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Effects of tobermorite and calcium silicate hydrate (I) crystals formed within polymer concretes

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In the development of hydrothermally stable vinyl-type polymer concretes (PC), the effect of calcium silicate hydrates produced by the hydrothermal reaction of an anhydrous cement–silica flour system used as a filler in the PC was determined. Results from measurements of the mechanical properties of PC specimens after exposure to a 25% brine solution at a temperature of 240° C for 10, 30 and 90 days were used to quantify these effects. In addition, X-ray diffraction, differential thermal analysis, and scanning electron microscopy were used to perform quantitiative and morphological analyses of hydrated calcium silicate compounds synthesized during exposure to hot brine of PC samples containing cements having molar ratios of CaO/SiO_2 of 1.33, 0.99 and 0.54. The data indicated that 11.3 Å tobermorite and calcium silicate hydrate-(I)-type [C–S–H(I)] crystals produced from the hydrothermal reactions of cement having the lowest CaO/SiO_2 ratio of 0.54 significantly affect the long-term hydrothermal stability of the composite. Exposure for approximately 30 days to a 240° C hydrothermal environment was required for synthesis of a highly crystalline tobermorite to occur on the amorphous polymer surfaces. Morphological examination of tobermorite revealed circular radiating crystals of diameter about 20 μm.

1. Introduction

Polymer concrete (PC) is generally prepared by mixing a binder, composed of an organic-type polymer, with an aggregate and a filler. For applications as protective liners or in geothermal processes as well-cementing materials, the proper choice of a filler material is very important in order to produce a hydrothermally stable product. A programme to develop a filler which promotes hydrothermal stability of PC at temperatures up to about 240° C has been in progress at Brookhaven National Laboratory since September 1976 [1–3]. The work has indicated that hydraulic cement-type fillers consisting mainly of calcium–silica compounds contribute most significantly to hydrothermal stability [4, 5].

A major reason for this effect is that Ca^{2+} ions released from cement grains during exposure to hydrothermal conditions produce a calcium polymer-complexed PC which imparts considerable thermal stability to the system. The complex is produced by an ionic bonding between the Ca^{2+} ions and the carboxylate anion ($-COO^-$) yielded from the thermal decomposition of polymers having carboxyl groups in their molecule. Materials such as polymethyl methacrylate (PMMA), polyesters (PE), and trimethylolpropane trimethacrylate (TMPTMA) have this characteristic [5, 6].

Hydrothermal stability is also influenced by the hydration products of the calcium silica compound fillers formed on the organic-type polymer layers, which have a significant effect on the mechanical properties and the thermal stability of PC exposed to hot brine [6, 9]. The formation of hydration products on an organic polymer layer indicates that there may be a morphological connection between the organic and the inorganic phases due to corrections of physical and chemical weak points of both materials. Thus for the use of PC in such high-pressure hydrothermal environments as those in geothermal wells, it is very important to know what hydration compounds are formed when general hydraulic cement fillers are used.

At the present time, silica-stabilized American Petroleum Institute (API) class G or H cement seems to be the preferred geothermal well-cementing material [10–12]. The silica is used to prevent a loss in strength that occurs with cement [12–14]. Amounts varying from 30 to 80 wt% of cement are generally used [12]. During exposure in an autoclave at temperatures above 110° C, the finely powdered silica reacts with hydrated cement compounds to form a calcium silicate complex called tobermorite [15]. The improvement in strength of hydrated calcium silicate groups was estimated to be in the order of [16]:

$$\text{tobermorite groups} \gg \text{xonotlite} > \text{gyrolite} > \text{afwillite} > \alpha\text{-}C_2SH.$$

Many cement chemists agree that the strength of tobermorite groups is considerably greater than that of other hydrated calcium silicate compounds. Tobermorite can also be used for aerated concretes and as thermal insulation.

It appears that the formation of highly-crystalline tobermorite is encouraged by:

(a) molar ratio of CaO/SiO_2 (C/S) ranging from about 1.0 to 0.8;

(b) the autoclave temperature;

(c) the content of alumina used as a promoter of crystallization [17–19];

(d) silica type (colloidal, quartz, amorphous by-products, or silica glass [20]);

(e) the grain size [10, 21].

This report gives the results of attempts to produce a thermally stable polymer concrete, the stability resulting from the formation of tobermorite on the polymer layers. Fillers prepared with a 1:1 ratio of β-dicalcium silicate (C_2S) to class-H cement, which are known to have a significant effect on the hydrothermal stability of PC, were used as a uniform basic cement [8].

