Dehydration and rehydration processes of cement paste exposed to high temperature environments

C. ALONSO, L. FERNANDEZ
Institute of Construction Science "Eduardo Torroja" (C.S.I.C.), Serrano Galvache No 4, 28033 Madrid, Spain
E-mail: mcalonso@ietcc.csic.es

Microstructural changes of an OPC cement paste after being exposed at various elevated temperatures and further rehydration have been evaluated using ^{29}Si MAS-NMR. Thermogravimetry and XRD are also employed to complement the information. NMR studies of cement paste exposed to high temperatures demonstrate a progressive transformation of C-S-H gel that leads at 450°C, to a modified C-S-H gel. For temperatures above 200°C to a progressive formation of a new nesosilicate. At 750°C, the transformation of C-S-H is complete into the nesosilicate form with a C_2S stoichiometry close to larnite, but less crystalline. Also is observed an increase of portlandite that takes place up to temperatures of 200°C. A progressive increase of calcite formation up to 450°C is noticed. The ettringite disappearance below 100°C is confirmed and the portlandite and calcite are converted to lime at 750°C. The initial anhydrous phases as larnite and brownmillerite remain unaltered during heating. Rehydration of the heated samples (450 and 750°C) shows recrystallization of calcite, portlandite and ettringite, and the C-S-H reformation from the new nesosilicate. The larnite and brownmillerite remain unaltered during rehydration. The developing of damaged due to the formation of microcracking is detected and improved because of rehydration phenomena. © *2004 Kluwer Academic Publishers*

1. Introduction

Fire is a risk for concrete structures because concrete is not stable at high temperatures and chemical/physical transformations in aggregates and paste are developed, which finally results in alteration of mechanical properties [1]. The main chemical process responsible for the internal damage of concrete is the alteration of hydrates [2]. A sequence of events takes place during heating, being the release of water vapor the main consequence, coming from vaporization of moisture, and transformation of C-S-H, dehydration of calcium hydroxide [3] and ettringite, this last occurring below 100°C [4–9].

Lack of knowledge has been published on the transformations of C-S-H occurring during heating [10–13]. Recently, Shaw *et al.* [10, 11] used synchrotron radiation (SR) to deal with the dehydration mechanism during heating of various natural C-S-H minerals with crystalline structure: tobermorite and xonotlite transforms into wollastonite, while hillebrandite evolves to larnite on cement pastes. Castellote *et al.* [12, 13], employed *in-situ* neutron diffraction experiments (ND) during heating up to 620°C, and confirmed that the ettringite losses its crystalline form around 80°C, the crystalline phases of C-S-H, as tobermorite, transforms around 400°C. Also noticed that portlandite is destroyed during heating after 510°C, and partially recovered during cooling within different crystalline phase.

But most microstructural studies on the stability at high temperatures of cement paste [3, 14–17] are performed after cooling (i.e., at room temperature). Besides, in the case of dehydration process as consequence of heating studies are focused on porosity or compositional changes using XRD, SEM, ND or TG [3, 12, 14–17], but there is a lack of studies on the evolution of C-S-H, using ^{29}Si MAS-NMR [18], although most of C-S-H in paste is amorphous, or poorly ordered [19], and represent about 60% of the cement paste.

When fired concrete is exposed after cooling to moist air, rehydration processes take place in cement paste, that together with the changes in volume, and mass may lead to an additional increase in porosity and to the formation of additional cracking to that occurring during heating [20].

This paper includes results obtained from a cured cement paste submitted to various elevated temperatures. The aim is to identify the microstructural changes concerning mineral transformations as a function of temperatures (100, 200, 450 and 750°C) using mainly ^{29}Si MAS-NMR and supporting with information from X-ray Diffraction and Thermogravimetric analyses, also employed to complete the full compositional microstructure picture, in order to increase the understanding of process of cement paste degradation at high temperatures.

TABLE I Chemical composition of the cement

Chemical analysis (%)	L.O.I	IR	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	CaO (free)
Cement	3.59	0.58	19.60	4.43	4.27	62.61	0.95	3.29	0.11	0.28	1.92

The effect of humidity on dehydrated cement paste is later considered and the microstructure changes in solid phases are addressed.

2. Experimental section

2.1. Sample preparation

Cement paste specimens were prepared by mixing Ordinary Portland Cement (OPC) with distilled water, using a $w/c = 0.4$. A cement type 42.5MR-SR was employed for the testing program, whose chemical composition is given, in Table I. The cement has low C_3A (<1%) and low alkaline content (0.42 Na_2O eq.). The fluid paste was introduced in cylindrical plastic tubes of 23 mm in ϕ and 30 mm in height. The samples were sealed and cured for 70 days at room temperature ($20 \pm 2°C$) inside the tubes, so no additional water gain was allowed during hydration.

2.2. Heating procedure

After this curing period, the specimens were submitted to the selected heating regime up to reach a maximum of four temperatures (T_c): 100, 200, 450 and 750°C. One sample was kept sealed without heating, as reference, up to the characterization analysis was performed.

The heating process was pursued in several steps that are summarized in Fig. 1:

1. Each specimen was placed into the furnace and was heated at a heating rate of 1°C/min, starting from room temperature ($20 \pm 2°C$).

2. When the desired temperature (T_c) was reached (200, 450 or 750°C), the samples were kept 2 h into the furnace at T_c in order to homogenize the temperature in the specimen and allow the respective transformation to occur.

3. After this time, the heating was stopped and the specimens were maintained in the furnace for slow cooling down up to room temperature.

The weight loss of each heated sample was registered by weighing each sample before and after heating (Table II).

