Role of PVA Flakes in Promoting Self-Degradation of Sodium Metasilicate-Activated Cement under a Hydrothermal Environment at ≥150°C

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Abstract: We investigated the effect of flakes of polyvinyl alcohol (PVA) on the self-degradation of sodium metasilicate (SMS)-activated slag/Class C fly ash cement, which is used as temporary sealer for fractures in Enhanced Geothermal System (EGS) wells under a hydrothermal environment at ≥150°C and at pressure of 1000 psi. The reactions between PVA and SMS dissolved in an aqueous medium at 85°C led to the formation of a colloidal hydroxylated silicate-cross-linked PVA gel in the cement body. This gel-incorporated cement had a compressive strength >2000 psi, so ensuring that it adequately plugs the fractures. Increasing the hydrothermal temperature to ≥150°C triggered the transformation of the gel into a sol. This *in-situ* gel→sol phase transition played a pivotal role in promoting the cement's self-degradation because of the extensive spreading of sol in the cement body, and its leaching from the cement. In contrast, when gel was dry heated at ≥150°C, the gel→xerogel phase transformation engendered the molecular fragmentation of PVA. This fragmentation yielded polysilicate cross-linked PVA derived from the combination of extended-chain scission, carboxylation and condensation, so that it no longer served as a self-degrading promoter of cement.

Keywords: Enhanced Geothermal System, polyvinyl alcohol, cement, sodium metasilicate, lost circulation, temporary sealer.

1. INTRODUCTION

In drilling and sealing operations, the well's temperatures vary between 70 and 110°C and the common temperature is around 85°C. The ideal temporary cementitious sealer in Enhanced Geothermal System (EGS) must not only plug the pre-existing fractures during drilling operation at a low well temperature around 85°C, but it must also self-degrade when the well temperature reaches ≥150°C. In the former scenario, these fractures in terms of lost circulation zones often cause the wastage of a substantial amount of the circulated water-based drilling fluid. To deal with this problem, operators first must seal or plug the lost circulation zones with appropriate materials to avoid depleting the drilling fluid and loosing mud. The sealing materials are required to possess the appropriate setting time at this temperature, so precluding the undesirable fast setting of sealer during the down-hole pumping operation. Further, the cured sealer must develop an adequate mechanical strength to assure a satisfactory plugging performance without any possibility of its dislodgement from fractures when drilling operation is resumed. Once this problem is resolved, the drilling operation continues until the wellbore structure is completed. Thereafter, the inevitable concern arising is the fact that all sealing materials used to plug the fractures now must be disintegrated in a hydrothermal environment at an elevated temperature of ~ 150°C to reopen the sealed fractures. The next step is a hydraulic-stimulation operation to assure the propagation of the reopened fractures.

When the sealer is placed into fractures in impervious rock, it may encounter two different environments: One is the hydrothermal condition at the inlet of fracture; the other is a hot dry condition at its end. Thus, the sealer is required to disintegrate under both environments. For the former condition, its disintegration takes place in hot water at 150°C. In contrast, for the latter, the degradation would occur after the 150°C-heated sealer comes in contact with water.

Based upon this concept, our previous work concentrated on investigating the usefulness of sodium carboxymethyl celluloses (CMCs) in promoting the breakdown of sodium silicate-activated slag/Class C fly ash cementitious sealer under the latter condition [1]. When heated, CMC emitted two major volatile compounds, CO_2 and acetic acid, creating a porous structure in a cement body. It also favorably reacted with NaOH from sodium silicate to form three water-insensitive solid reaction products, disodium glycolate salt, sodium glucosidic salt, and sodium bicarbonate.

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Other water-sensitive solid reaction products, such as sodium polysilicate and sodium carbonate, were derived from hydrolysates of sodium silicate. When these products formed in cement came in contact with water, their dissolution generated exothermal energy triggering cement's self-degradation. Thus, CMCs of high molecular weight contributed two important features to the water-catalyzed self-degradation of heated cement: One was the generation of more exothermal energy in cement; the other was introduction of extensive porosity into it.

To achieve a good plugging performance the cement sealer requires bridging additives, which ensure adequate filling of different-size fractures. Desirable bridging additives not only must improve sealer's plugging performance at a low temperature of 85°C, but also self-decompose when the self-degradation of cement matrix in sealer system begins at ≥150°C. We previously evaluated several organic fibers as self-decomposable bridging additives [2]; among them, the polyvinyl alcohol (PVA)-based fiber significantly improved the slurry's plugging performance in slot nozzles of 1-in. wide x 6-in. long x 0.08 in. and 0.24 in. high under pressures up to 700 psi. PVA fiber-bridged slurry easily penetrated in the slot and filled it to a depth of nearly one inch from the slot's inlet; then the slurry was transformed into solid cement composite that was responsible for abating any lost-circulation problems at 85°C. Also, PVA fibers conferred great compressive toughness and self-degrading properties on cement composite. One factor governing the development of toughness was the excellent adherence of PVA to the cement matrix reported earlier [3-5]. The alkali-catalyzed self-decomposition of PVA in the cement composite at 200°C led to the *in-situ* morphological transformation of the material from a fibrous structure to a microscale flake-like structure that aided the desirable conversion of the bulk cementitious sealer into small fragments, ranging from ~7 mm to ~5 mm size. Finally, the transformed PVA flakes were dissolved and vanished during their exposure to hydrothermal environment at 200°C.

The information detailed above prompted us to assess the potential of PVA flakes with high molecular weight as an alternative self-degradation promoter. Thus, the objective of this study is to investigate their efficacy in improving further the self-degradation performance of cement in hot water at ≥150°C under pressure of 1000 psi. Under the conditions of our test, we assumed that the sealer is placed in the inlet of fracture and exposed directly to hot water. The desirable performance of the improved self-degradation is as follows: The cement composites cured hydrothermally at 85°C and possessing the compressive strength of at least 2000 psi are crumbled in small fragments of less than 5 mm during their immersion in hot water at ≥150°C and at pressure of 1000 psi.

As well documented [6-8], the plentiful alcoholic group, -COH within PVA favorably reacts with alkaline reagents including metallic hydroxides (metals: B, Cu, and Ti, et.al) to form an inter- and intra-hydrogen bonds between PVA and hydroxyl metal ions at temperature around 40°C. Subsequently, these hydroxyl metallic ions promote the cross-linking between inter- or –intra-PVA molecular chains [9]. This cross-linked structure in aqueous media was responsible for converting PVA solution into its gelatinous phase. Further, increasing the temperature to > 65°C caused cleavage of this cross-linked structured structure resulting in the transformation of the gel into a sol. Thus, the gel-sol transition was thermally reversible. On the other hand, the interactions between two hydroxyl groups of PVA and B-, Si- or Al-hydroxide in an oven at elevated temperatures around 150°C [10-12] led to the dehydration condensation reactions to form the oxygen-bridged B-, Si- and Al-PVA linkages in the xerogel state. These linkages not only offered improved thermal stability of PVA, but also caused the transformation of the crystalline phase of PVA into an amorphous one.

Based upon this information, our particular interest was the gelation of PVA flake in sodium silicate-activated cement under a hydrothermal condition. This gelation may be caused by interactions between PVA and sodium silicate in cement slurry. Assuming such a gel is incorporated into solid cement during the hydration period of cement at 85°C, and then it is transformed into sol at elevated hydrothermal temperature ≥150°C under pressure of 1000 psi, this gel→sol transition may promote the disintegration of solidified cement. On the other hand, an intriguing question is whether cross-linked PVA xerogels formed by heating at >85°C contribute to the crumbling of cement in hot water.

