO}_3 \). Thus, the hydroxysodalite sequestered \( \text{CO}_3 \). The X-ray pattern of 5-cycled 60/40 ratio cement had three major characteristics. Firstly, the intermediate hydrogrossular phase formed in this cement after the autoclaving at 200°C was eliminated; secondly, the intensities of the carbonated sodalite-related lines increased, reflecting the incorporation of more carbonated sodalite into the cement bodies; and thirdly the line intensities for the calcite and \( \gamma\text{-Al}_2\text{O}_3 \) phases decreased. Relating the second and third observations to the compressive strength results, the carbonated sodalite displayed a far greater performance as a cementitious binder in developing compressive strength, than calcite or \( \gamma\text{-Al}_2\text{O}_3 \) formations. In fact, higher incorporation of carbonated sodalite into the cement bodies in conjunction with a minimized amount of calcite and \( \gamma\text{-Al}_2\text{O}_3 \) was responsible for maintaining the value of the compressive strength developed during autoclaving the cement. The XRD features of 40/60 ratio cement closely resembled those of 60/40 ratio.

Figure 3B compares the FT-IR spectra for the 5-cycled cements earlier characterized in the XRD study. The spectrum (a) of 5-cycled bulk #80 cement revealed two predictable features. One was the elimination of all boehmite- and katoite-related major bands at 3302, 3087, 1068, and 729 cm\(^{-1}\); the other was the presence of strong bands at 1498 and 1415 cm\(^{-1}\) related to \( \text{CO}_3 \) in the calcite, while the band at 3660 cm\(^{-1}\) belonged to free water. The spectrum (b) of cycled 80/20 ratio encompassed four bands at 1498, 1415, 1173, and 945 cm\(^{-1}\). The first two bands corresponded to \( \text{CO}_3 \) in the carbonated sodalite and calcite. The 1173 and 945 cm\(^{-1}\) bands belong to carbonated sodalite; the former band can be attributed to the Si-O asymmetric stretching mode in Si-O-Si or -Al linkages, and the latter was the Si-O stretching in Na\(^+\) – O-Si linkage.

In comparison with a poor performance of calcite and \( \gamma\text{-Al}_2\text{O}_3 \) phases formed in cycled #80 the carbonated sodalite phase derived from the carbonation of Class F fly ash-derived hydroxysodalite phase played a key role in retaining material’s compressive strength in heat-water quenching tests in the presence of \( \text{CO}_2 \). The carbonated sodalite phase conferred an excellent thermal shock resistance on the #80/Class F fly ash blend cements.

### 3.1.3 TGA Analysis

We studied dehydration of the hydration products’ interlayer and their dehydroxylation (elimination of hydroxyl groups) in the 200°C-autoclaved Class G well cement- and #80/Class F fly ash blend-based cements by running TGA for the analysis of these cements in the temperature range between 25°C and 599°C. For bulk Class G well cement, the TGA curve showed three stages of thermal decomposition; the first stage began at the onset temperature near 75°C and ended around 150°C, the second occurred between ~150°C and ~325°C, and the third took place from ~325°C to ~475°C. The first stage, corresponding to ~1.47 %, was due to the elimination of free pore water from cement, and the second stage might have been caused by dehydration of calcium silicate hydrate (I). The third stage representing a large weight loss of ~6.44 % mostly involved the dehydroxylation of portlandite and possibly the dehydration of \( \alpha\)-dicalcium silicate hydrate, which converts into non-hydrus \( \beta\)-dicalcium silicate at 800°C. (28) By comparison the Class F fly ash- Class G cement did not express any pronounced weight loss in this temperature range, although the loss in weight progressively took place. As described earlier in the TGA study, this cement included four major hydration products, 1.1 nm tobermorite, calcium silicate hydrate (l), portlandite, and hydrogrossular. According to literature, (29-31) the dehydration of tobermorite and dehydroxylation of hydrogrossular takes place at temperatures between 50° and 700°C and between 260° and 350°C, respectively. The hydrogrossular disappeared after 3 cycles likely because of the phase transformation of hydrogrossular into unknown chemical compounds by its dehydroxylation. This TGA data also verified that the amount of portlandite, which underwent dehydroxylation in the temperature range of ~325°C to ~475°C, was little. Correspond-
ingly, the total weight loss at 599°C was 10.6 %, which was ~20 % lower than that of bulk Class G cement at the same temperature. The similar curve feature and changes in weight loss can be seen from the quartz-Class G well cement, implying that two crystalline phases, 1.1 nm tobermorite and calcium silicate hydrate (I), seem to have a good thermal stability at temperatures up to 599°C as well as may withstand thermal shock fatigue. However, although the amount of portlandite formed in cement body was little, its transformation into lime, followed by lime → portlandite recrystallization, was a major reason why Class G well cement generated cracks in an extended heat-quenching tests.

We also obtained TGA curves of 100/0, 80/20, 60/40, and 40/60 #80/Class F fly ash ratio cements after autoclaving at 200°C. For 100/0 ratio cement, there were two decomposition stages. In the first stage, onset and end temperatures were ~190°C and ~340°C, reflecting ~8.46 wt% loss; second stage occurred between ~400°C and ~570°C, relating to ~5.62 wt% loss. Since two major hydrothermal reaction products, boehmite and katoite, were formed in this cement, there were two different dehydroxylation processes. The first stage belongs to katoite, (32) which yielded calcite as its carbonation by-product, and second one was due to boehmite, (33-34) which converted into γ-AlO(OH) as its thermal decomposition product, leading to the total loss weight of 16.1 % at 599°C. This loss was significantly reduced by adding Class F fly ash to #80 because of a lesser formation of katoite and boehmite phases. With 80/20 ratio, the hydrosodalite as additional hydration reaction product formed in the #80-based cement. Since the dehydroxylation of hydrosodalite took place at temperatures up to ~350°C, (35) the weight loss of this cement between ~190°C and ~350°C involved the dehydroxalation of both the katoite and hydrosodalite. More importantly, the hydrosodalite was transformed into carbonated sodalite during the quenching test, emphasizing that such hydrosodalite → carbonated sodalite phase transition might have minimized the total weight loss of cement. Since the 60/40 and 40/60 ratio cements made by adding more Class F fly ash enable them to assemble the hydrosodalite-rich cementitious structure, their weight loss at 599°C depended on the Class F fly ash content. Namely, the lowest weight loss of 7.1 % was obtained from the 40/60 ratio cement containing the highest content of Class F fly ash in this test series.