The heating regime for the specimen at 100°C was different. This specimen was introduced into the furnace directly at 100°C and maintained inside till
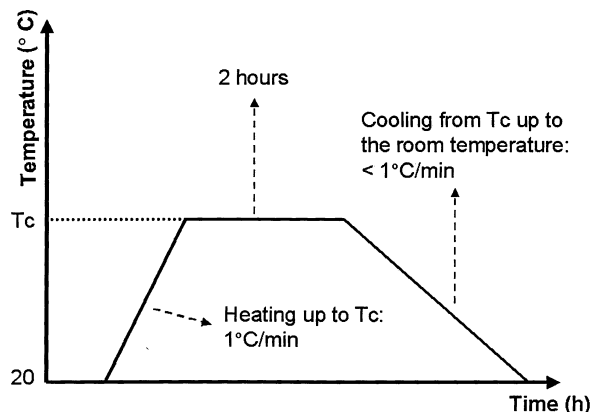

Figure 1 The heating process applied to the cement paste for $T_c = 200$, 450 and 750°C.

reaching a constant weight loss. Then, heating was stopped and the specimen was kept into the furnace with slow cooling down to room temperature.

Once the cooling process finalized, the specimens were covered with a plastic film and kept into a desiccator to avoid contact with the atmosphere and further up take of humidity or carbonation, before characterization test.

Rehydration process was also studied in the specimens heated at ($T_c = 450$ and 750°C) by placing them into a saturated chamber (100% R.H) at room temperature for $3\frac{1}{2}$ months.

2.3. Characterization techniques

- X-ray Diffraction (XRD) was used to identify the crystalline phases. XRD data were recorded using a Phillips PW1820, powder diffractometer with Cu K_α radiation. The goniometer speed was 0.020°/s. Software from Phillips has been used to the characterization of the mineralogical crystalline phases.
- A Netzsch simultaneous analyzer, model STA 409 was used to obtain thermogravimetric (TG) and differential thermogravimetric analysis (DTA) curves of the specimens. The heating ratio was 4°K/min in a nitrogen atmosphere flowing at 100 cm^3/min. The analyzed mass per specimen was about 50 mg.
- ^{29}Si MAS NMR spectra were recorded at the ^{29}Si resonance of 59.572 MHz using a Varian VXR

TABLE II Weight loss of samples after each high temperature experiment

Samples	Constant weight loss		Heating process (by using the cycle from Fig. 1)			
	$T_c = 100°C$	$T_c = 200°C$	$T_c = 100°C$	$T_c = 200°C$	$T_c = 450°C$	$T_c = 750°C$
Weight loss of samples (%)	19.1	13.2	22.2	15.3	24.4	32.0

300 S spectrometer, with a spinning speed of 4 kHz in a double bearing 7 mm ZrO_2 rotor. Spectra were accumulated using Bloch decay pulse sequences of $\Pi/2$ and high power ^1H decoupling with a 60 kHz radio frequency field. A recycle time of 59 s was used. The number of scans was 1000. Tetramethylsilane (T.M.S, $Si(CH_3)_4$) was used as reference. The spectra were simulated using a modified version of the Winfit program [21].

3. Results

3.1. Weight losses of heated specimens

As commented before, the transformations induced by heating in the cement paste goes to a weight loss from the evaporation of free water and that of hydrated products occurring at specific temperatures. Table II includes the values obtained from the specimens heated at each temperature. An increase in the amount of weight loss at each temperature is noticed except between 100 and 200°C. The specimen at 100°C showed higher weight loss at 100°C than at 200°C. The test was made by duplicate and results of weight losses were (19.1 and 22.2%). The reason was associated to evolution of hydration of partially hydrated cement phases, mainly C_3S. The weight loss at 200°C until reaching a constant weight (13.2%), was similar to that obtained following the regime of heating (1°C/min increase, 2 h heating and temperature decrease) (15.3%).

3.2. X-ray diffraction studies

The diffractogram from the five analyzed specimens are shown in Fig. 2, where the main peaks have been identified. Typical reflections associ-
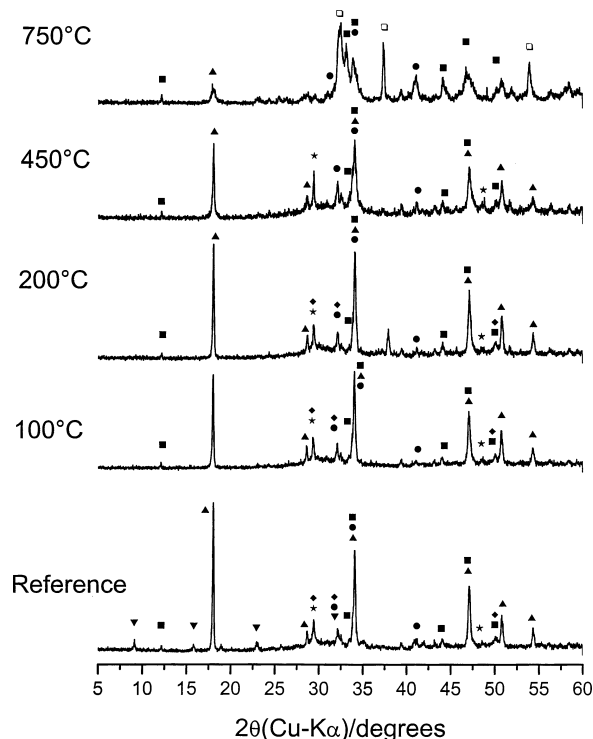

Figure 2 X-ray diffractograms of the reference specimen (initial cement paste), and the heated specimens at various temperatures (T_c). Key to phases: C_2S (●); Portlandite (▲); Calcite (★); Brownmillerite (■); Ettringite (▼); $Ca_{1.5}SiO_{3.5} \cdot xH_2O$ (♦); lime (□).
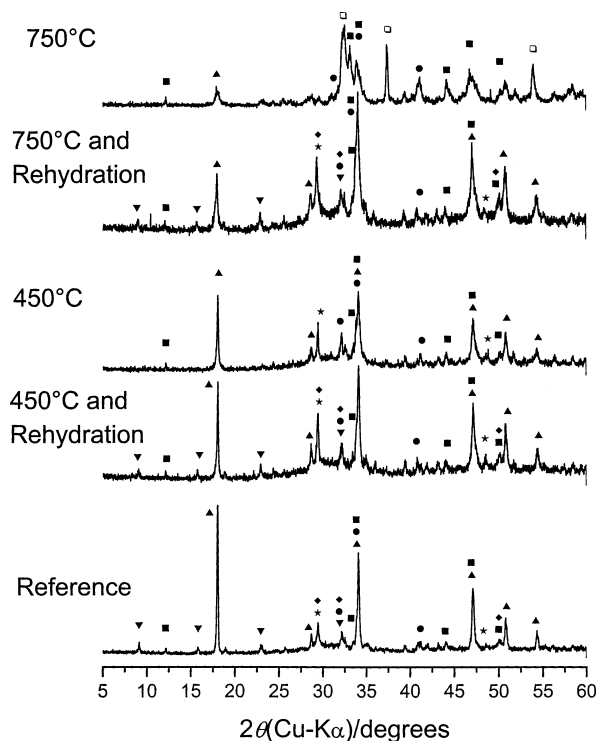

