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Controlled Rate Thermal Treatment of Reactive Powder Concretes

A. Feylessoufi,* M. Crespin,† P. Dion,† F. Bergaya,† H. Van Damme,†
and P. Richard*
**Laboratoire des Matériaux, Groupe Bouygues, Direction Scientifique, Challenger, Saint Quentin-Yvelines; and †Centre de Recherche sur la Matière Divisée, CNRS and Université d'Orléans, Orléans, France*

Controlled rate thermal analysis (CRTA) was applied to the thermal curing of a reactive powder concrete. Heating was adjusted to keep the rate of gas evolution constant and in dynamic equilibrium at a pressure of 3 Pa. In this way, all internal gradients were kept constant and homogeneous samples were produced. Six different solid-state transformations were detected below 900°C, four of them occurring below 250°C. Under these conditions, no xonotlite or other crystalline silicate hydrates were detected even up to temperatures of 250°C, contrary to what is observed when heating is carried out in regular, nonkinetically controlled conditions, which generate local hydrothermal water vapor pressures inside of the samples. Our results show that controlled rate thermal treatment in dynamic equilibrium with fixed water vapor pressures is a promising method for the accurate control of hydrate crystallization. ADVANCED CEMENT BASED MATERIALS 1997, 6, 21–27. *© 1997 Elsevier Science Ltd.*

KEY WORDS: Concrete, Controlled rate thermal analysis, Curing, Infrared spectroscopy, Reactive powder concrete, ^{29}Si nuclear magnetic resonance, Xonotlite

Thermal curing is a classical method of improving the mechanical properties of cement based materials [1]. The most important effects are better crystallization of the hydrates and activation of the pozzolanic reaction of the silica fillers. How this leads to improvement of the mechanical properties is still unclear, but the effect is undoubtedly beneficial in most cases. In hydrothermal conditions, the reaction of lime with silica leads to the formation of tobermorite at temperatures below 200°C and to truscottite, gyrolite, xonotlite, and hillebrandite at higher temperatures, depending on the CaO/SiO_2 ratio [2,3].

It has recently been shown that by the concomitant improvement of several parameters such as particle-size homogeneity, porosity, and microstructure, concretes with compressive strengths ranging between 200 and 800 MPa, breakdown energies between 1200 and 40,000 J/m^2, and ultimate tensile strain before fracture on the order of 1% could be prepared [4]. This was achieved by reducing the size of the largest aggregates, lowering the water/cement ratio, and, for some special uses, pressing or introducing reactive quartz into the formula. High-temperature curing led to further and dramatic improvement. This family of materials was called reactive powder concrete (RPC).

Xonotlite was found to be one of the major crystalline hydrates in RPC elaborated at high temperature [5]. Xonotlite has an H/C ratio (1/6) much smaller than that of the usual calcium silicate hydrates (CSH) formed in normal conditions ($\cong$1), which goes along with the intense dehydration of RPC. X-ray diffraction analysis performed on fragments of cured concrete samples showed that xonotlite does not form on the edges of the samples, which suggests that the vapor from the dehydration process generates local hydrothermal conditions in the internal parts of the sample. How this heterogeneous distribution of crystalline products affects the mechanical performance still has to be established.

In this article the applicability of a particular type of thermal treatment to control the generation of xonotlite and other crystalline hydrates is explored, using controlled rate thermal analysis (CRTA) in its preparative mode for that purpose [6]. The principle of the method is to control the heating by a kinetic parameter X and to *measure* the temperature–time, T–t, curve rather than *imposing* it by a pre-established (and most often linear) temperature program. CRTA is, in some sense, the opposite of conventional thermal analysis, in which the T–t curve is imposed and the time evolution of some property X (mass, as in thermogravimetry, or the quantity of evolved gases) is recorded. The special interest of using a kinetic parameter to control the temperature rise lies in the fact that all the gradients of

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Address correspondence to: A. Feylessoufi, Laboratoire des Matériaux, Groupe Bouygues, Direction Scientifique, Challenger, 1 avenue Eugène Freyssinet, 78061 Saint Quentin-Yvelines cedex, France.