The hydraulic cement-type fillers containing C/S molar ratios of 2.44, 1.33, 0.99 and 0.54 were prepared by the addition of silica flour having a particle size less than 44 μm. To obtain detailed information regarding the hydrated calcium silicate formed in the PC, compressive strength tests, X-ray diffraction (XRD), differential thermal analysis (DTA) and scanning electron microscopy (SEM) analyses were performed on the vinyl-type PC samples containing various C/S ratios after exposure to a 25% brine solution at a temperature of 240° C for 10, 30 and 90 days. These results also permit discussion regarding the formative process of hydrated calcium silicate on the polymer layers and its physical characteristics.

2. Experimental procedure

2.1. Materials

A mixture of vinyl-type monomers consisting of 55 wt% styrene (St), 35 wt% acrylonitrile (ACN), and 9 wt% trimethylolpropane trimethacrylate (TMPTMA) was used in the study to produce, upon polymerization, a co-polymer. Polymerization was initiated by using 2 wt% benzoyl peroxide of 98% purity with subsequent heating at 85° C for 24 h.

The mixture of the β-C_2S (of specific surface 3200 $cm^2\,g^{-1}$) containing a free-lime concentration of 0.6% with the API class-H cement (of specific surface 2778 $cm^2\,g^{-1}$) was prepared as a uniform basic cement filler. The chemical constituents of a cement filler having a β-C_2S/class-H cement ratio, by weight, of 1:1, are shown in Table I. General commercial-grade silica flour (98% pure SiO_2) was used to inhibit loss in strength at elevated temperatures. The particle size of silica was controlled to be less than 44 μm in diameter. The aggregate used in the preparation of the PC was a commercial silica sand with particle sizes ranging from 1.19 to 0.149 mm diameter.

PC samples containing CaO/SiO_2 molar ratios of 2.44, 1.33, 0.99, and 0.54 were prepared by thoroughly mixing the dry ingredients by hand and by subsequent mixing for 2 min. These compositions are given in Table II.

TABLE I Calculated chemical constraints of β-C_2S/class-H cement fillers

Constituent*	Concentration (wt%)
C_3S	27.5
C_2S	62.2
C_3A	1.4
C_4AF	7.2

*In the abbreviated formula $C \equiv CaO$, $S \equiv SiO_2$, $A \equiv Al_2O_3$, $F \equiv Fe_2O_3$; plus gypsum lime and alkali.

TABLE II Molar ratios of CaO/SiO$_2$ and compositions of polymer concrete

C/S ratio	Composition* (wt%)
2.44	13 % P–70 % sand– 0 % silica flour–17 % cement
1.33	13 % P–66 % sand– 4 % silica flour–17 % cement
0.99	13 % P–63 % sand– 7 % silica flour–17 % cement
0.54	13 % P–53 % sand– 17 % silica flour–17 % cement

*P ≡ 55 wt% styrene–36 wt% acrylonitrile–9 wt% TMPTMA; sand ≡ 50 wt% No. 16 sand (of size 1.19 nm) –25 wt% No. 30 sand (of size 0.595 nm)–25 wt% No. 100 sand (of size 0.149 nm); cement ≡ 50 wt% class-H cement –50 wt% β-C$_2$S.

2.2. Test method

Compressive strength tests were performed on PC specimens, originally measuring 2.20 cm in diameter and 4.40 cm in length, both before and after exposure to a simulated 25% geothermal brine for 20, 30 and 90 days in an autoclave at a temperature of 240° C. The measurements were performed in triplicate and the average values are listed in the figures and tables.

X-ray diffraction analysis was performed using the powder diffraction pattern method.

Differential thermal analysis measurements were performed with a DuPont 910 differential thermal analyser at a heating rate of 10° C min^{-1} in nitrogen gas. The samples for DTA analysis weighed between 12 and 15 mg and were crushed to a size small enough to pass through a 0.104 mm sieve. Samples were analysed after exposure for 90 days to a 25% brine solution at a temperature of 240° C.

Scanning electron microscopy observations were made to determine the microstructural features of hydrated calcium silicates produced on the organic polymer layers. The method of sample preparation involved fracturing a sample and, as soon as possible thereafter, depositing a gold film on the freshly fractured surface by evaporation and condensation.

3. Results and discussion

3.1. Compressive strength

The compressive strength of PC specimens after exposure to a 25% brine solution at 240° C for 0, 10, 30 and 90 days, respectively, and the rate of strength reduction obtained from a comparison of these results with those for unexposed specimens, are given in Figs 1 and 2, respectively.