Figure 3 X-ray diffractograms of the reference specimen (initial cement paste), the heated and afterwards rehydrated specimens ($T_c = 450$ and 750°C). Key to phases: C_2S (●); Portlandite (▲); Calcite (★); Brownmillerite (■); Ettringite (▼); $Ca_{1.5}SiO_{3.5} \cdot xH_2O$ (♦); lime (□).

ated to larnite (C_2S), portlandite ($Ca(OH)_2$), brownmillerite ($Ca_4Al_2Fe_2O_{10}$), calcite ($CaCO_3$), ettringite ($Ca_6(Al(OH)_6)_2(SO_4)_3(H_2O)_{26}$), and $Ca_{1.5}SiO_{3.5} \cdot xH_2O$ were found in reference sample. After heating, some reflections disappear, shown in Fig. 2, as those corresponding to ettringite, which were identified in the initial specimen but not in the samples heated at $T > 100°C$, and $Ca_{1.5}SiO_{3.5} \cdot xH_2O$ after 450°C. A progressive reduction of the intensity of the peak related to portlandite is noticed by increasing the temperature above 450°C and is not present at 750°C. The presence of calcite is detected and even increases in intensity up to $T_c = 450°C$. At the highest temperature tested (750°C), the reflection peaks of calcite practically disappear. Lime is also well identified in the specimen heated at 750°C, the origin is explained from portlandite and calcite transformation. The brownmillerite is present in all specimens heated and the same for larnite.

The XRD diffractograms corresponding to the rehydrated specimens ($T_c = 450$ and 750°C) are presented in Fig. 3. Both specimens contain the reflections of larnite, portlandite, brownmillerite, calcite, ettringite and $Ca_{1.5}SiO_{3.5} \cdot xH_2O$ similar to that of reference, indicating that the initial crystalline composition of hydrated forms are recovered.

3.3. Thermal analyses

The thermogravimetry analyses are presented in Fig. 4 and the weight losses associated to the various ranges of temperature are given in Table III.

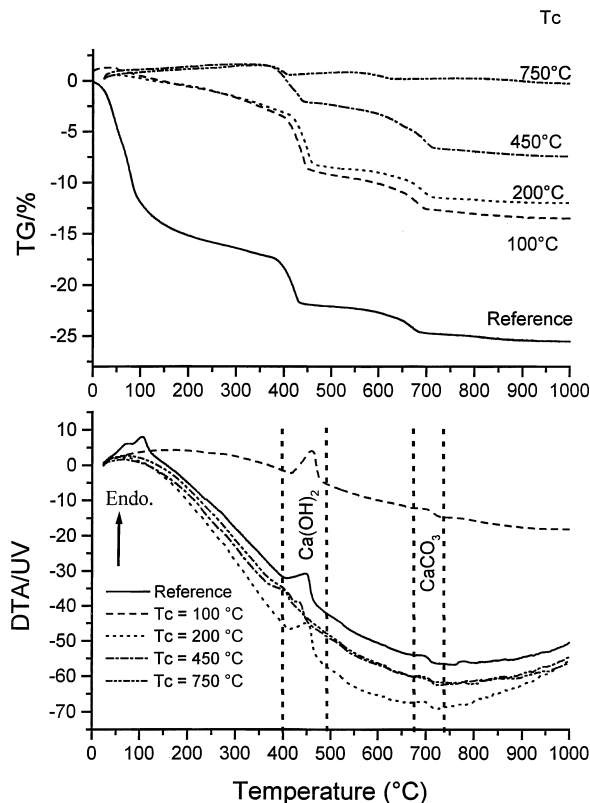The thermogravimetric test are interpreted as follows:

Figure 4 Thermogravimetric analysis (TG and DTA) of the reference specimen (initial cement paste) and the heated specimens at various temperatures (T_c).

Figure 5 Thermogravimetric analysis (TG and DTA) of the reference specimen (initial cement paste), and the heated and afterwards rehydrated specimens ($T_c = 450$ and $750°C$).

- The free water, still present in the samples, is removed up to about 100°C.
- From 100–250°C, takes place the loss of water mainly from the C-S-H. Most of the bound water is lost up to 250°C.
- A further important weight loss occurs with the transformation of portlandite at 450°C.
- Finally, a weak endothermic peak at 650°C is attributed to the decomposition of calcite.

The sample heated at 750°C show a complete transformation of the portlandite and calcite. In this sample, the weight losses are very low in the whole range of temperatures from the TG tests, indicating that during heating a complete chemical transformation of the cement paste has occurred.

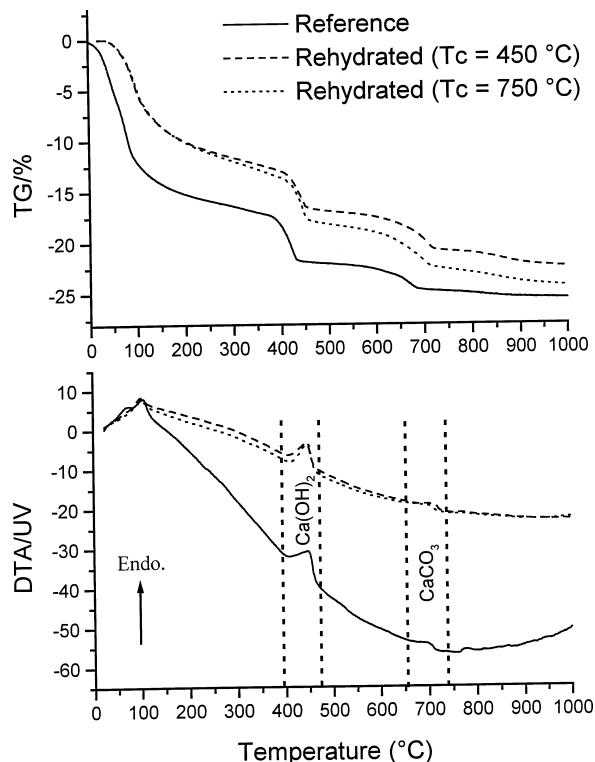The weight losses related to the rehydrated specimens, previously heated at 450 and 750°C, are presented in Fig. 5 and Table III. The TG and DTA figures are similar to the reference specimen: new formation of portlandite, the presence of calcite, and bound and free water are clearly observed.