Received October 16, 1995; Accepted March 7, 1997

655 Avenue of the Americas, New York, NY 10010

ISSN 1065-7355/97/$17.00
PII S1065-7355(97)00006-0

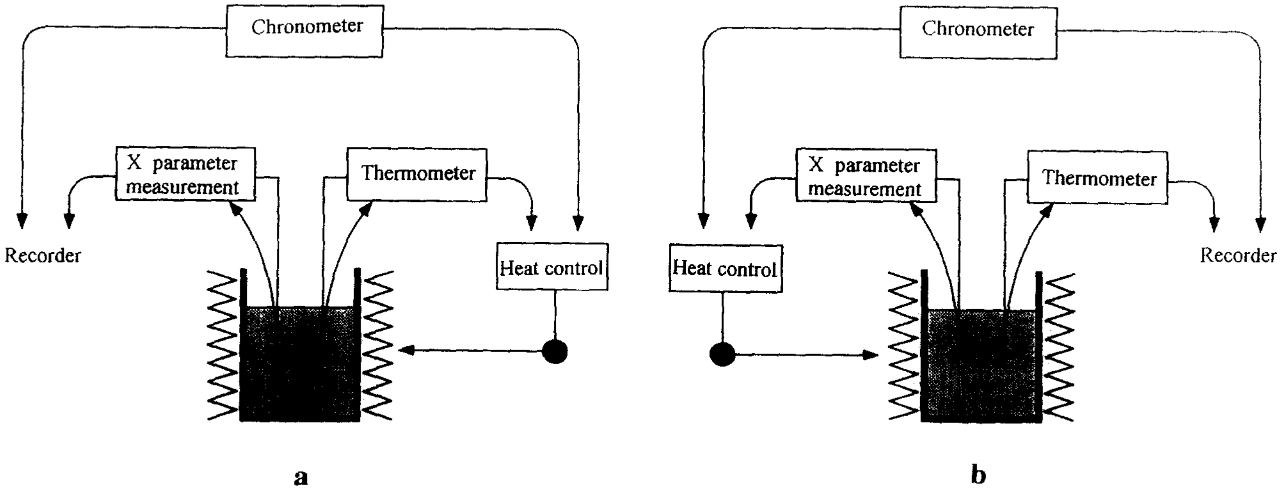

FIGURE 1. Schematic comparison between the conventional TGA method (a) and the CRTA method (b).

temperature, partial pressure, evolved gases, etc., which originate from the reaction itself, are also controlled indirectly [7]. Thus, the reaction takes place within the whole sample and the local heterogeneity of the reaction conditions is limited by the size of the grains or crystallites of the material and not by the size and shape of the whole sample or container. In this case, the rate of gas evolution is used as a kinetic control parameter, to control as accurately as possible the homogeneity of the water vapor pressure distribution within the RPC sample. As will be shown, this technique appears to be an effective tool in the control of the formation of the crystalline silicate hydrates.

Experimental Methods

Materials

The RPC used in this study was prepared from the following components (mass ratio with respect to cement): type V Portland cement; fine sand, 150 to 400 μm (1.1); undensified silica fume, 18 m^2/g (0.25); polymelamine superplasticizer (0.044); and water (0.15). The concrete was mixed, cast, and vibrated like conventional concrete. Dry concrete powder components are mixed for 3 to 5 minutes, water is added with half of the volume of the superplasticizer and mixed for 3 minutes, and the second half of the volume of the superplasti-