Thus, the objective of this study is to investigate the effectiveness of PVA flake in increasing the extent of self-degradation of sodium silicate-activated slag/Class C fly ash cement in hot water at 150° and 200°C under a pressure of 1000 psi. The factors to be investigated included the exothermal energy evolved during the gelation of PVA in sodium silicate solution at 85°C, the chemical structure of PVA gel, the molecular alterations of PVA gel after heating at 85°, 150° and 200°C, the amount of PVA sol leached from 85°-, 150°- and 200°C-autoclaved and –heated cements, and the microstructure of PVA developed in 150°C-autoclaved and -heated cements and their chemical compositions. The integrated information on all the data above was correlated directly with the visual observation of self-degrading performance and the changes in compressive strength of sodium silicate-activated slag/Class C cement containing PVA flakes and PVA fibrous bridging additive after immersing in hot water at 85°, 150°, and 200°C under pressure of 1000 psi. For comparison, we also observed the self-degradation performance and determined the compressive strength of this same cement without PVA flakes (with PVA fibers) after heating at 85°, 150°, and 200°C.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Poly(vinyl alcohol) flakes of Mw 195,000 were obtained from Sigma Aldrich Chemicals and used as self-degradation promoter of the hydraulic pozzolana cement consisting of two cement-forming components, granulated blast-furnace slag and Class C fly ash. The former component under the trade name “New Cem” was supplied by Lafarge North America, and the latter was obtained from Boral Material Technologies, Inc. Their chemical compositions detected by micro energy-dispersive X-ray spectrometer (μ EDX) were as follows: Slag; 38.5 wt% CaO, 35.2 wt% SiO_2, 12.6 wt% Al_2O_3, 10.6 wt% MgO, 1.1 wt% Fe_2O_3, and 0.4 wt% TiO_2; and, Class C fly ash; 30.2 wt% CaO, 31.9 wt% SiO_2, 21.7 wt% Al_2O_3, 4.6 wt% MgO, 6.1 wt% Fe_2O_3, 1.7 wt% Na_2O, 0.7 wt% K_2O_3, and 3.1 wt% SO_3. The PQ Corporation provided the sodium metasilicate (SMS) granular powder under the trade name “Metso Beads 2048,” as the alkali activator of these pozzolana cements; its chemical composition was 50.5wt % Na_2O and 46.6 wt % SiO_2. The PVA fiber (24 μm diam. x 6 mm long, under the trade name PVA RMS702), supplied from Nycon Corporation, was applied as self-decomposable bridging additive to cement. The formulation of the dry pozzolana cements employed in this test included slag/Class C fly ash ratio of 20/80 by weight. The SMS was added at 12 % by total weight of pozzolana cement to prepare the dry blend. A 2.0 % PVA fiber by the total weight of the pozzolana cement and SMS was incorporated into this dry blend. Further, PVA flakes were added to the dry blend at up to 4.0 % by the total weight of the pozzolana and SMS.

In preparing the cement slurry, an appropriate amount of water was added to the dry cement mixture with PVA-fiber and -flakes additives at room temperature. The slurries were placed in the sealed glass container with 100 % relative humidity at 85°C to convert them into hydrated cements. Subsequently, they were exposed to two different environments: One was in a hot water at three different temperatures of 85°, 150° and 200°C for 24 hours under pressure of 1000 psi, called the autoclave treatment; the other was in an air oven at these same three temperatures for 24 hours, called the pre-heat treatment, prior to the immersion for 24 hours in a hot water at these same temperatures under pressure of 1000 psi. We visually observed the self-degrading behavior of these autoclave- and pre-heat/autoclave-treated cements and determined their compressive strength. Additionally, to obtain information on leaching of PVA from cement during the immersion in hot water, we prepared the samples in the following manners: First, ~ 2.8 g of PVA flake-incorporated cement without PVA fiber were placed in 22 cc ampoule, and then 11 ml deionized (D.I.) water were poured into cement-containing ampoule, followed by sealing the top of the ampoule; second, the ampoule was autoclaved at 85°, 150°, and 200°C for 24 hours; and, finally, the D.I. water from autoclaved ampoule was analyzed to measure the total amount of carbon leached from cement during autoclaving.

To study the interactions between PVA flakes and SMS solution and clarify the role of interaction products in promoting and inhibiting the self-degradation of cement, a 0.5, 1.0, and 2.0 g PVA flakes was mixed with 12 g of 28 wt% SMS aqueous solution.

2.2. Measurements

TAM Air Isothermal Microcalorimeter was employed to determine the heat flow evolved by the reactions of PVA with sodium metasilicate solution at an isothermal temperature of 85°C. To identify the reaction products, we employed Fourier Transform Infrared Spectroscopy (FT-IR) and Thermo Gravimetric Analysis (TGA) at the heating rate of 20°C/min in a N_2 flow. The crystalline phases formed in 85°-, 150°-, and 200°C-heated PVA/SMS xerogels were surveyed by X-ray diffraction (XRD). The compressive strength for the cylindrical specimens (16 mm diameter by 35 mm long) was determined using Instron Model 5967. The microstructure of PVA developed in autoclaved- and heated-cements, and its chemical composition were explored using µEDX. We employed the SHIMADZU TOC-L Total Organic Carbon Analyzer to detect the amount of PVA sol leached from cement.

3. RESULTS AND DISCUSSION

3.1. Self-Degradation and Compressive Strength

Figure **1** shows the appearance of PVA fiber-bridged cements containing 1.5, 3.0, 3.5, and 4.0 wt% PVA flakes after immersing them in hot water at 85° and 150°C under pressure of 1000 psi for 24 hours. As is seen in the photo images, there were no pronounced degradations in any of the 85°C-autoclaved cements. In contrast, autoclaving at 150°C caused the cements to self-degrade. The magnitude of this self-degradation depended primarily on the PVA content; in this test series, 4 % PVA displayed the most effective degradation, which converted the bulk cement into small fragments, ranging from ~1 mm to ~5 mm. Similar results were observed at 200°C (not shown). Next, we determined the compressive strength for these samples except those of 150°-and 200°C-autoclaved cements with 3.5 and 4.0 % PVA because they were self-degraded (Figure **2**). Without PVA, the cements autoclaved at 85°C had the compressive strength of 2886 psi; this value declined with an increasing autoclave temperature, to 1913 and 1470 psi at 150° and 200°C, respectively. As was described in our previous paper [2], this reduction of strength was due to the hydrothermal degradation of PVA fiber in the cement body. At 85°C, there were no significant changes in compressive strength as a function of PVA content. Since a drilling and sealing operation commonly is undertaken at a well temperature around 85°C, this result ensures that the cement adequately plugs the fractures without degrading. Increasing the hydrothermal temperature to 150°C considerably reduced compressive strength to 460 and 300 psi for 1.5 and 3.0 wt% PVA, demonstrating the effectiveness of PVA in promoting the degradation of the cement at this temperature. We obtained a similar result for the 200°C-autoclaved cement.

In contrast, when the PVA-containing cements were pre-heated at 85°, 150°, and 200°C for 24 hours, these pre-heated cements did not show any signs of self-degradation during their immersion in a hot water at the same temperature (not shown in the figure). As is evident from the results of compressive strength test (Figure **3**), although 4 wt% PVA was added to cement, its strength after autoclaving at 150° and 200°C was almost equivalent to that of the PVA-free cements at the same temperature. This fact strongly suggested that the nature of PVA present in the pre-heated cement was different from that in the non-heated one, and furthermore, it was not as effective in promoting the self-degradation of cement as did the non-heated one.