One relevant feature is the endothermic peak at about 100°C in the reference sample that disappears after heating, but it recovers again after rehydration. The peak has been associated with the transformation of ettringite [5–9].

3.4. ^{29}Si MAS NMR studies

The interpretation of ^{29}Si MAS-NMR spectra give the silicate tetrahedra designated as Q^n, where Q represents the silicon tetrahedron bonded to four oxygen atoms and n is the connectivity, i.e., the number of other Q units attached to the SiO_4 tetrahedron under study. Thus, Q^0 denotes the monomeric orthosilicate anion SiO_4^{4-} (nesosilicate) and typical of anhydrous

TABLE III Thermogravimetric data

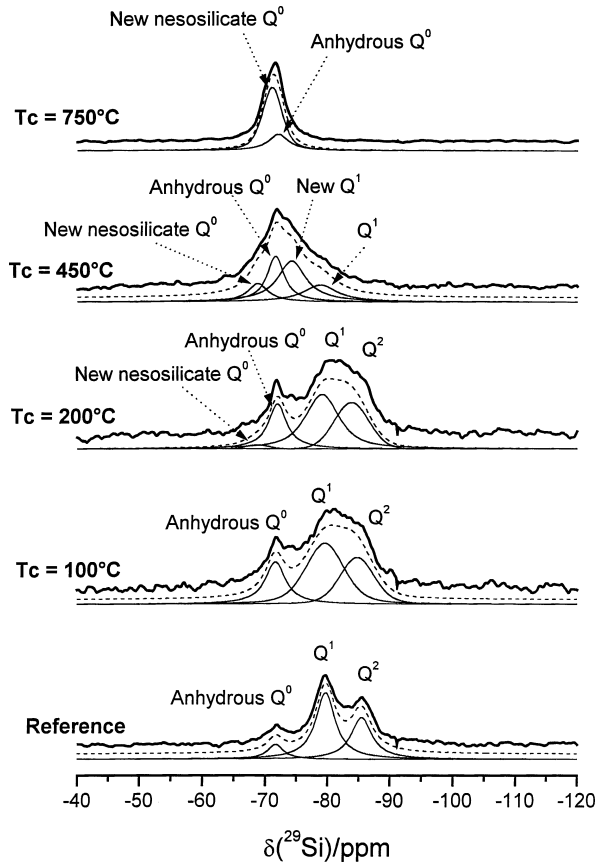| Samples	Weight loss (%) Temperature range (°C)				
	100–250 bound H_2O	250–400	400–475 Ca(OH)$_2$	475–600	650–750 calcite
Reference	6.7	1.8	4.6	0.5	1.7
$T_c = 100°C$	1.6	2.3	5.6	1.1	2.2
$T_c = 200°C$	1.3	2.1	5.2	0.7	1.9
$T_c = 450°C$	0.4	<0.1	2.53	1.1	2.3
$T_c = 750°C$	0.4	<0.1	<0.1	<0.1	<0.1
$T_c = 450°C$ and afterwards rehydrated	6.1	2.0	4.0	1.0	2.6
$T_c = 750°C$ and afterwards rehydrated	6.6	2.5	4.4	1.0	2.6

Figure 6 ^{29}Si MAS NMR spectra of the reference specimen (initial cement paste) and the heated specimens at various temperatures (T_c). The isotropic chemical shifts are referenced to the T.M.S (Si(CH$_3$)$_4$). The thick solid line represents the experimental spectrum. The other solid lines are the gaussian components of the silicate tetrahedra Q^n and the deconvolutions.

silicate of cement (C$_3$S and C$_2$S), Q^1 represents an end group of a chain of C-S-H, Q^2 a middle group, Q^3 a chain branching site and Q^4 a three-dimensionally fully cross-linked group. The isotropic chemical shift (δ^{iso}) of the ^{29}Si nuclei allows obtaining information concerning the organization of tetrahedral links [22, 23].

The spectra of the different specimens are given in Fig. 6 and the results of the deconvolution by Gaussian lines representing the isotropic chemical shift characteristic for each Q^n, δ^{iso}, the percentage (%) and full width at half height (FHWH) are included in Table IV.

The interpretations of the spectra are based on the bibliography of the C-S-H gels [24–27].

The ^{29}Si MAS-NMR spectrum of the reference sample shows the characteristic peaks of cement paste in an OPC or the C-S-H gel [24–27] with the resonance of Q^0 (-71.7 ppm), Q^1 (-79.7 ppm) and Q^2 (-85.5 ppm). The Q^0 resonance represents the remaining anhydrous cement that mainly corresponds to C$_2$S also identified by XRD as larnite.

The heated specimens of the cement paste in comparison with the reference sample show evolution of the spectra. After heating at 100°C besides the free water of the pores decreases, the structure of C-S-H gel is altered. From $T_c = 100$°C up to 200°C, it appears that the C-S-H gel progressively decomposes (Fig. 6). The evolution of the spectra up to $T_c = 200$°C is characterized by low decrease of the intensities of Q^1 and Q^2 tetrahedra but compensated by the formation of a new anhydrous nesosilicate phase, type Q^0, that appears at lower $\delta^{iso} = -68.7$ ppm, shifted 3.2 ppm from initial Q^0.