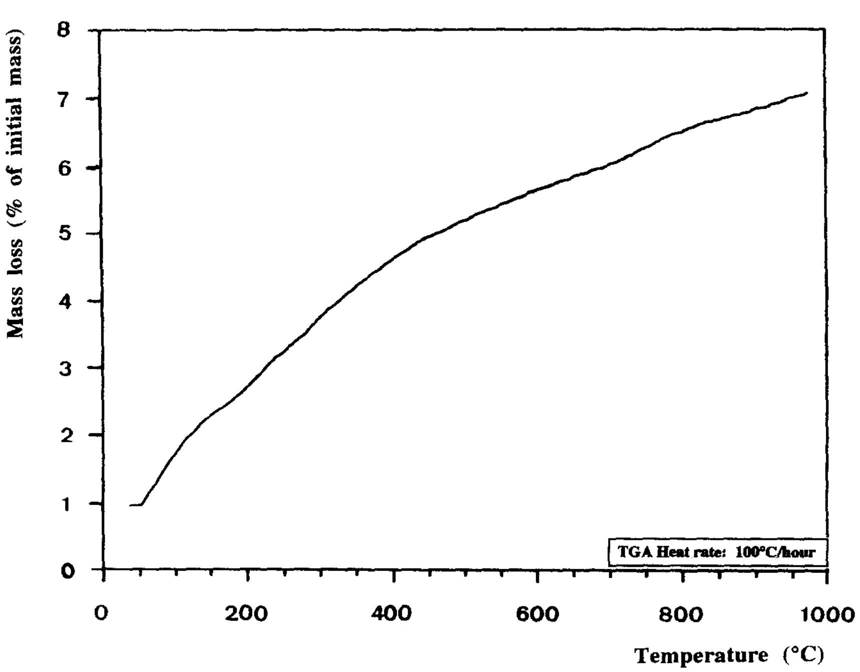

FIGURE 2. TGA curve of an RPC heated at 100°C per hour in vacuum.

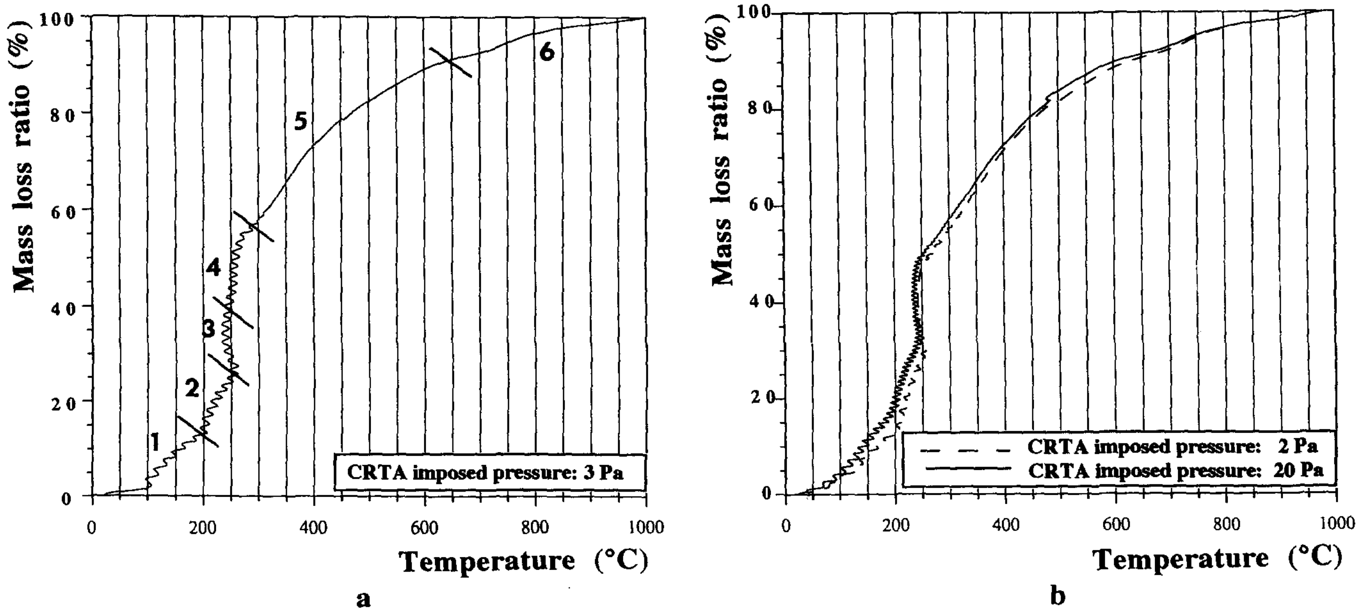

FIGURE 3. Determination of six different reaction domains by CRTA of RPC samples: (a) CRTA curve at a pressure of 3 Pa; (b) CRTA curves at pressures of 2 Pa and 20 Pa.

cizer is added and mixed for 5 minutes. The cylindrical samples were 70 mm in diameter and 140 mm long. The following mild curing treatment was applied to stabilize the mechanical and physical properties of the specimen: in water at 20°C for 7 days; in water at 90°C for 4 days; and air-drying at 90°C for 2 days. After curing, the samples had a density of 2.47 mg $\cdot$ cm^{-3}. No additional high-temperature curing treatment was applied before the CRTA experiments. The following mechanical properties were measured on specimens from the same mixture and mild curing treatment: 240 MPa average compressive strength (Perrier machine); 59 GPa dynamic Young modulus; and 0.16 Poisson ratio (Grindosonic instrument).