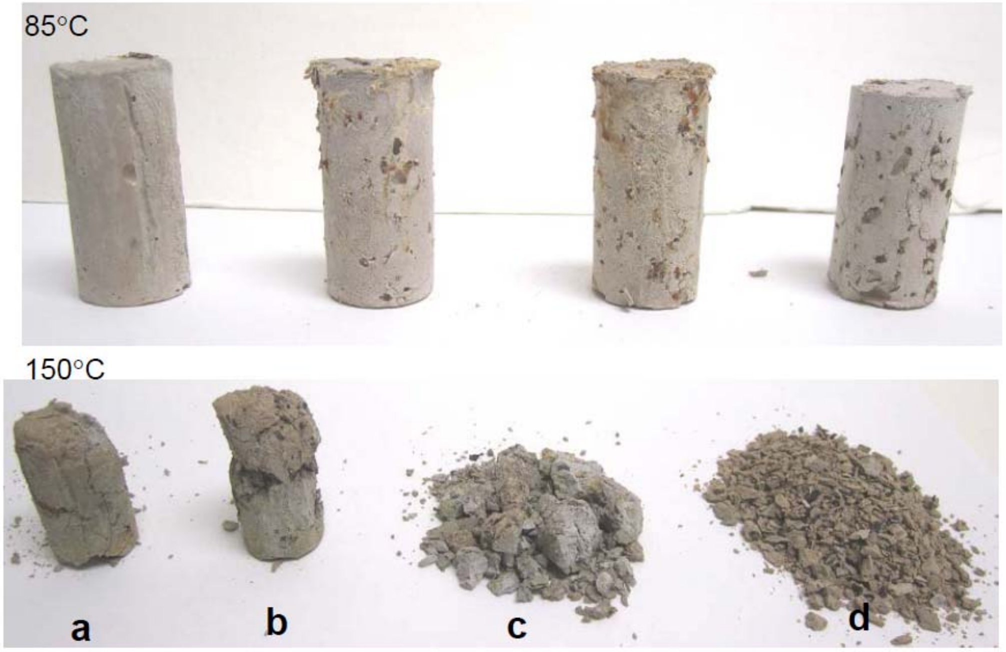

Figure 1: Appearance of 1.5 (**a**), 3.0 (**b**), 3.5 (**c**), and 4.0 (**d**) wt% PVA flake-containing cements after immersing them in hot water at 85° and 150°C under pressure of 1000 psi for 24 hours.

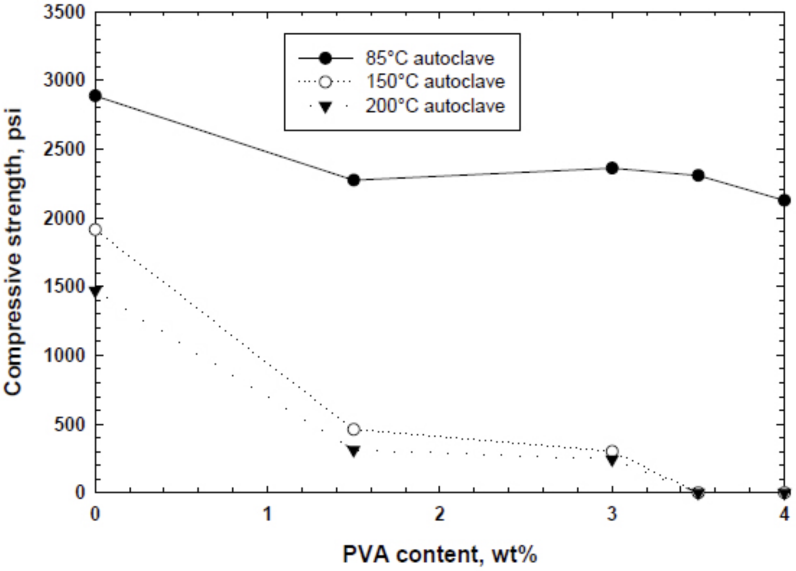

Figure 2: Changes in compressive strength of 85°-, 150°-, and 200°C-autoclaved cements as a function of PVA content.

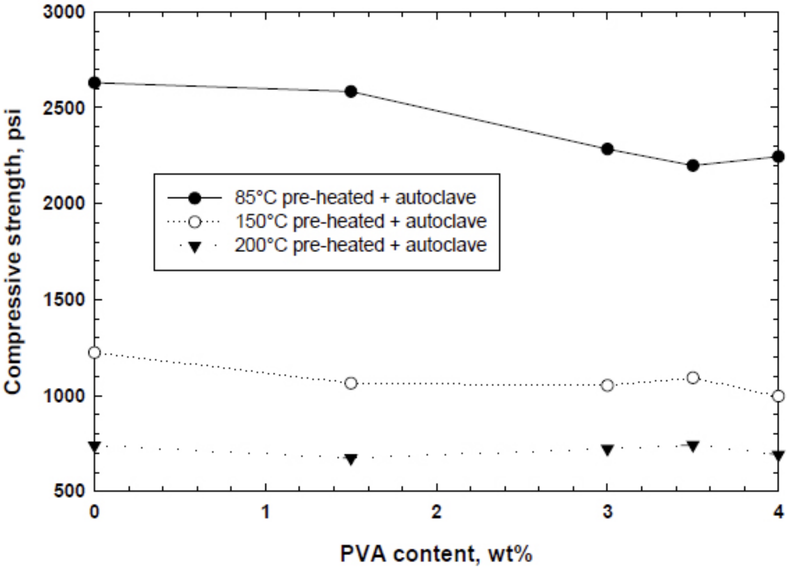

Figure 3: Compressive strengths of PVA-containing cements prepared by pre-heating and autoclaving at 85°, 150°, and 200°C.

3.2. Microstructure Development and Chemical Composition

To support this finding and visualize the effect of PVA on self-degradation of cement, we explored the morphology of PVA present in the 150°C-autoclaved and –pre-heated cements, and also detected the chemical compounds of PVA by µEDX. Figure **4** shows the image and oxide compound analyses for the surface of self-degraded cement fragment after autoclaving at 150°C.

We observed in the color images that there were two major distinctive areas: One was a purple-colored area attributed to PVA; the other was white-colored and referred to the cement matrix. The PVA area was extensively spread penetrating into the body of cement. Our particular interest was the oxide composition of PVA areas, compared with that of cement area; we found that it included a substantial amount of silicon dioxide, with a value of 29.5 % that was as much as six-fold higher than that in cement, seemingly suggesting that SiO_2 in cement preferentially reacted with PVA rather than the other oxide compounds. A quite different morphology of PVA was observed in the 150°C-heated cement (Figure **5**). As is seen, PVA was locally isolated from cement phase and did not display any spreading compared with that of autoclaved PVA. On the other hand, like the autoclaved PVA, the uptake

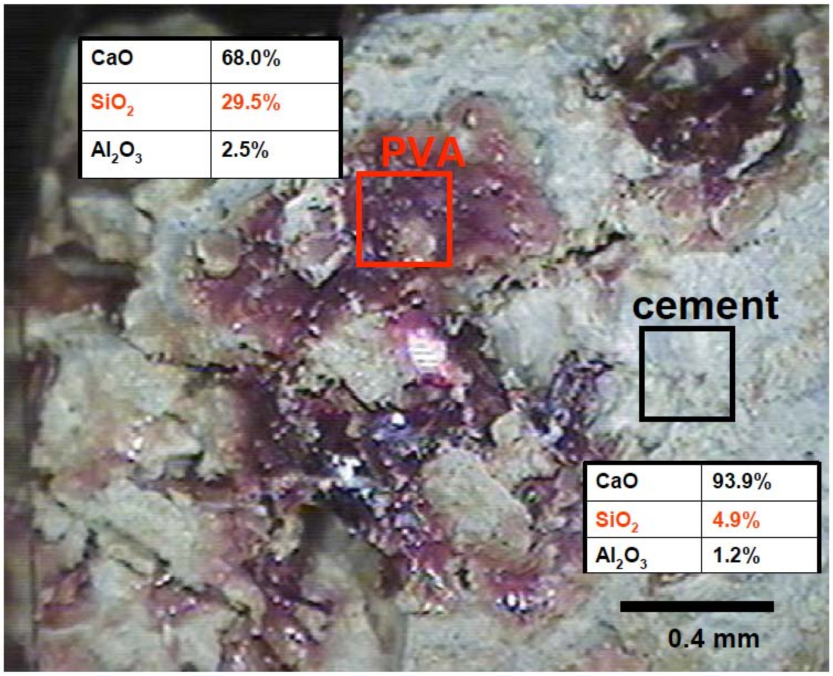

Figure 4: Morphology and oxide composition of PVA in 150°C-autoclaved cement.