The sample heated at 450°C, shows that the Q^2 tetrahedra disappear, but a new Q^1 resonance is identified. This sample presents two types of Q^1 tetrahedra, one typical of C-S-H gel ($\delta^{iso} = -78.8$ ppm) and other at -74.2 ppm (6 ppm shifted from Q^1 typical). Clearly the spectrum of this specimen differs from the initial, but some C-S-H gel still remains with shorter length chains in the form of Q^1. The resonances that correspond to the new nesosilicate increase in size ($\delta^{iso} = -68.7$ ppm) and the initial anhydrous appears at $\delta^{iso} = -71.6$ ppm.

The heated specimen at 750°C shows a total transformation of the initial C-S-H gel (Q^1 and Q^2 structure). However an asymmetric peak with a shoulder is better noticed in Fig. 7. This indicates that an overlapping of two peaks is possible, one corresponding to Q^0 ($\delta^{iso} = -72.0$ ppm), the initial anhydrous cement, C$_2$S, and a new nesosilicate phase ($\delta^{iso} = -71.0$ ppm).

Although literature indicates [12, 28] the formation of larnite during heating as result of dehydration of C-S-H, ^{29}Si NMR tests enable to deduce that the anhydrous new nesosilicate formed is different in the morphology than initial anhydrous residue with less crystalline structure.

TABLE IV Simulation results of ^{29}Si MAS NMR spectra. The given data are the isotropic chemical shifts (ppm), integration (%) and FWHH (ppm)

| | Nesosilicate | | | | | | Range of C-S-H gel | | | | | | | | |
| | New resonance | | | Anhydrous cement | | | | | | | | | | | |
| | Q^0 | | | Q^0 | | | New Q^1 | | | Q^1 | | | Q^2 | | |
Samples	δ^{iso}	%	FWHH	δ^{iso}	%	FWHH	δ^{iso}	%	FWHH	δ^{iso}	%	FWHH	δ^{iso}	%	FWHH
Reference	–	–	–	−71.7	10	3.01	–	–	–	−79.7	55	3.80	−85.5	35	4.00
$T_c = 100$°C	–	–	–	−71.6	25	3.90	–	–	–	−79.6	45	7.29	−84.8	30	6.45
$T_c = 200$°C	−68.7	<5	3.90	−71.9	25	3.50	–	–	–	−79.1	45	6.46	−83.8	30	6.50
$T_c = 450$°C	−68.7	20	3.80	−71.6	20	3.30	−74.2	40	5.40	−78.8	20	6.51	–	–	–
$T_c = 750$°C	−71.0	75	3.73	−72.0	25	3.83	–	–	–	–	–	–	–	–	–
$T_c = 750$°C and afterwards rehydrated	–	–	–	−71.1	10	3.01	–	–	–	−79.7	50	4.81	−85.5	40	4.78
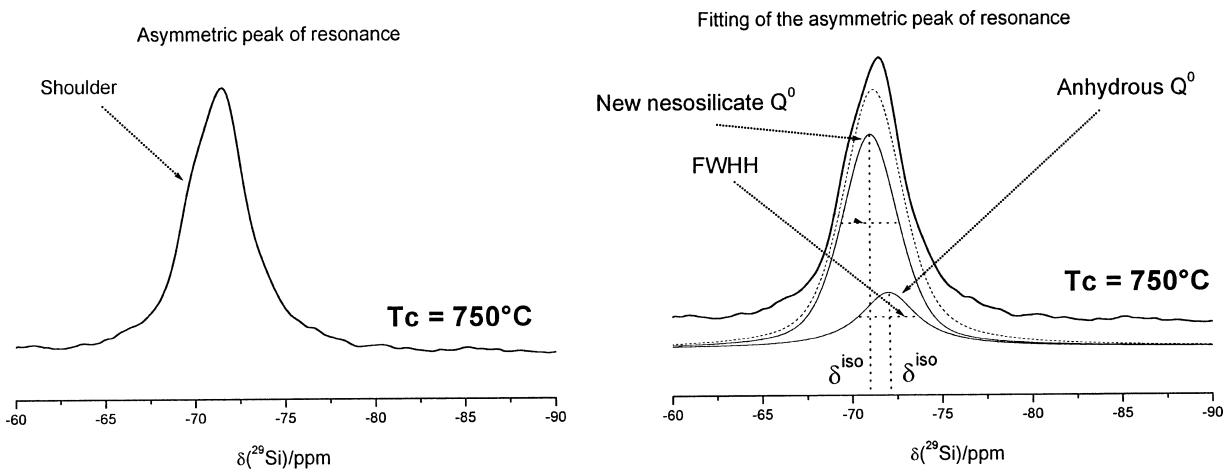
Figure 7 Details of the deconvolution of the ^{29}Si MAS NMR spectra of the heated specimen at 750°C. The new nesosilicate and the anhydrous Q^0 are depicted. Also are showed the asymmetric peak of the resonance and, the shoulder (right), the full widths at half height (FWHH) and the isotropic chemical shifts (δ^{iso})(left).
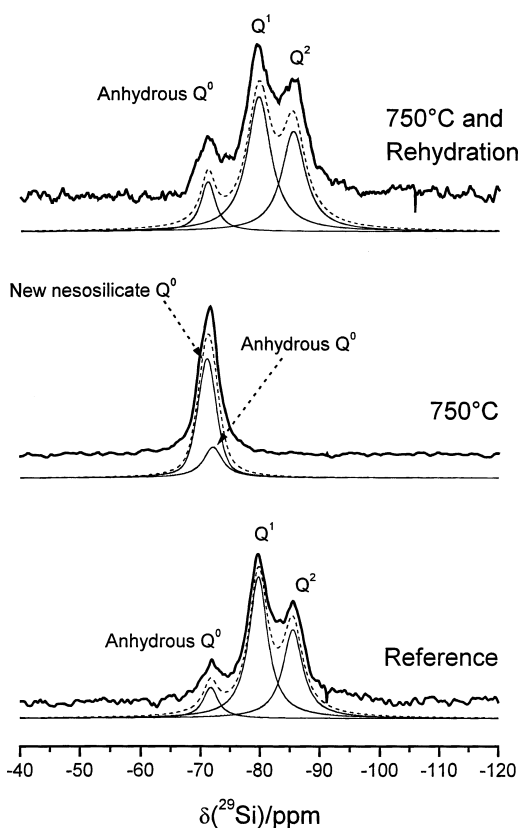

Figure 8 ^{29}Si MAS NMR spectra of the reference specimen (initial cement paste), the heated specimen at 750°C and this one afterwards the rehydration into wetting atmosphere during $3\frac{1}{2}$ months. The isotropic chemical shifts are referenced to the T.M.S. (Si(CH$_3$)$_4$). The thick solid line represents the experimental spectrum. The other solid lines are the gaussian components of the silicate tetrahedra Q^n and the deconvolutions.