Controlled Rate Thermal Treatment

Home-made CRTA equipment was used for this purpose (Figure 1). In practice, the sample is kept in a vacuum-tight thermal reaction chamber equipped with a pressure gauge and connected to a high-vacuum manifold (turbomolecular pump) through a leak diaphragm and a vacuum valve. The evolved gases are continuously evacuated through the leak. The heating rate is adjusted to keep the pressure drop through the leak diaphragm constant. A residual pressure of 3 Pa was maintained in the reaction chamber. This imposes a very low gas extraction rate in our system: 7.2 10^{-6} L $\cdot$ s^{-1}, which corresponds to 3.2 mg of water per hour for 1 g of sample (note that the evolved gases are also expected to contain the volatile decomposition products of the superplasticizer and carbon dioxide). The samples were 0.5- to 1-g fragments from the master cylindrical pieces. The vacuum chamber/sample size is about 5. This size is only chosen to obtain the correct sensitivity for the observed phenomenon. Due to the constant rate of gas evolution, the recorded T–t curve may be converted to a weight loss versus T curve, provided the total weight loss is measured at the end of the experiment. Alternatively, it may also be converted into a degree of mass loss (α) versus T curve.

Diffraction and Spectroscopy

All investigations were performed on powdered samples obtained by crushing the fragments of RPC after thermal treatment. The powder X-ray diffraction spectra were obtained on a D500 Siemens diffractometer with Cu Kα radiation at 0.154 nm and a nickel filter of classic thickness (0.02 mm). The spectra were obtained after 20 hours under the X-ray beam to obtain an appropriate signal/noise intensity. The infrared spectra were recorded on a Nicolet FTIR instrument. The ^{29}Si MAS NMR spectra were recorded with a Bruker MSL360 solid-state spectrometer at 8.4 T, using a double-bearing probehead spinning at 3.5 to 4.1 kHz in the following typical acquisition conditions: frequency, 71.5 MHz; spectral width, 83.3 kHz; pulse duration, 2 μs; recycle time, 30 s (optimized pulse width/recycle time ratio on natural samples), with at least 400 to 500 accumulated scans, using single-pulse excitation with phase cycling.