The curves show decreasing strength after exposure in the autoclave for between 0 and 30 days and then a slow increase in strength between 30 and 90 days. Specimens containing different molar C/S ratios, with the exception of the 2.44 C/S-filled PC specimens, showed similar trends. The reduction in strength which occurs during the first 30 days is probably due to the hydrothermal decomposition of the co-polymer used as a binder. The tendency for strength to increase after exposure for 30 days is possibly due to the production of crystalline hydration products formed on the polymer layers together with a retarded rate of decomposition of co-polymer due to the formation of Ca-co-polymer-complexed PC.

The strength of 2.44 C/S-filled PC after exposure for 90 days was almost equal to that of PC after exposure for 30 days. This suggests that PC containing the relatively high 2.44 C/S ratio with no additional silica flour does not produce a significant amount of crystalline calcium silicate hydrates which would contribute towards an improvement in strength. The strength of unexposed PC specimens decreases with an increase in the absolute quantity of silica flour added to the PC because of air entrapment on the large surface area. As shown in Fig. 1, PC having the lowest C/S ratio, 0.54, and adjusted by the addition of silica flour has a strength that is approximately 13% lower than that for PC without silica flour and with a C/S ratio of 2.44 (91.0 MPa compared with 104.7 MPa, respectively). However, as seen in Fig. 2, the rate of strength reduction of PC after exposure for 10, 30 and 90 days decreases with decreasing C/S ratio. This means that the basic hydrated cement compounds which have a low strength are transformed by the reaction with fine silica into crystalline hydration products which yield high strength. The strength recovery of PC specimens containing C/S ratios of 0.99 and 0.54 occurring in the 30 to 90 day period is higher than that for PC with a C/S ratio of 1.33. A comparison of the strength reduction (~ 26%) for 1.33 C/S-filled PC after exposure for 90 days with that for 2.44 C/S-filled PC demonstrates that a C/S ratio of 1.33 has little effect on the strength recovery of PC.

3.2. XRD and DTA measurements

In order to investigate the hydrothermal reaction process and the hydration products yielded within

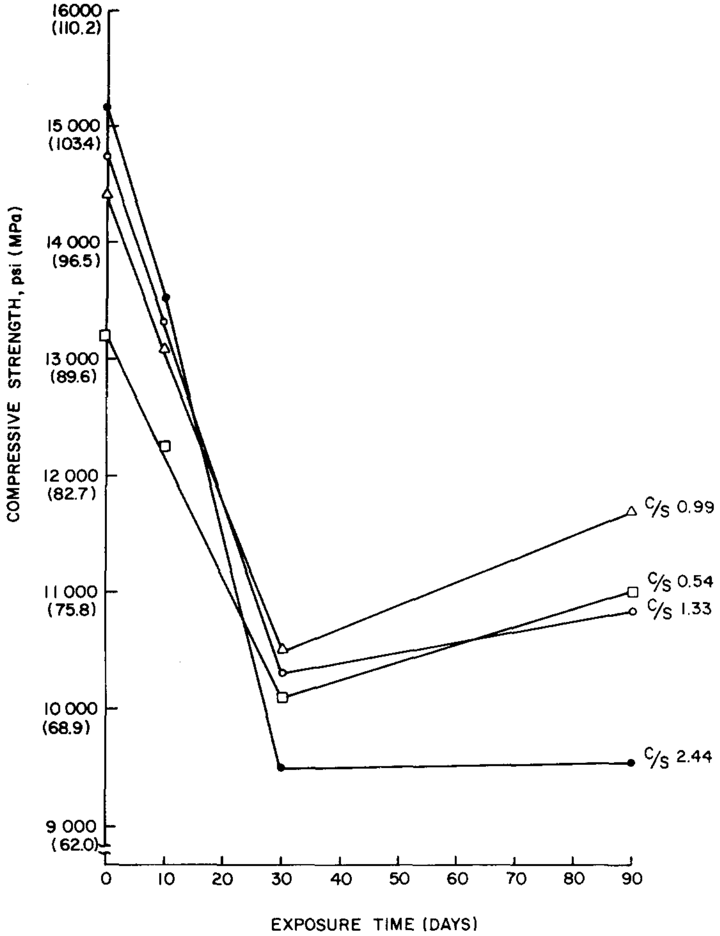

Figure 1 Compressive strength of PC containing various C/S ratios after exposure to a 25% brine solution at a temperature of 240° C.