The FWHH of Q^1 and Q^2 increase with the heating treatment, indicating more disordered structure of the amorphous C-S-H, given in Table IV.

Concerning the rehydrated specimen previously heated at 750°C given in Fig. 8, the anhydrous phase Q^0 remains in similar proportion than at the initial. The new nesosilicate phase is again transformed into C-S-H gel by hydration. The anhydrous cement remains in similar proportion to that in reference sample.

In all specimens, including initial, heated and rehydrated, the anhydrous phase Q^0 is always present with only a soft increase after heating.

4. Discussion

Handoo *et al.* [3] followed the transformation occurring within a gradient of temperature between the core and the surface of the concrete, here, this gradient has been assumed by heating the samples at different temperatures until reaching the transformations in equilibrium at each temperature. The sequence of transformations in the solid phases of a cement paste are followed.

4.1. Microstructure transformations of the C-S-H at elevated temperatures

Several authors have studied chemical transformations of cement paste exposed to high temperatures, and present results agree with their previous found from XRD, ND and TG [3, 12, 14–17].

The evolution of the crystalline phases observed with XRD show that some reflections disappear as consequence of high temperatures such as $Ca_{1.5}SiO_{3.5} \cdot xH_2O$ (after heating at 450°C) and ettringite (by heating above 100°C), this last also confirmed by neutron diffraction [12] and others [5–7]. Anhydrous phases as larnite and brownmillerite seem to be stable respect to temperature, as also indicated by [12, 29]. Increasing the heat above 450°C, the cement paste shows that portlandite and calcite decompose into lime [3, 12, 14–17].

But in present work by heating from 20°C up to 200°C an increase of portlandite around 1% has been detected due to the progress of hydration of residual anhydrous components. This hypothesis is sustained by the parallel increase in weight loss in the region of T_c up to 250°C (Table III) coming from C-S-H, indicating higher content of C-S-H gel.

As consequence of heating the C-S-H gel looses water molecules and OH$^-$ groups from the interlayer space. Cong *et al.* [18] showed by studying several synthetic C-S-H gels heated up to 200°C that the peak

intensities of Q^1 and Q^2 change, and also shows an increase of FWHH of the ^{29}Si MAS NMR signals attributed to a more disordered structure of samples. The deconvolution of the spectra of C-S-H gels of the heated cement paste up to 200° in present work shows also the evolution of Q^1 and Q^2 and the increase of FWHH.

Besides, in ordinary Portland cement pastes the C-S-H gel is characterized by the CaO/SiO_2 ratio, that ranges between 1.5 to 2.0 [30]. Grutzek [31] points out for C-S-H gels that a correlation exists between Q^1/Q^2 and CaO/SiO_2. In present study, the Q^1/Q^2 ratios of initial cement paste and those of the specimens heated at 100 and 200°C, are approx. ≈ 1.5, calculated from Table IV. Using the correlation of Grutzek the CaO/SiO_2 ratio of heated cement pastes is practically not modified and preserves their stoichiometry up to 200°C.

By increasing the temperature at 450°C the NMR spectrum confirms the progressive transformation of C-S-H gel. But this C-S-H gel follows a structural modification that differs from a C-S-H gel spectrum of a hydrated cement paste. The C-S-H gel spectrum after 450°C, is similar to that of early stages of hydration of a C_3S, mainly composed of Q^1, since Q^2 resonance appears only after about 10 h of hydration [25]. However, in heated C-S-H gel of cement paste apparently two types of Q^1 tetrahedra are observed, which suggest that the Si bonding around each Q^1 tetrahedra vary, while Q^2 resonance is not detected.

The two Q^1 resonances are shifted of 5 ppm respect to Q^1 and Q^2 resonance of the initial C-S-H gel in the reference sample (Table IV). The Q^1 resonance at -78.8 ppm more likely corresponds to a similar surrounding than others Q^1 tetrahedra in C-S-H gels. To attribute the new Q^1 resonance (-74.2 ppm), several hypotheses would be considered:

- If aluminum is introduced in the C-S-H chain: the substitution SiOSi $\rightarrow$ SiOAl brings about a deshielding of ca. 5 ppm for the central silicon atom [22]. However, the new Q^1 resonance (-74.2 ppm) can not be explained by a silicium tetrahedra bonded to an aluminum tetrahedra, one reason is that approximately 93% of aluminum is in the aluminum phases of the cement paste, in the form of brownmillerite ($Ca_4Al_2Fe_2O_{10}$) and ettringite ($Ca_6(Al(OH)_6)_2(SO_4)_3(H_2O)_{26}$), calculated from Table I. In case that a small portion of aluminum would incorporate into the C-S-H chain, the amount must be too low to give a so large NMR signal of the ^{29}Si NMR seen in Fig. 6.
- Other possibility for the new Q^1 resonance attribution can be obtained from Cong [18], who considers water molecules bonded to Ca^{2+}, so that, the loss of water in the interlayer space by heating favors the formation of Ca—O—Si bonds, which causes some changes of bond angles and distances in Si tetrahedra. The presence of two different Q^1 tetrahedra in C-S-H gel has only been described by Klur [32] who pointed out the appearance of a new Q^1 peak in a C-S-H gel hav-

ing a CaO/SiO_2 ratio >1.0, located at -76 ppm and assigned as Q^{1p} (Si—O—Ca—O—H groups). As the isotropic chemical shift observed in the sample heated at 450°C is close to that of Q^{1p} tetrahedra, the new Q^1 resonance could be attributed to this form.