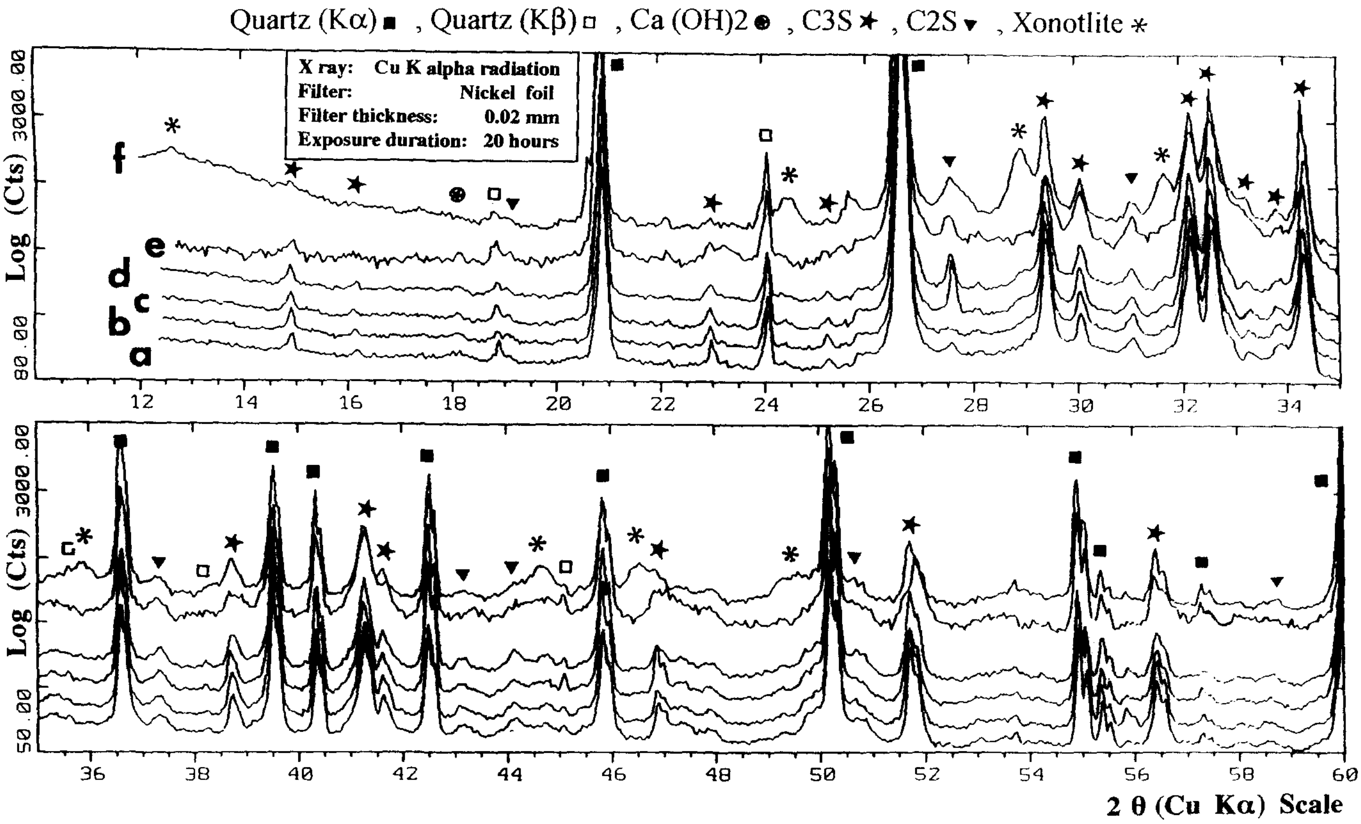

FIGURE 4. X-ray diffraction diagrams of RPC samples: (a) starting material; (b) heated at 200°C by CRTA; (c) heated at 250°C by CRTA; (d) heated at 300°C by CRTA; (e) heated at 800°C by CRTA; (f) rapidly heated in an oven at 300°C.

Results and Discussion

This article focuses on the comparison of the samples heat-treated in conditions of controlled rate of gas evolution with those heated in "regular" conditions. Three heating modes were used. The most ill-controlled and brutal way was to put the sample inside an oven preheated to temperature of 300°C. The second mode was to heat the sample in a conventional thermogravimetric analysis (TGA) apparatus in vacuum, heated at a rate of 100°C per hour. The third mode used the CRTA equipment.

The TGA curve shown in Figure 2 does not present distinct features. Note that there is no portlandite in the specimen, and thermal events linked to its decomposition were not observed. This is in accordance with published results [5] on RPC: the portlandite is present in small quantities in RPC at 20°C and disappears completely after a curing treatment of 48 hours at 90°C. A total mass loss of 6.8% was obtained at 900°C, to which a 1% initial loss when the sample is outgassed at room temperature has to be added. Only slight slope changes are observed. One may eventually identify three domains: below 200°C; from 200°C to 700°C; and from 700°C to 1000°C.

In comparison, the two CRTA curves shown in Figure 3 contain much more information. The virtually identical shape of the curves, obtained on different samples and with different pressures (2, 3, and 20 Pa), also shows the remarkable reproducibility of the results. The noise that eventually can be observed in some curves comes from oscillation of the heat control mechanism. It seems that the thermoanalytical CRTA curve is only characteristic of the material studied. Six domains may clearly be detected. The two domains at high temperature (domains 5 and 6, above 300°C) resemble those observed in traditional TGA. The most characteristic features appear below 300°C, i.e., in the temperature range where the curing of RPC is usually performed. Domain 1, below 200°C, and domain 2, between 200°C and 250°C, have the same shape as the high-temperature domains. The intermediate domains (domains 3 and 4) have a different shape (clearly for domain 3, less clearly for domain 4) and appear in a very narrow temperature range, around 250°C and between 250°C and 300°C, respectively. The total mass loss at 900°C is 6.8%, in excellent agreement with the TGA result. The intermediate equilibrium mass losses are 2.4% at 200°C, 3.6% at 250°C, and 4.3% at 300°C.