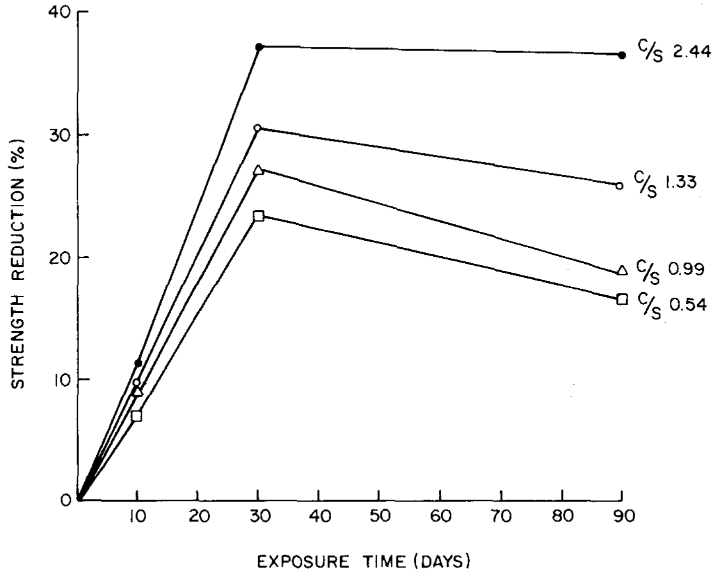

Figure 2 Compressive strength reduction plotted against exposure time in autoclave at 240° C for PC samples containing various C/S ratios.

the PC during exposure to hot brine, X-ray powder diffraction analyses were performed on the PC specimens containing various C/S ratios after exposure to hot brine for 10, 30 and 90 days. In addition, differential thermal analysis was used to investigate the thermal characteristics of the hydrated calcium silicate compounds having OH^- ions and H_2O molecules within the crystalline structure. Thus, the confirmation of hydrated calcium silicates present on the organic polymer surfaces was made by using DTA measurements with XRD analysis.

XRD patterns in the *d*-spacing range between 3.18 and 2.69 Å for PC specimens exposed to brine for 90 days are illustrated in Fig. 3. DTA thermograms for these specimens are shown in Fig. 4.

The data indicate that the strong reflections corresponding to *d*-spacings of 3.07 and 2.81 Å are produced when PC with a relatively low C/S ratio is exposed to hydrothermal conditions. The intensity of the bands at *d*-spacings of about 2.78 and 2.74 Å, which indicates the presence of anhydrous β-C_2S within PC, is reduced as the C/S ratio is lowered. In addition, XRD analysis of 0.99 and 0.54 C/S-filled specimens shows weak bands corresponding to *d*-spacings of 2.98 and 2.72 Å which are not apparent in 2.44 and 1.33 C/S-filled PC samples. Although not shown in Fig. 3, samples containing C/S ratios of 0.99 and 0.54 also exhibited a strong band corresponding to a *d*-spacing of about 1.82 Å, which seems to demonstrate that tobermorite is formed within the PC during long-term autoclave exposure.

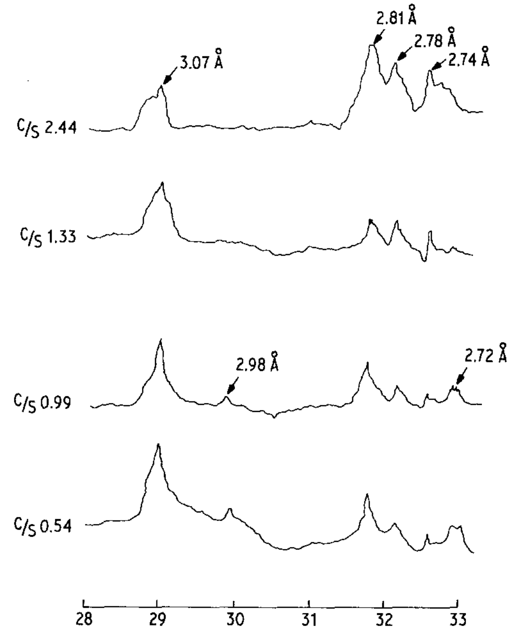

Figure 3 X-ray diffraction patterns representative of tobermorite and C–S–H(I) formed on organic polymer layers after exposure for 90 days to a 25 % brine solution at 240° C.

The spacings of 2.44 C/S-filled specimens were represented by wide, weak bands around 3 Å, and strong bands at 2.81, 2.78 and 2.74 Å. Weak bands at 3.27 and 2.41 Å, indicating the presence of α-C_2SH, were also observed on XRD analysis. Thus, the hydrated calcium silicate yield within PC having a C/S ratio of 2.44 after 90 days exposure in an autoclave is assumed quantitatively to consist of C–S–H(II) and α-C_2SH.