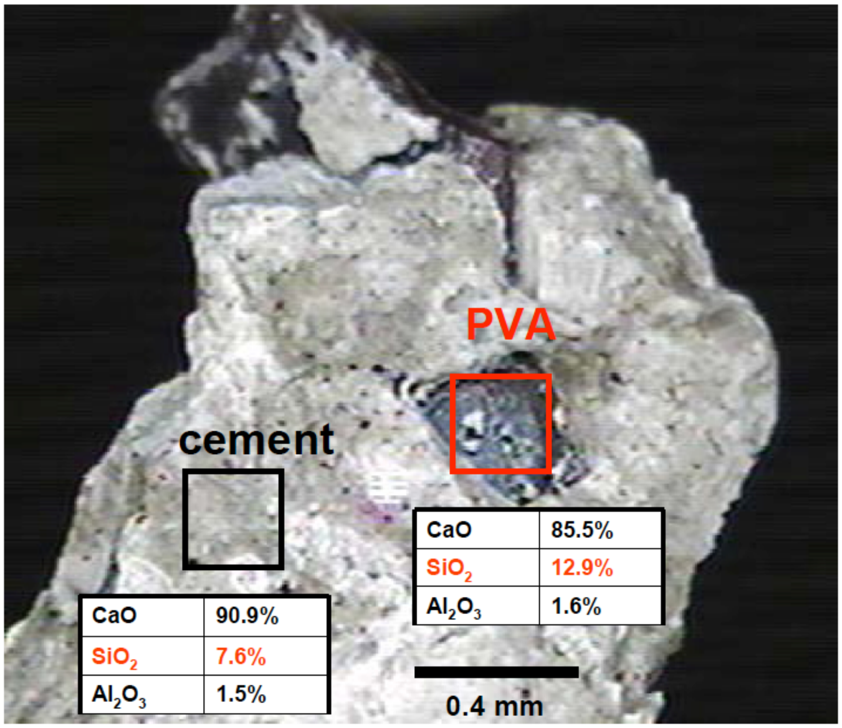

Figure 5: Morphology and oxide composition of PVA in 150°C-heated cement.

of SiO_2 by PVA was evident from comparing the oxide compositions of PVA and cement. Relating this finding to the self-degrading performance of cement, the spreading and penetrating behaviors of PVA in autoclaved cement is likely to play a key role in promoting cement's self-degradation. Hence, an extensive spreading and penetrating PVA in cement was responsible for improving the cement's self-degradation.

3.3. Leaching of PVA from Cement

To estimate the extent of PVA's spreading, we measured the amount of the total carbon leached from

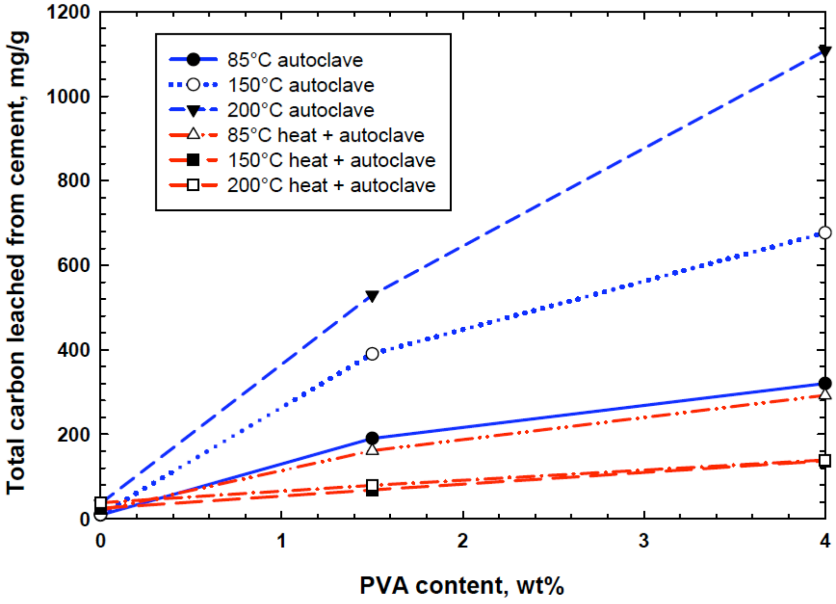

Figure 6: Carbon content liberated from autoclaved and pre-heated PVA-containing cement.

cements containing 0, 1.5, and 4.0 wt% PVA during autoclaving and pre-heating-autoclaving treatments at 85°, 150°, and 200°C for 24 hours (Figure **6**).

Without PVA flakes, the total carbon detected from all of the cement samples ranged from 9 to 38 mg per 1g sample, meaning that these amounts of carbon were liberated from cement during the treatments. Such a small amount of leaching did not trigger the degradation of cement. When the PVA-incorporated cements were autoclaved and pre-heated at these temperatures, except for at 85°C, the amount of carbon liberation depended primarily on the temperature and PVA content. With the autoclave treatment, at 1.5 wt% PVA, 85°C-treated cement liberated 190 mg/g carbon, corresponding to an amount nearly a 21-fold higher than that of PVA-free cement at the same temperature. A further increase in PVA to 4.0 wt% resulted in the release of 320 mg/g carbon. Our particular attention was paid to the relationship between the value of carbon liberation and the self-degradation performance: In fact, the release of up to 320 mg/g did not show any visual self-degradation. By contrast, after autoclaving at 150°C, the carbon value was 390 and 677 mg/g for 1.5 and 4.0 wt% PVA contents, respectively, and these values corresponded to cement's self-degradation. Increasing the temperature to 200°C further promoted the rate of carbon liberation to 530 and 1108 mg/g for 1.5 and 4.0 wt%, leading to advanced self-degradation, compared with that at 150°C. Our attention next focused on the cements made with the pre-heating prior to autoclaving. The data revealed that all of the 85°-, 150°-, and 200°C-pre-heated cements significantly restrained the leaching of carbon when immersed in hot water at the same temperature. Although 4 % PVA was incorporated, the liberated carbon at 85°, 150°, and 200°C was only a 292, 137, and 139 mg/g, demonstrating that the pre-heating restrained carbon liberation, thereby inhibiting the cement's self-degradation.

3.4. Reaction of PVA with Sodium Silicate

Regarding a preferential uptake of SiO_2 by PVA, although the slag and Class C fly ash used as the cement-forming starting materials included some SiO_2, its ionic dissolution takes place after these materials are activated with SMS solution [13-16]. Thus, we believe that the ionic silicate dissociated from SMS in aqueous media primarily reacted with PVA, rather than that from the slag and Class C fly ash. Our study next centered on visualizing and rationalizing the reactions between PVA and SMS solution at 85°C, and also on identifying the interaction products derived from these reactions.