The final stage of dehydration of the C-S-H gel, pointed out from present work, is the formation of a new nesosilicate, Q^0 instead of forming the anhydrous cement structure of C_2S, this last only increase in small proportion. The identification of the dehydrated morphology of the C-S-H represents enlightenment that allows to complement that of the crystalline formation of C_2S as larnite addressed until now [12, 28]. Moreover, the identification of the new nesosilicate with the ^{29}Si NMR spectrum coincides with a discontinuity and change of slope in the d-spacing of larnite (Fig. 6e given in Ref. [12]), probably indicating that the formation of more C_2S is not as that of larnite. The range of the isotropic chemical shifts of the new nesosilicate, obtained from the deconvolution of the heated specimens, is narrow and corresponds to a similar structure (Table IV) but with less crystalline formation. FWHH of the new Q^0 resonance is larger than initial Q^0.

The NMR chemical shifts depend primarily on atomic nearest neighbor and next-nearest neighbor structure; then, nuclei of atoms in similar local structure resonate at similar chemical shifts. Consequently, the resonance of the new nesosilicate may be attributed to a structure close to belite (C_2S) [22] or alite [33, 34]. Although, some authors [12, 28, 35] postulated at high temperatures the formation of β-C_2S from C-S-H. In order to resolve the final attribution of the new nesosilicate phase a chemical balance of the solid phases could help.

4.1.1. Determination of the CaO/SiO_2 ratio of dehydrated C-S-H (new nesosilicate)

The chemical balance of CaO and SiO_2 for the specimen heated at 750°C would allow to determine the CaO/SiO_2 ratio of the new nesosilicate.

The amount of $[SiO_2]$ is calculated from Tables I and IV; SiO_2 is in: C_2S and in the new nesosilicate (Fig. 6).

The amount of [CaO], may be calculated from (Tables I, III and IV); CaO is: in C_2S, in CaO (lime), in dehydrated ettringite, and in brownmillerite.

In order to estimate [CaO] corresponding to lime in the sample at 750°C, it can be assumed that this one comes mainly from the transformation of calcite and portlandite, easily calculated from TG test. Calcite and portlandite vary during heating, the greater amounts have been considered from Table III. Ettringite and C-S-H dehydration contribute to CaO but in less proportion, because ettringite does not decompose, only dehydrates and maintains the short-range order in its structure [5, 8]. As the amount of CaO from C-S-H is assumed low. The calculated CaO/SiO_2 ratio obtained for the new nesosilicate resonance is 1.78. So that, it can be accepted that the new nesosilicate corresponds to a structure close to C_2S.

4.2. Changes in solid phases during dehydration and rehydration processes of cement paste due to heating

4.2.1. Dehydration processes of cement paste

Cement paste is a complex multiphase material leading to a composite constituted of solid phases, pores and water. The chemical transformations occurring in solid phases of cement paste after heating are the interest of present work. It is assumed a heating cement paste showing a gradient temperature profile moving from a heated and unsealed face that penetrates inside the bulk to a sealed interior not affected by temperature. In Fig. 9, the dehydration processes of solid cement paste phases are schematically described taking into account results from present study and literature data [1–3, 10–12, 18].

The degree of transformation of solid phases in cement paste is considered in function of temperature and the chemical equilibrium is assumed to be reached at each temperature. The following processes could take place, from the external heated surface, at 750°C to the interior not affected by temperature:

1. From the external face, and between 750 to 650°C, the solid phases contain mainly: dehydrated C-S-H (New Nesosilicate), CaO, Anhydrous phases (Larnite), and Dehydrated Ettringite [5, 8].

2. Regions exposed at 650°C up to 600°C, the same solid phases than above are found plus calcite, this last formed during heating from reaction of CO_2 gas existing in pores.

3. In regions exposed to temperatures below 600°C up to 450°C, modified C-S-H coexists with decreasing proportions of the dehydrated C-S-H (new nesosilicate). CaO in decreasing proportions with temperatures is also formed. Besides anhydrous phases (larnite and brownmillerite) and dehydrated ettringite are present.

4. In cement paste exposed at 450°C up to 200°C, Portlandite coexists with contents of partially dehydrated C-S-H and contents of modified C-S-H and dehydrated C-S-H (new nesosilicate). Calcite, anhydrous phases and dehydrated ettringite are present.

5. The region from 200°C up to 100°C, the C-S-H is present and follows slight dehydration. The New Nesosilicate is not formed. Portlandite coexists with some calcite (from carbonation during heating), anhydrous cement phases (larnite and brownmillerite) and dehydrated ettringite.

6. Inside the unaffected zone by heating, that is below 100°C, C-S-H, portlandite, ettringite and anhydrous phases are the solid components coexisting. In this range of temperature free water is also present and progression of hydration of unhydrated cement phases is possible, what may justify the increase of C-S-H and portlandite at this range of temperature. This could be explained if sealed conditions inside the concrete are possible, similar to those of an autoclave steam curing [19]. The reason is that the vapor formed in heater zones, coming from dehydration of solid phases penetrates inside the bulk of the concrete moving to cooler zones, where condenses due to gas pressure and temperature decrease. This water might participate in further hydration of anhydrous cement.

The weight loss is another parameter also included in Fig. 9. There is an increase progress of weight loss in a heating cement paste, as a consequence of transformation of solid phases. Three critical temperatures with higher weight losses are differentiated:

1. Around 650°C, from the decomposition of calcite and generation of CO_2.

2. H_2O from dehydration of portlandite above 450°C.

3. Above 100°C from the dehydration of C-S-H.

Below 100°C two situations are possible: (a) in unsealed condition, loss, of capillary water that is released outside the material, and (b) in sealed conditions, as commented above condensations would take place with increasing moisture content inside the pores.