Generally, DTA thermograms of formed tobermorite are characterized by an exothermal peak at around 840° C [22]. Examination of the DTA thermogram of a 2.44 C/S-filled specimen, shown in Fig. 4, does not reveal the existence of an exothermal peak around 840° C. This means that PC having a C/S ratio of 2.44 does not yield tobermorite.

XRD of a sample with C/S ratio of 1.33 is characterized by the peak corresponding to a *d*-spacing of 3.07 Å becoming a sharper and narrower band than the equivalent peak for C/S ratio of 2.44, and with a greater intensity than that seen at 2.81 Å. The very weak bands corresponding to spacings of 3.27 and 2.41 Å also suggest that a little α-C_2SH together with other hydration products may exist. From the results showing lower band intensities corresponding to spacings of 2.78 and 2.74 Å, than are observed for specimens with C/S ratio of 2.44, it appears that the amount of residual anhydrous β-C_2S for C/S

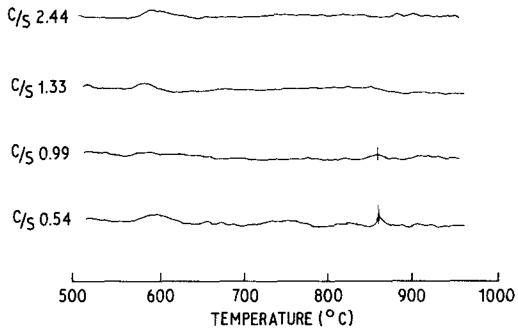

Figure 4 DTA thermograms of hydration products produced in PC after exposure for 90 days to a 25 % brine solution at 240° C.

ratio 1.33 decreases. Thus, the hydration products of C/S ratio 1.33 after exposure for 90 days seem to consist of C–S–H(I) as the main hydrated calcium silicate compound together with a little α-C_2SH.

From the XRD results of the samples with C/S ratio of 0.99, the peak corresponding to a *d*-spacing of 11.3 Å (not shown in Fig. 4), which identifies the formation of tobermorite, is very difficult to find after exposure for 90 days. However, as shown in Fig. 4, a small exothermal peak at about 860° C can be found on the DTA thermogram. Thus, the main calcium silicate hydrate formed during exposure for 90 days of PC having a C/S ratio of 0.99 is quantitatively presumed to be the semi-crystalline tobermorite-like C–S–H(I).

For C/S ratio of 0.54, XRD shows a weak band corresponding to a *d*-spacing of 11.3 Å. The data also indicate that the band intensities corresponding to 2.98 and 2.72 Å occupy approximately 20% and 30%, respectively, of the area of the peak at 3.07 Å (Fig. 3). DTA thermograms illustrate a prominent exothermal peak at about 860° C (Fig. 4). Thus, it is assumed that tobermorite formed by a hydrothermal synthesis occurring within PC having the C/S ratio of 0.54 has a highly crystalline structure. From the results for PC with C/S ratio of 0.54, the crystalline 11.3 Å tobermorite and semi-crystalline tobermorite [mainly as C–S–H(I)] were the main hydrates of calcium silicate yielded after exposure for 90 days in an autoclave at 240° C.

Fig. 3 also indicates that for anhydrous β-C_2S the peak intensities corresponding to 2.78 and 2.74 Å decrease with a lowering in C/S ratio. This phenomenon indicates a higher degree of hydrothermal reaction of anhydrous β-C_2S with an increase in silica flow content.

In order to obtain information regarding the amount of tobermorite X-ray peak intensities corresponding to a *d*-spacing at 3.07 Å of PC having a C/S of 0.99 and 0.54 were measured after exposure to a 25% brine solution at 240° C for 10, 30 and 90 days. Simultaneously, the residual anhydrous β-C_2S existing in PC was also quantified by the peak intensity corresponding to a spacing of 2.74 Å.