Figure **7** shows the photos of the single PVA solution and sodium silicate-mixed PVA solution at 85°C. As is evident, the PVA reacted with SMS to create its gelation phase segregated from the SMS solution phase. We next measured the maximum heat (MH, mW/g) evolved during the gelatinizing interactions between PVA and SMS (Figure **8**).

Without PVA, the dissolution of SMS in aqueous media at 85°C generated the MH of 0.038 mW/g. This value rose by ~8 % to 0.041 mW/g when 0.5g PVA was

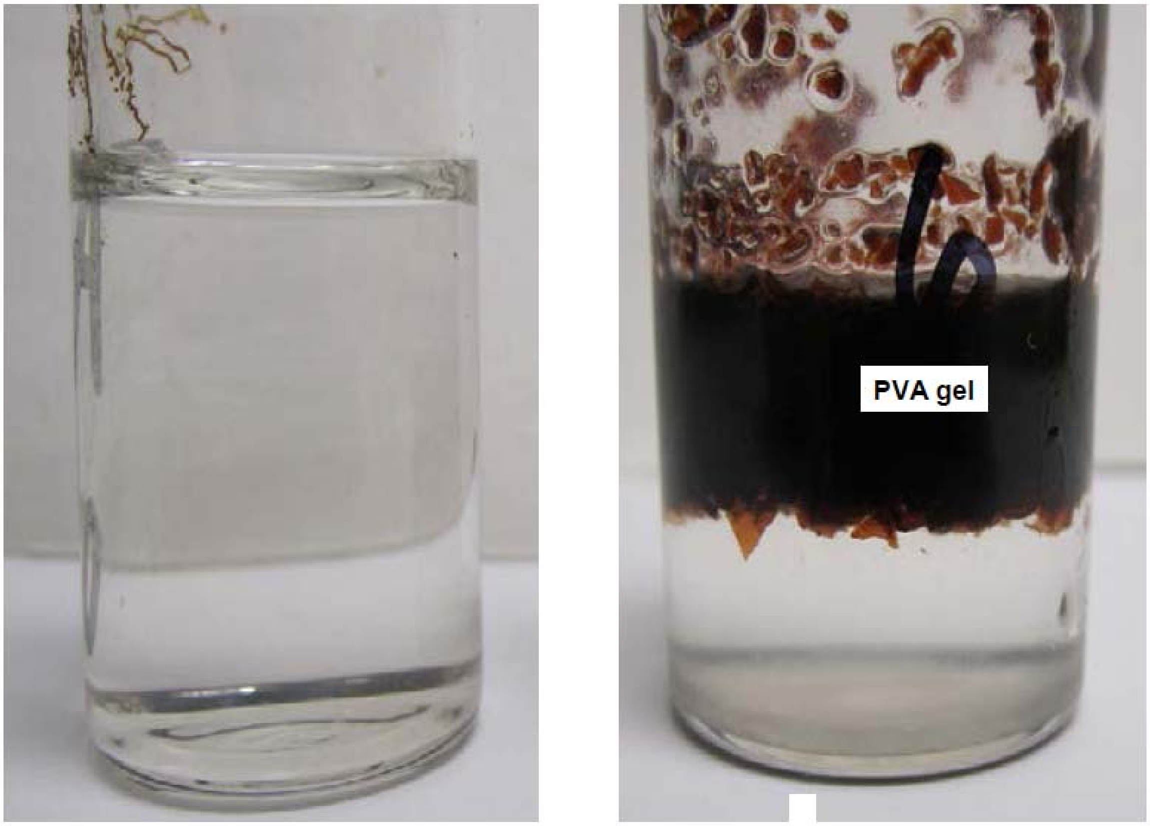

Figure 7: PVA solution (left) and PVA gel formed in PVA/SMS mixed solution (right) at 85°C.

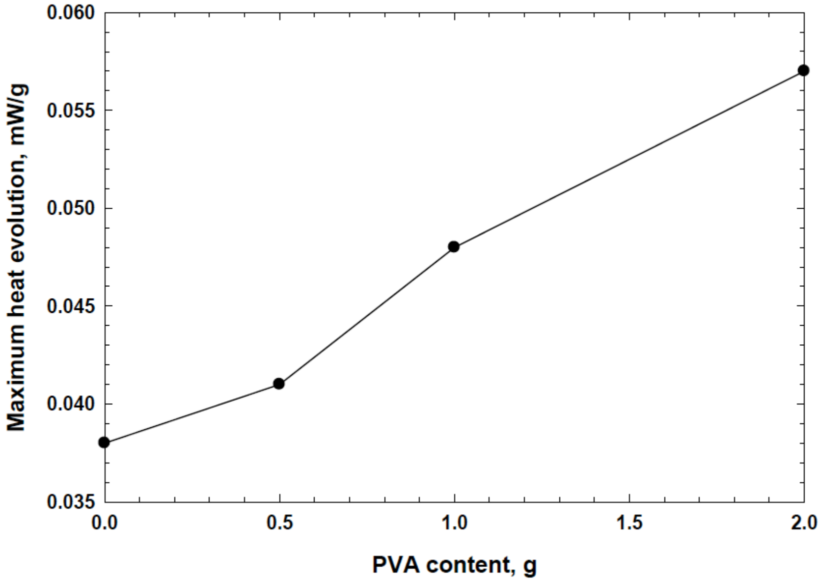

Figure 8: Maximum heat evolution generated during gelatinizing reactions between PVA and SMS.

added to this SMS solution. Adding more PVA further augmented the value of MH, strongly supporting the evidence that PVA had a strong chemical affinity with SMS to create its gel.

Figure **9** illustrates FT-IR spectra in the wavenumber region, 1797-1303 cm^{-1}, of 0.5, 1.0, and 2.0 g PVA gels formed in SMS solution at 85°C. We paid particular attention to two absorption bands at 1549 and 1413 cm^{-1} attributed to the C-O asymmetric and symmetric stretching node in the carboxylate anion group, -COO^{-} [17, 18], while a prominent band at 1662 cm^{-1} was due to the H-O-H bending in water. The data revealed that the intensity of COO^{-} group-related bands

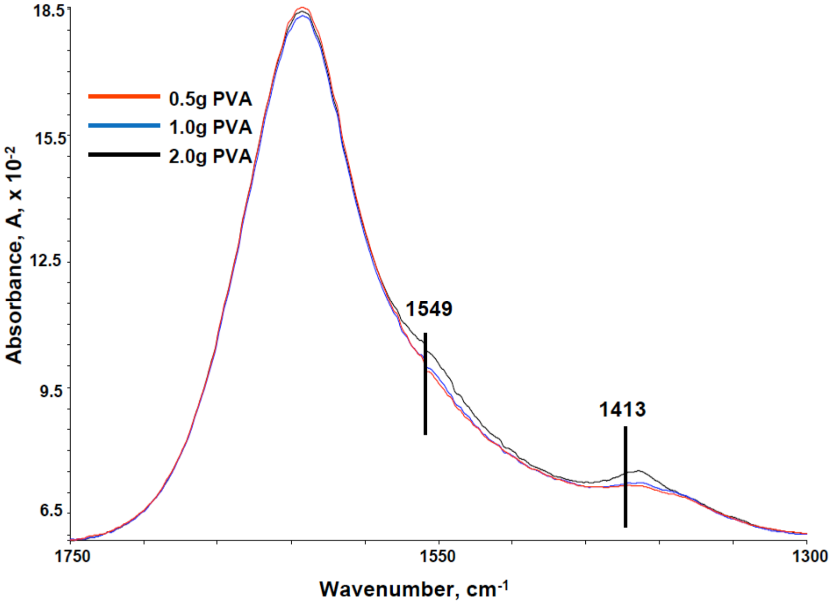

Figure 9: FT-IR spectra, ranging from 1750 to1300 cm^{-1}, for gels made by varying the content of PVA at 85°C.

grew with an increasing amount of PVA. Since SMS didn't have any groups associated with the positions of these two wavenumbers, it appeared that PVA was susceptible to reactions with SMS that altered its molecular structure. This alteration occurred at the alcoholic, -COH group, within PVA, and consisted of its conversion into carboxylate group in conjunction with the scission of alkane backbone chains [19].