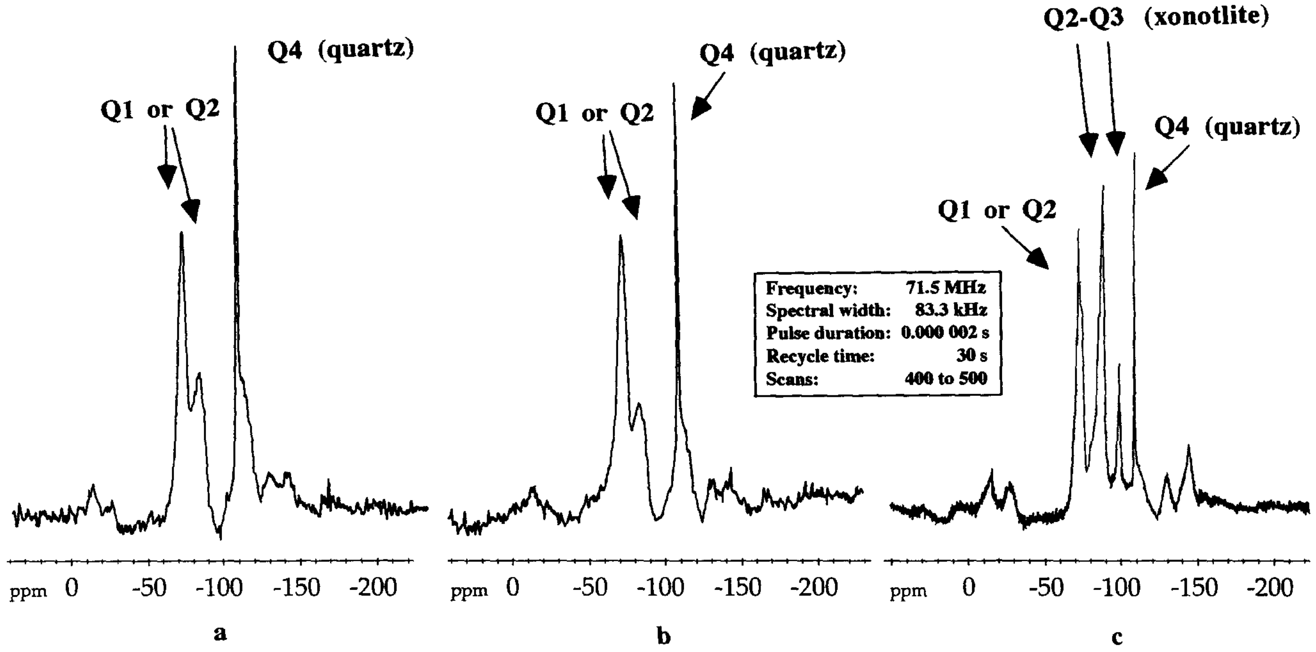

FIGURE 5. ^{29}Si MAS NMR spectra of RPC samples: (a) starting material; (b) heated at 300°C by CRTA; (c) rapidly heated in an oven at 300°C.

According to the well-established relation between some classic solid-state reaction mechanisms [8] and the shape of CRTA curves [9], the six domains may be associated with the three general classes of reaction mechanisms. Domains 6, 5 and, probably, 1 have the sigmoidal shape characteristic of a two- or three-dimensional diffusion mechanism. Domains 2 and, probably, 4 correspond to a mechanism involving the inward motion of an interface. Domain 3, with its characteristic "c" shape (the temperature decreases to maintain the pressure), may reveal a nucleation and growth process. It may tentatively be attributed to the dehydration of a complex of gypsum, probably the hydrated calcium monosulfoaluminate whose dehydration is known to begin at about 200°C to 250°C. The SO_3 level obtained by chemical analysis of the cement used for this RPC is about 2.19%, and successive reactions of gypsum with C_3A and water generally lead to the formation of the hydrated calcium monosulfoaluminate.