As illustrated in Fig. 5, the data indicate an increase in peak intensity corresponding to 3.07 Å and a decrease corresponding to 2.74 Å as the time in hot brine is increased. This means that the amount of tobermorite formed within the PC increases relatively with an increase in exposure time, and, conversely, the amount of anhydrous β-C_2S decreases. The data which indicate a relatively higher peak intensity at 3.07 Å for a sample containing C/S ratio of 0.54 than for one containing C/S ratio of 0.99 also suggested that the formation of tobermorite in the former is far easier than in the latter. It is presumed that, for samples with C/S ratio of 0.54, the quantity of tobermorite formed during the exposure time begins to be produced on the organic polymer layers after exposure for about 30 days, as noted from the results of relative intensity values of about 5, 19 and 30 after exposure in an autoclave for 10, 30 and 90 days, respectively. Therefore, a low strength reduction obtained from PC specimens having a low C/S ratio of 0.54 after exposure

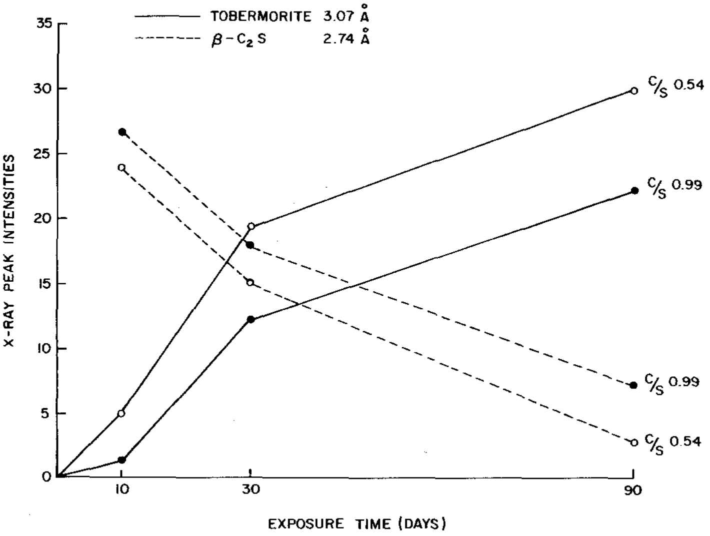

Figure 5 Variation in X-ray intensities (arbitrary units) of tobermorite (3.07 Å) and β-C_2S (2.74 Å) of PC with time of exposure to a 25% brine solution at 240° C.

for more than 30 days can be attributed to the formation of highly crystalline tobermorite which occurred as a binder of PC, taking place at the same time as the hydrothermal decomposition of co-polymer.

In the field of inorganic cement chemistry, generally, the optimum range of C/S ratio to produce tobermorite under high-pressure steam at a temperature of about 170° C is between 0.8 and 1.0 for $CaO-SiO_2-H_2O$ systems [23, 24]. However, when anhydrous cement–silica grains are covered with an organic polymer phase formed within PC, the hydrothermal synthesis of tobermorite at a lower 0.54 C/S ratio seems to be easier than at the higher C/S ratio of 0.83. Furthermore, the conditions required to form tobermorite within PC are an exposure time greater than approximately 30 days and a temperature above 170° C.

As seen in Fig. 5, at C/S ratios of 0.99 and 0.54, the amount of residual anhydrous β-C_2S decreases with increased exposure time. This is due to a hydrothermal reaction of the anhydrous β-C_2S, existing in PC, with the hot brine which penetrates into the PC because of thermal decomposition of the co-polymer binder. The hydration products may subsequently fill in any pores resulting from the thermal decomposition of the co-polymer.

The hydrated calcium silicate formed in this study was synthesized by exposure for 90 days to hot brine at 240° C. However, a very weak peak seen, corresponding to a *d*-spacing of 2.74 Å, for a C/S ratio of 0.54 after 90 days indicates that a little anhydrous β-C_2S still exists within the PC. Thus, to further study the hydrothermal reactions and the complete conversion of tobermorite into xonotlite and truscottite, which produces excellent hydrothermal stability [25, 26], hydrated calcium silicate compounds formed in an autoclave by exposure for times greater than 90 days at temperatures in excess of 240° C should be investigated.

The results described above show that an anhydrous cement–silica flour system having a low C/S ratio of 0.54 within the PC yields semi-crystalline C–S–H(I) together with highly crystalline tobermorite resulting from the hydrothermal reaction occurring during exposure to hydrothermal conditions. These calcium silicate hydrates are believed to have a great effect on the hydrothermal stability and the physical properties of PC during long-term exposure in an autoclave.