Figure **10** shows FT-IR spectra in the region of 1130-750 cm^{-1} for the same samples. The spectra encompassed three bands, at 975, 921, and 818 cm^{-1}, respectively, corresponding to Si-O stretching mode in non-oxygen bridged SiO^- Na^+ group, Si-O stretching in silanol Si-OH group [20] for SMS, and C-H stretching in backbone chain of $-CH_2-$ groups [21] for PVA. As shown, the absorbance of SMS-related bands tended to rise with an increasing content of PVA, emphasizing the uptake of SMS by PVA.

Additionally, we also studied the molecular structure of 2.0 g PVA gels prepared at 150° and 200°C by FT-

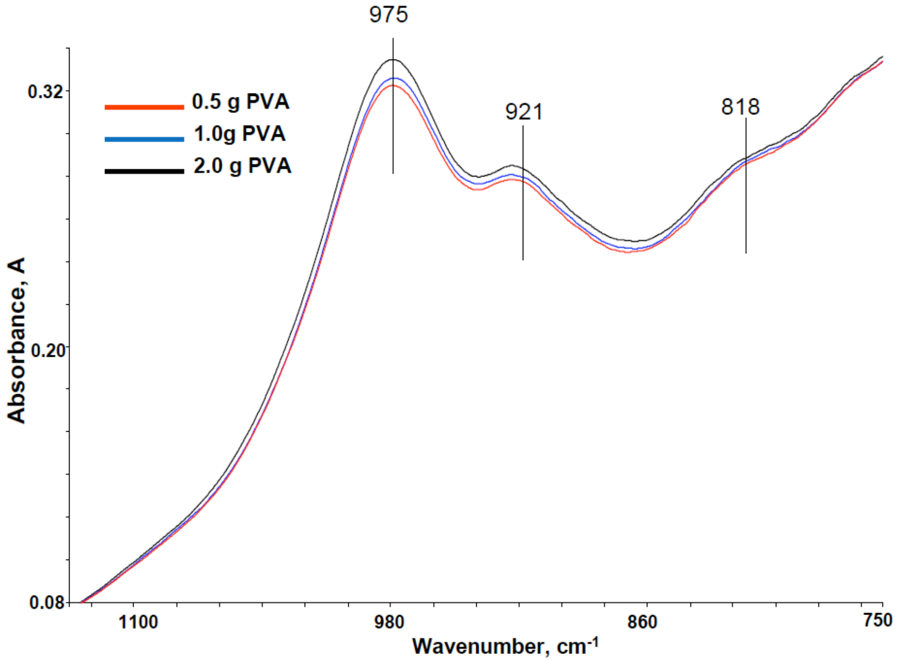

Figure 10: FT-IR spectra at range of 1130-750 cm^{-1} for PVA gels.

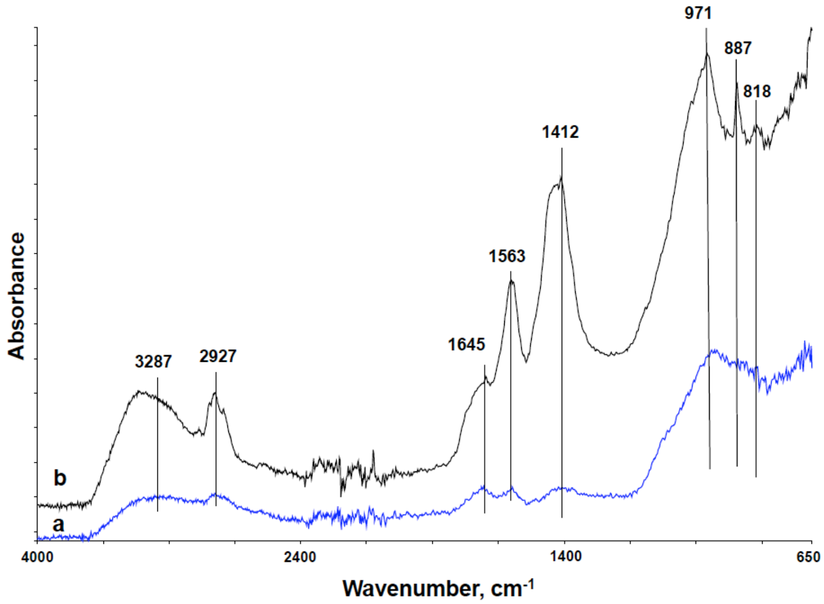

Figure 11: FT-IR results of PVA gels prepared in autoclave at 150°(a) and 200°C (b).

IR (Figure **11**). The data revealed that an elevated hydrothermal temperature engendered an increase in the absorbance of COO^- -associated with1563 and 1412 cm^{-1} bands, underscoring that an extended oxidation and chain scission of PVA underwent at such high temperatures and, correspondingly, the absorbance of SiO^- Na^+- and silanol-related bands at 971 and 887 cm^{-1} increased, reflecting more uptake of SMS by PVA. These spectra also included the O-H stretching vibration in alcohols at 3288 cm^{-1} and C-H stretching modes in backbone $–CH_2$- chain groups at 2927 and 818 cm^{-1}.

Based upon this information, we proposed the following hypothetic reaction route and chemical structure of the colloidal silicate-cross-linked PVA gel formation as reaction products between SMS and PVA (Figure **12**).

According to this interaction route, first, when SMS dissolves in water, it forms two reactants, sodium

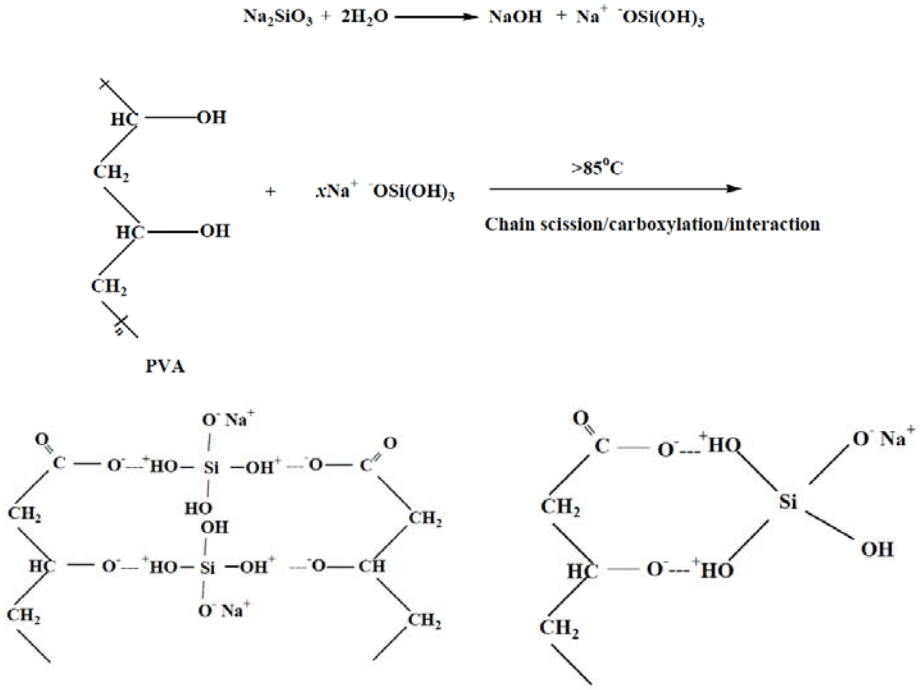

Figure 12: Hypothetic reaction route to form PVA gel and the gel's chemical structure.

hydroxide and colloidal hydroxylated sodium silicate, $Na^+ \ ^-OSi(OH)_3$. Second, alkali oxidation of PVA at ≥85°C causes the formation of functional carboxylate anion derivative brought about by the scission of $–CH_2$-backbone chains within PVA. Finally, the COO^- reacts with the silanol in $Na^+ \ ^-OSi(OH)_3$ to develop hydrogen bonding, $-O^-$---- $^+HO-Si-$, creating an inter-and intra-colloidal silicate cross-linked PVA structure in a gel state.