From overall information described above, carbonated sodalite was identified as the most effective phase in improving thermal shock resistance of cements.

4. Conclusion

The dry mix cement consisting of three starting materials, Secar #80 refractory cement, Class F fly ash, and sodium silicate, was formulated to evaluate its potential as thermal shock resistant cement for use in EGS injection wells.

For comparison with #80/Class F fly ash blend cement, we employed the Class G well cement unmodified and modified with Class F fly ash and quartz flour. After autoclaving them at 200°C, the unmodified Class G well cement formed three hydrothermal reaction products, the portlandite as the major crystal phase, and α-dicalcium silicate and calcium silicate hydrate (I) as the minor crystal phases. Incorporating the Class F fly ash and quartz into Class G cement significantly reduced the formation of portlandite. With Class F fly ash, the hydration-related crystalline phase composition comprised the 1.1 nm tobermorite, calcium silicate hydrate (I), hydrogrossular, and portlandite. The similar phase composition, except for no hydrogrossular, was observed from quartz-modified Class G cement. To evaluate the resistance to thermal shock for these autoclaved Class G cements, we adapted an extremely large temperature differential between 500°C annealing and 25°C water-quenching to accelerate any thermal shock failure of the cements. This annealing-water cooling quenching cycle was repeated five times. The unmodified Class G cement failed after only one cycle, impairing the cement’s integrity. The major reason for failure was the hydration of lime formed by the dehydroxylation of portlandite at 500°C, generating the volume expansion-caused cracks in the cement. Although the thermal shock resistance of Class G well cement was improved by adding Class F fly ash and quartz, the presence of portlandite still was detrimental to the integrity of Class G cement; namely, portlandite → lime → reformed portlandite as the phase transformation during annealing-water quenching period. Meanwhile, 1.1 nm tobermorite and calcium silicate hydrate (I) underwent their dehydroxylation, and the hydrogrossular in the family of hydrogarnet formed in autoclaved Class G/Class F fly ash system disappeared in this accelerated thermal shock cycle testing.

For #80/Class F fly ash blend cement system, we evaluated the following four formulas, 100/0, 80/20, 60/40, and 40/60 #80/Class F fly ash ratio, for thermal shock cycle testing. The 200°C-autoclaved bulk #80 cement had two major crystalline hydration products, boehmite and katoite phases. Adding 20 wt% Class F fly ash to the #80 cement as 80/20 ratio led to the incorporation of one additional hydrothermal reaction product such as hydroxy-sodalite known as hydroceramic. Further addition of Class F fly ash resulted in the incorporation of another reaction product like intermediate hydrogrossular. After 5-cycle thermal shock test, two new crystalline phases in the bulk #80 cement were identified: One was γ-AlO(OH); the other was calcite, while the boehmite and katoite phases formed in the autoclaved #80 cement were eliminated. Thus, the boehmite was transformed to γ-AlO(OH) by its dehydroxylation, γ-AlO(OH) → γ-AlO(OH), and the katoite in the family of hydrogarnet was carbonated to form calcite, Ca₃Al₂(OH)₁₂ → CaCO₃. Although these phase transformation took place, the #80 cement did not show any signs of failure such as the generation of cracks, revealing it to be reliable as a refractory cement. However, the original compressive strength developed in the autoclaved cement fell by 33 % to 4325 psi after 5 cycles. For the cement made with 80/20 #80/Class F fly ash ratio, the hydrogarnet formed in autoclaved cement was transformed to the carbonated sodalite by the replacement of OH group in hydrosodalite with CO₃, Na₂Al₂Si₃O₁₀CO₃ → Na₂Al₂Si₃O₁₀CO₃, while some γ-AlO(OH) and calcite coexisted with carbonated sodalite. With 60/40 and 40/60 ratios, their phase composition closely resembled that of 80/20 ratio. Only one differential was the fact that like the Class F fly ash-modified Class G cement, the intermediate hydrogrossular produced in autoclaving these cement disappeared after 5 cycles. Nevertheless, we found that Na₂Al₂Si₃O₁₀CO₃ → Na₂Al₂Si₃O₁₀CO₃ phase transformation not only played a pivotal role in sustaining the compressive strength of cement during annealing-water quenching cycles test, but also contributed significantly to improving further the thermal shock resistance of #80 cement. In fact, no changes in compressive strength after 5 cycles were
observed from the cements made with 60/40 and 40/60 ratios, compared with that of autoclaved cements. Thus, among the three crystalline phases, γ-Al₂O₃, calcite, and carbonated sodalite, assembles in the #80/Class F blend cements during cycle testing, the carbonated sodalite not only acted to improve the thermal shock resistance of #80 refractory cement, but also, it was primarily responsible for densifying the cementitious structure. In addition, such a CO₂-sequestering property of hydroxidosodalite seemed to suggest that this cement could be categorized as CO₂-resistant cement.

Consequently, the sodium silicate-containing #80/Class F fly ash blend cement has a potential as alternative thermal shock resistant cement in EGS wells.

References