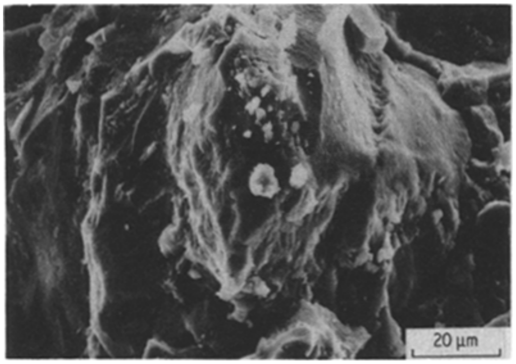

Figure 6 **Fractured surface of PC before exposure in an autoclave, showing a continuous layer of polymer connecting cement and aggregate.**

3.3. SEM study

The morphology and microstructure of C–S–H(I) and tobermorite formed on the amorphous polymer surfaces were observed by scanning electron microscopy observations of the fractured surfaces of PC specimens having a C/S ratio of 0.54 after exposure to hot brine for 90 days. Furthermore, in an attempt to investigate and identify the crystalline C–S–H(I) and tobermorite formed, the PC specimens containing monocalcium silicate (CS) and beta-dicalcium silicate (β-C_2S) fillers, adjusted by adding silica flour (of size $< 44\,\mu m$) to the C/S ratio of 0.54, were prepared by the same method as that used for PC containing cement–silica flour-type fillers. The PC specimens were exposed to a 25% brine solution at 240° C for 20 days, and then SEM and XRD measurements were performed for the clarification of hydrated calcium silicate compounds.

A micrograph of a fractured surface of an unexposed PC specimen is shown in Fig. 6. This fractured surface is characterized by a continuous layer of co-polymer connecting cement and aggregate. Thus, the anhydrous cement grains cannot be distinguished outright by their appearance. The sharply fractured surface apparent from the micrograph indicates that the PC is a brittle material.

The fractured surface of CS-filled PC specimen, after exposure for 30 days to a hot brine solution, is shown in Fig. 7. The electron micrograph shows that the morphological features of the crystalline hydration products produced by the hydrothermal reaction of the CS–silica systems are characterized by circular radiating and wrinkled foil-like crystals of about $20\,\mu m$ in diameter. These crystals were

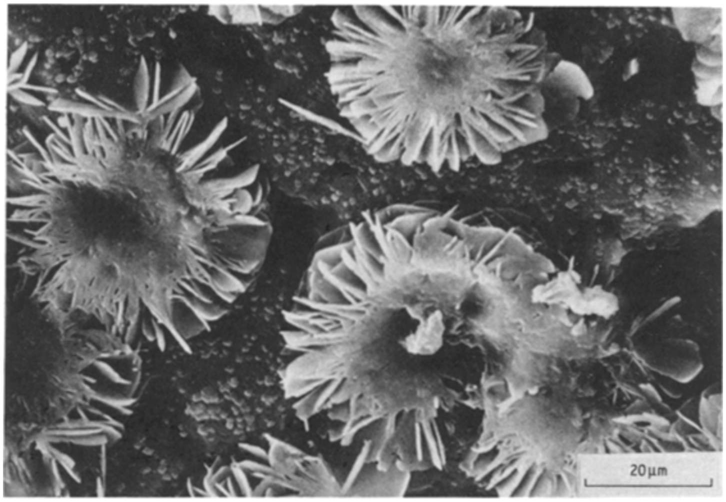

Figure 7 Circular radiating crystals of tobermorite formed within CS-filled PC after exposure for 30 days in an autoclave.

verified by XRD analysis to be 11 Å tobermorite. Fig. 8 shows a micrograph of a β-C_2S-filled PC sample after exposure for 20 days to the hot brine solution, illustrating the thin plates (A) and interlocking plates (B) of semi-crystalline C–S–H(I), about 5 µm in length, which are confirmed by XRD analysis to have formed on the amorphous polymer surface. The morphological features of these C–S–H(I) crystals are considerably smaller than those of tobermorite formed by the hydrothermal synthesis of CS-filled PC. The larger degree of crystallization of tobermorite than of C–S–H(I) seems to be due to the fact that the density of tobermorite crystal is 9% greater than that of C–S–H(I) (2.4 g cm^{-3} compared with 2.2 g cm^{-3}, respectively) [15]. This micrograph shows very interesting wrinkled foils and plate-like crystals, almost plant-like in appearance, growing from the Ca-co-polymer complexed polymer surface.

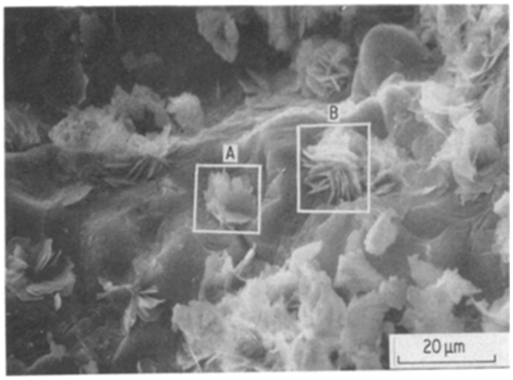

Figure 8 Thin plates (A) and interlocking plates (B) of C–S–H(I) formed within β-C_2S-filled PC after exposure for 20 days in an autoclave.