Assuming such cross-linked PVA is formed, our focus was concentrated on investigating visually the hydrothermal stability of this cross-linked structure. To obtain this information, a certain amount of gel was poured into D.I. water-containing glass beaker at room temperature, and agitated vigorously by magnetic stirrer. After mixing, we observed that the gel phase was segregated from the aqueous phase, and then it precipitated on the bottom of the glass beaker. Next, the beaker was slowly heated to 95°C. At around 90°C, the partial dissolution of the gel was observed, strongly demonstrating that the gel phase was turned into sol phase in water at >90°C. It is reasonable to consider that this conversion of gel into sol was due to the rupture of hydrogen bond-based cross linking between PVA and colloidal silicate. Thus, the PVA gel appeared to be altered to a non-cross-linked PVA structure by elevating hydrothermal temperature. This gel→sol phase transformation was major reason why PVA spread extensively throughout the entire cement matrix during immersion in hot water at 150° and 200°C. Hence, the magnitude of such spreading and leaching behaviors of PVA sol can be interpreted as the principal factor governing the self-degradation performance of cement.

Our FT-IR study next shifted to surveying the changes in chemical structure of 85°-, 150°, and 200°C-hydrothermaly made gels after heating them at these temperatures (Figure **13**). For 85°C-heated gel (a), the features of the spectrum, excepting Si-OH band at 890 cm^{-1} that became the major peak, closely resembled those of the gel before heating. At 150°C, these spectral features differed remarkably from that of the unheated one. There were five differences: First, the absorbance of the alcoholic OH group-, water- and CH_2-related bands was strikingly declined and vanished; second, the line intensity of carboxylate group bands markedly grew; third, a new band emerged at 1030 cm^{-1}, it was attributed to oxygen bridged Si-O-Si linkage; fourth, the $SiO^- \ Na^+$ and Si-OH bands became intensive peaks; and, finally, two carbonate-related bands appeared at 1447 and 708 cm^{-1}, due to CO_3^{2-} possibly in the sodium carbonate. At 200°C, the spectrum highlighted a further enhancement in the absorbance of carboxylate-, Si-O-Si linkage-, and carbonate-related bands, compared with those at 150°C, manifesting that heating the gel at temperature of ≥150°C led to the molecular fragmentations of PVA caused by sever chain scissions. This fragment not only was mainly constituted by carboxylate and hydrocarbon, but also

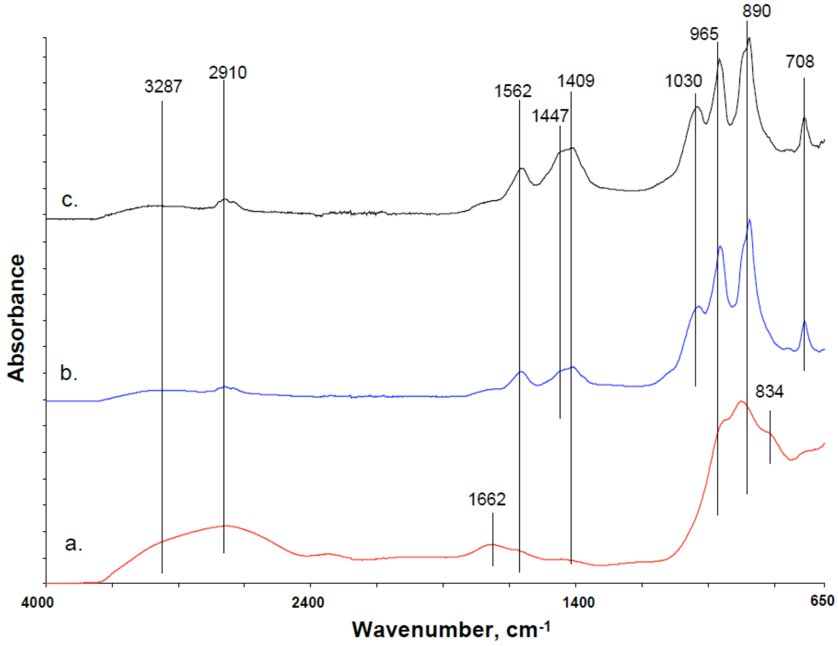

Figure 13: FT-IR spectra for 85° (a)-, 150° (b)-, and 200°C (c)-heated PVA gels.

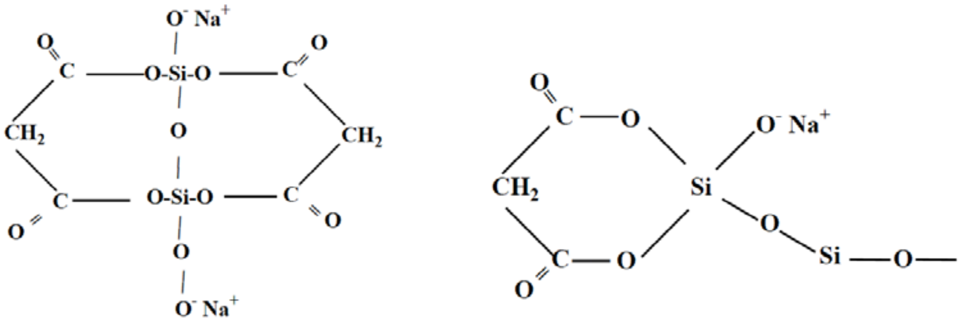

Figure 14: Hypothetical heat-catalyzed reaction derivatives of PVA gels.

contained Si-O-Si linkage-based polysilicate. Figure **14** shows hypothetical heat-catalyzed reaction products of polysilicate-cross-linked PVA xerogel fragment formed by combination of extended-chain scission,-carboxylation and –condensation.

Relating this finding to non self-degrading phenomena of heated cement in hot water, these xerogel fragments withstood hydrothermal temperatures ≥150°C, suggesting that there was no transformation of xerogel to sol. Thus, no xerogel→sol transition deterred the spreading of PVA in the cement body and leaching it from cement, thereby restraining the cement's self-degradation.