It also seems that the decomposition of the organic superplasticizer does not result in any change in the shape of the curve. A mass spectrometer analysis while heating a similar RPC in powder form, [10] shows that the decomposition of superplasticizer begins after 300°C and continues over a wide temperature range, probably due to complex formulation of the superplasticizer. Therefore, the organic superplasticizer decomposition is not considered to modify the shape and delimitations of the different CRTA domains and their relation with reaction mechanisms.

Even if some special and ideal solid-state mechanisms are already computed [7] to find the shape of CRTA curves in relation to a precise mechanism, it is clear that different mechanisms also can give the same CRTA shape. In this state of the art, it is not possible to identify the different mechanisms by the shape of the CRTA curve alone. Nevertheless, as will be shown, CRTA can provide information that is not detectable by other experiments.

In fact, this set of transformations detected by CRTA is *not* paralleled by changes in the X-ray diffraction diagram. Figure 4 shows the diagrams obtained with CRTA samples when the heating was stopped at different temperatures. No significant difference could be detected between the starting RPC samples and those treated by CRTA at 200°C, 250°C, and 300°C. The diffraction diagram is dominated by the α- and β-quartz peaks, and only a very minor broadening of some peaks attributed to C_3S could be detected. Neither xonotlite nor tobermorite was detected.

The absence of significant modification was also noticed in the ^{29}Si MAS NMR spectra (Figure 5). The spectrum obtained with the RPC treated at 300°C by CRTA is virtually undistinguishable from the spectrum of the starting material. Three main peaks are observed at -72, -83, and -107.8 ppm. While the latter is clearly due to Q^4 species, i.e., to silicon atoms linked via siloxane bridges to four other silicon atoms, the two former may be due either to Q^1 or Q^2 (silicon tetrahedra with one or two siloxane bridges, respectively) species

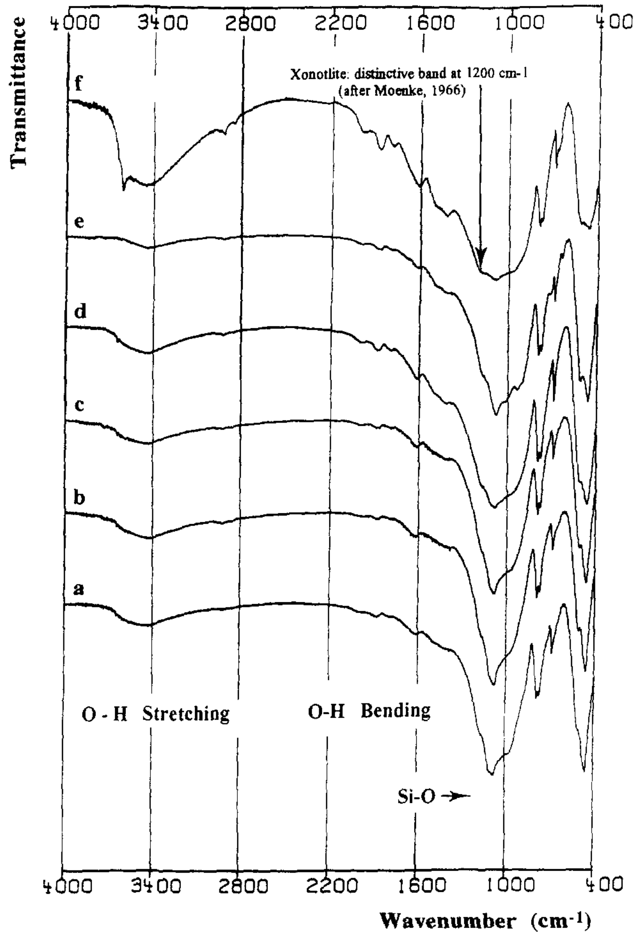

FIGURE 6. Evolution of the FTIR spectrum of RPC heated by CRTA at increasing temperature: (a) starting material; (b) heated at 200°C by CRTA; (c) heated at 250°C by CRTA; (d) heated at 300°C by CRTA; (e) heated at 800°C by CRTA; (f) rapidly heated in an oven at 300°C.

[11]. The Q^4 species may be attributed to quartz, whereas the Q^1 and Q^2 species may be attributed to dimers or linear chains of CSH [12,13].