The fractured surface of PC containing a C/S ratio of 0.54 as a cement filler, after exposure for 90 days to the hot brine solution is shown in Fig. 9. The micrograph shows the hydration crystallization to consist of two different crystal types: circular radiating and large blocking crystals about 20 µm in diameter (C), and interlocking crystals composed of thin plates about 5 µm in length (D).

The circular radiating crystal (C) is morphologically very similar to the crystal structure of 11 Å tobermorite, of about 20 µm in diameter, observed on CS-filled PC (for example in Fig. 7) and it is concluded that it is in fact formed of 11 Å tobermorite. The crystalline interlocking plates (D) correspond to those of C–S–H(I) (for example Fig. 8(B)) formed by the hydrothermal reaction of β-C_2S-filled PC.

Comparison of the crystalline morphologies of C–S–H(I) formed by 20 and 90 day exposures to the hot brine solution reveal that the interlocking plates produced after 90 days represent well-crystallized C–S–H(I) consisting of thin plates that join together more tightly than the looser-fitting plates existing after exposure for 20 days. The growth process of C–S–H(I) that occurs with an increase in processing time may be presumed to progress as follows. The initial morphological forms, Fig. 8(A), appear to consist of thin plates of C–S–H(I) crystal which rise to the organic polymer surface to become a massive structure, Fig. 8(B). With increased exposure time, the morphology changes to one of interlocking plates, Fig. 9(D), of well-crystallized C–S–H(I). It is very interesting that the growth process of crystal-

Figure 9 Circular radiating crystals (C) and interlocking plates (D) formed on the amorphous polymer surfaces of 0.54 C/S-filled PC after exposure for 90 days in an autoclave.

line hydration products can be easily observed on the amorphous organic polymer surface. However, there was no evidence in this SEM study of a conversion of C–S–H(I) crystals to tobermorite crystals.

As seen in Fig. 9, the quantitative ratios representing C–S–H(I) and tobermorite in this micrograph were determined by microscopical observation to be approximately 70% and 30%, respectively. The formation of C–S–H(I) and tobermorite, determined from the crystal morphology of PC having a C/S ratio of 0.54, described above, is confirmed by the results obtained from XRD analysis.

4. Conclusions

Anhydrous cement-type fillers prepared by mixing silica flour (of particle size less than 44 µm) with cement (according to a β-C_2S/class-H cement ratio of 1 : 1) were shown to have a significant effect on the hydrothermal stability of organic polymer concretes after long-term exposure in an autoclave at 240° C. The cement fillers, adjusted by the addition of silica flour to polymer concrete with a low CaO/SiO_2 ratio of 0.54, produced C–S–H(I) and tobermorite crystals within the PC after exposure to a hot brine solution in an autoclave for about 30 days. These calcium silicate hydrates contributed to the strength recovery of the PC itself by restraining thermal decomposition of the polymer binder and thus preventing an extreme strength reduction in the PC. However, for PC specimens containing cement with a high CaO/SiO_2 ratio of 2.44, the hydrated calcium silicate, yielded by the hydrothermal reaction of cement occurring during exposure in an autoclave, seems to have a very poor crystalline structure.

It was observed by electron microscopy that the morphology of highly crystalline 11 Å tobermorite, produced in a PC having a CaO/SiO_2 ratio of 0.54 after exposure for 90 days to a solution of hot brine in an autoclave, consisted of circular radiating crystals of approximately 20 µm diameter. The C–S–H(I) crystals which are considerably smaller than those of tobermorite are characterized by interlocking structures composed of thin plates, of about 5 µm in length. The C–S–H(I) converted gradually into tobermorite with increasing processing time in an autoclave at 240° C.

Conditions required for the formation of highly crystalline tobermorite on the amorphous polymer surfaces seem to be exposure to hot brine at a temperature greater than 200° C for a time greater than 30 days at a low CaO/SiO_2 ratio of about 0.54.

Materials having β-C_2S to class-H cement to silica flour ratio of 1 : 1 : 2 were identified as an anhydrous cement–fine silica system filler of PC for application of hydrothermal environment at elevated temperatures.

In order to study the complete conversion of tobermorite into xonotlite and truscottite, an investigation of calcium silicate hydrates formed in an autoclave after exposure times greater than 90 days and temperatures greater than 240° C is in progress.

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