3.5. Thermal Decomposition of Xerogel Reaction Products

We investigated the thermal stability of xerogel derivatives produced by heating at 85°, 150°, and 200°C, by TGA at a temperature range of 25° to 500°C (Figure **15**). For comparison, the "as received" PVA flake was tested as the control. The TGA curve for control represented two step thermal decompositions: First, the major decomposition along with a large weight loss of ~ 70 % in the total mass occurred in the temperature region between 260° and 410°C; and second, the region of low weight loss at temperatures ranging from 410° to 460°C, was due to the decomposition of PVA's remnants [22]. In contrast, the TGA curve's feature of 85°C-made xerogel was characterized three stages of decomposition: The first stage denoted as No. 1, associated with the loss of absorbed water, began at ~ 113°C and ended at ~ 170°C; second stage occurred between 176° and 263°C; and, the third one was observed at >396°C. Conceivably, the weight loss on the second stage was related to the decomposition of some gel phases present in the xerogel, and third one was due to the xerogel phase. Assuming this interpretation is valid, no gel phase was detected in the 150°- and 200°C-derived

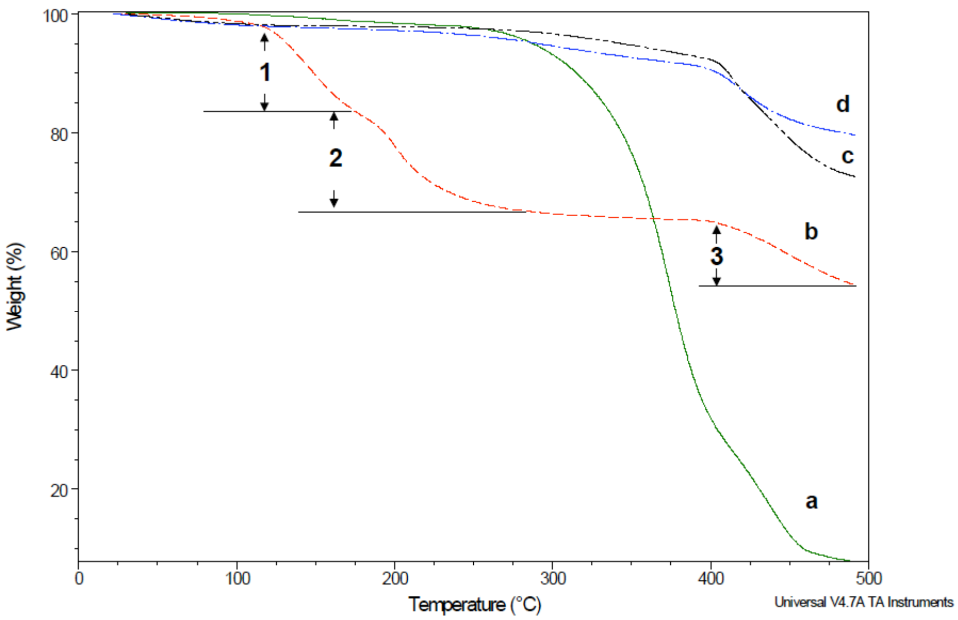

Figure 15: TGA curves of "as received" PVA (a), and xerogels made by heating at 85°(b)-, 150°(c)-, and 200°C (d).

xerogels because their TGA curves expressed a single stage decomposition pattern representing the degradation of only xerogel around 400°C. Thus, it appeared that highly polysilicate cross-linked PVA xerogel fragments displayed great thermal stability.

3.6. Crystallization of PVA

To further support our findings, XRD study was conducted to assess whether cross-linked PVA is crystallized. We used heated samples described above, and also the 85°-, 150°-, and 200°C-autoclaved samples, after drying them in a vacuum oven at 35°C. Figure **16** reveals the XRD tracings of 85°-, 150°-, and 200°C-heated PVA xerogel samples. The 85°C sample (a) included two crystalline compounds, PVA [23] and SMS, strongly demonstrating that PVA had regular molecular orientation that promoted its crystallization at this temperature. After heating at ≥150°C, both PVA and SMS no longer were crystallized as is seen in their XRD patterns (b and c). In contrast, all the autoclaved-dried samples exhibited the crystallized structure of PVA and SMS (not shown). Thus, a moderately silicate cross-linked PVA structure along with minor chain scissions still enabled it to crystallize; contrarily, a well polysilicate cross-linked PVA along with sever chain scission no longer could crystallize, thereby it became amorphous. For the latter, amorphous PVA xerogel was irreversible to sol in hot water ≥150°C, underscoring that the crystalline PVA was one important factor governing the C cement's self-degradation.

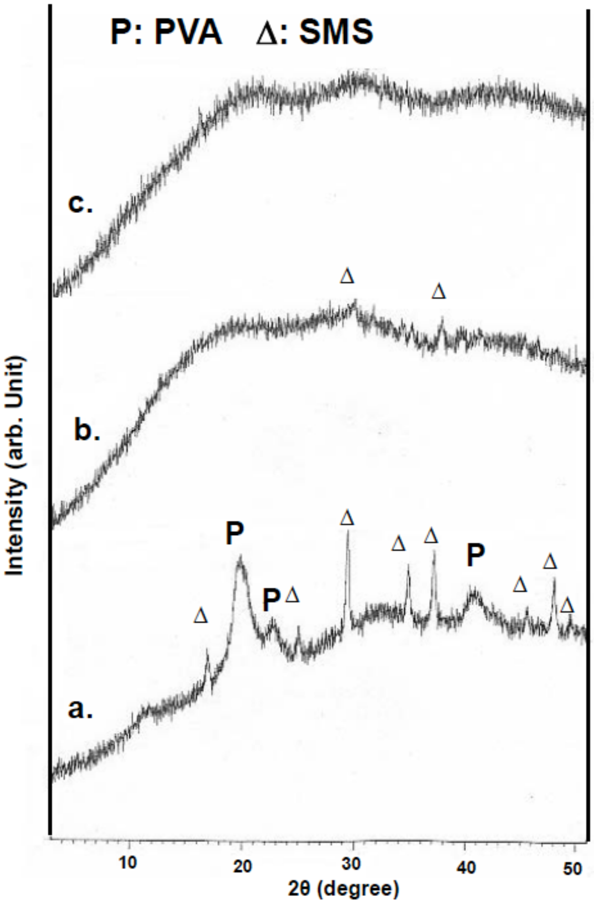

Figure 16: XRD patterns for 85°(a)-, 150°(b)-, and 200°C(c)-heated PVA xerogels.

4. CONCLUSIONS

The polyvinyl alcohol (PVA) flakes had high potential as an alternative self-degrading promoter of PVA fiber-bridged temporary cementitious fracture sealing materials consisting of slag, Class C fly ash, and sodium metasilicate (SMS) as alkali activator in a hot water at ≥ 150°C under pressure of 1000 psi. This material was designed in the aim of converting the bulk cement sealer placed in EGS well fractures around 85°C into the fragments of <5 mm of size, when well temperature increases to 150°C. The self-degradation mechanism of cement by PVA flake can be interpreted as follows: First, when PVA comes in contact with SMS dissolved in aqueous medium at 85°C, it undergoes alkali oxidation leading to the scission of alkane backbone chains that incorporate the carboxylate anions, $-COO^-$, into PVA; second, this carboxylate favorably reacts with colloidal hydroxylated sodium silicate, $Na^+ \, {}^-OSi(OH)_3$, in SMS solution to develop hydrogen bonding between $PVA\text{-}COO^-$ and $^+HO\text{-}Si\equiv$, so supporting the creation of the gelation phase of PVA in the cement body; importantly, this PVA gel-incorporated cement has compressive strength >2000 psi to ensure that it adequately plugs the fractures; third, at elevated hydrothermal temperature of ≥150°C, PVA gel phase present in cement transforms into its sol phase brought about by the breakage of hydrogen bond; fourth, these PVA sols extensively disperse in cement and some of them leach from it; and finally, such *in-situ* spreading and leaching behaviors of PVA sol at high temperature play a pivotal role in crumbling the hard cementitious materials.

In contrast, when PVA gel was heated at ≥ 150°C, the gel → xerogel phase transition caused the molecular fragmentation of PVA due to the combination of its sever chain scissions, extended carboxylation, and condensation. These fragments constituted polysilicate cross-linked PVA structure possessing a great thermal stability at temperatures up to 400°C. Such fragmentations of crystalline PVA not only impaired its ability to re-crystallize, but also inhibited the self-degradation of cement, reflecting that there was no xerogel → sol transformation.

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