Infrared spectroscopy reveals greater differences (Figure 6). The first and trivial one is the decrease of the bands due to water, both in the high-frequency OH stretching region (3800 to 2800 cm^{-1}) and in the medium frequency HOH bending region (1605 cm^{-1}). The most striking evolution appears at 1480 cm^{-1}. This band, which is barely present in the starting material, appears clearly at 200°C. It decreases back to its initial weak state at 250°C and 300°C, and finally reappears at 800°C. A smaller band at 1428 cm^{-1}, which may be attributed to carbonate species, appears in the spectrum of the starting material. It remains up to 300°C but disappears at 800°C. Subtle differences may also be detected in the domain below 1200°C, the absorption region of the Si-O stretching modes. The Si-O-Si band at 1107 cm^{-1} decreases slightly, whereas the $Si\text{-}O^-$ band at 1082 cm^{-1} increases slightly. Both modifications indicate limited reorganization of the silicate compounds.

The last point of comparison is the sample heated in the most brutal conditions, i.e., in a oven preheated to 300°C. As pointed out previously, this type of heating is expected to induce high water vapor pressures inside the sample due to the combination of rapid dehydration and limited diffusion. As shown in Figures 4f and 7f (X-ray diffraction spectra in the region of the main xonotlite peak) and in Figure 6f (infrared spectrum with a peak at 1200 cm^{-1}), xonotlite is present [14] and formed in those conditions. This observation is also confirmed by the ^{29}Si MAS NMR spectroscopy of Figure 5c in which two new peaks at −86 and −97 ppm correspond to the Q2 and Q3 species of xonotlite [11].

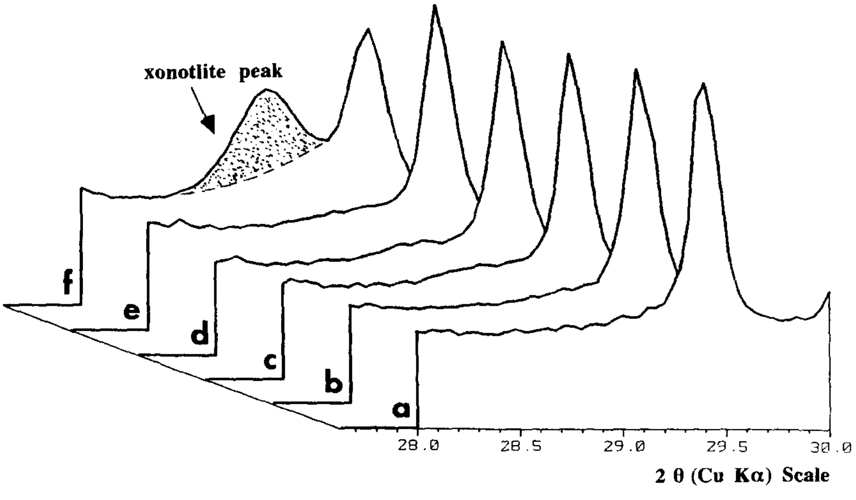

FIGURE 7. Comparison of the x-ray diffraction spectra in the region of the main xonotlite peak: (a) starting material; (b) heated at 200°C by CRTA; (c) heated at 250°C by CRTA; (d) heated at 300°C by CRTA; (e) heated at 800°C by CRTA; (f) rapidly heated in an oven at 300°C.

The xonotlite formation in those conditions is in accordance with what is observed when large test pieces (or beams) of RPC are cured at high temperature.

Conclusion

It has been confirmed that xonotlite formation in thermally cured RPC is due to local, large water vapor overpressures. The data show that kinetically controlled heating at low (3 Pa) dynamic equilibrium vapor pressures may totally suppress the formation of crystalline hydrates. As a result, it should be possible to develop what might be called "kinetically controlled thermal curing" and a fine control of hydrate crystallization, by imposing larger dynamic equilibrium pressures. On the other hand, it is seen that this kind of analysis can provide information that is not detectable by classic experimentation, and complex pressure-temperature thermodynamics in phase formation can be detected, especially those linked with the formation or dehydration of CSH in cement based materials. The latter point also has a practical implication for the curing treatment of large RPC beams: one can identify the temperature domains of substantial gas release and monitor the temperature increase during the curing process to avoid high pressure and damage inside the concrete.

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