However for a full-integrated picture of dehydration process of cement paste implies to take into account the transformations in pore microstructure, and correlate with mechanical strength decay and cracks formation. After that, it will be possible to deal into a more complex degradation model of concrete exposed to fire
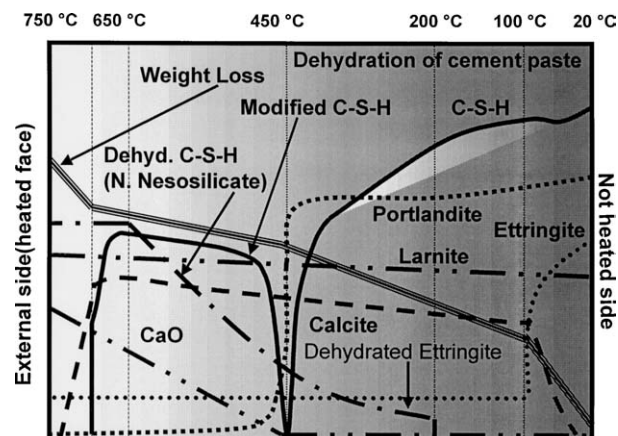
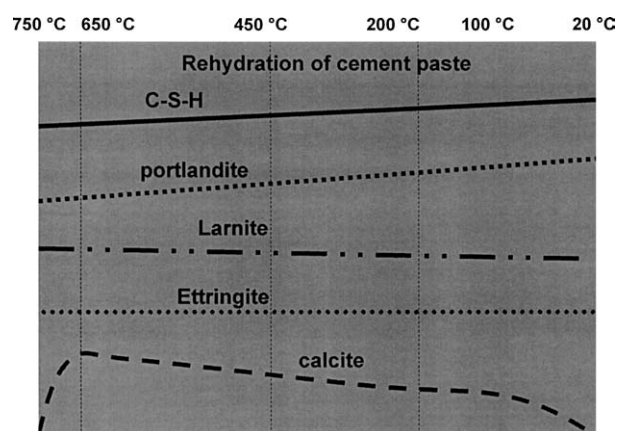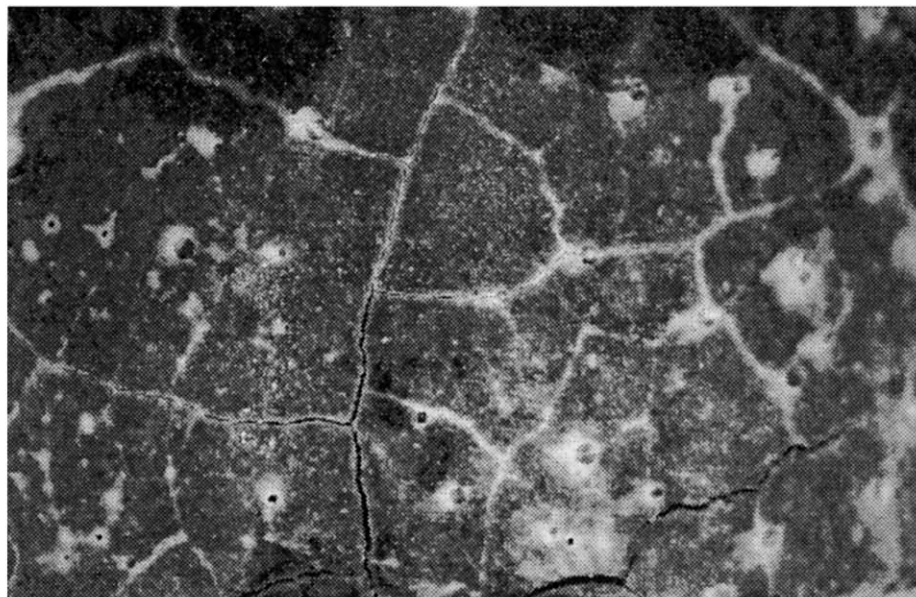*Figure 9* Picture of dehydration processes of cement paste exposed to high temperature environments.
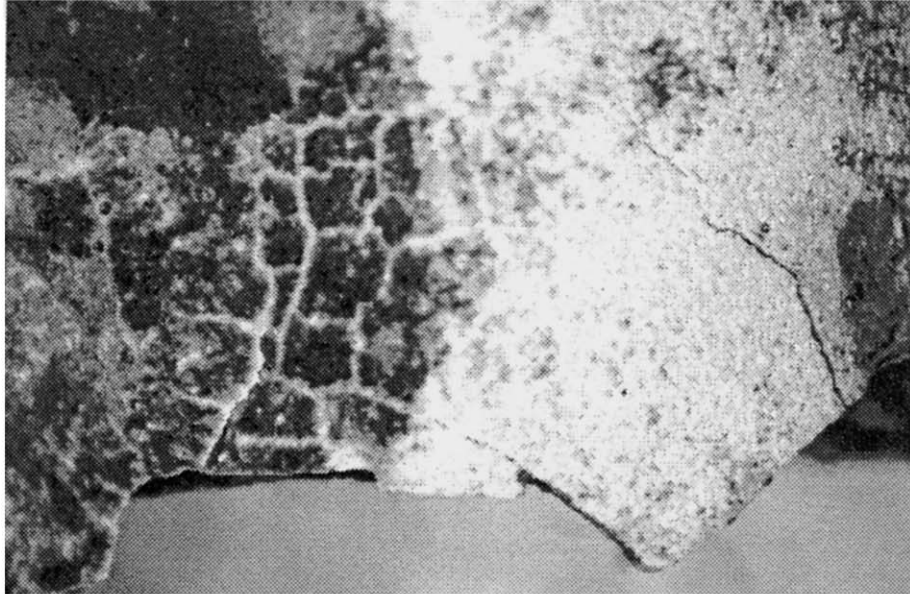
Figure 10 Picture of rehydration of dehydrated cement paste phases after exposure to high temperature environments.

Tc = 750°C and afterwards rehydrated

Tc = 450°C and afterwards rehydrated

Figure 11 Esteroscopic microscopy of the heated and afterwards rehydrated specimens ($T_c = 450$°C down and 750°C up).

conditions. In this paper the microstructural changes concerning solid phases of cement paste are addressed, but the correlation in other microstructure properties are needed.

4.2.2. Rehydration processes in dehydrated solid phases of cement paste

The heated cement paste is not stable in the wet atmosphere and rehydration processes take place, Fig. 10 summarizes the evolution of the different phases. The first is that the rehydration process goes to similar compounds to those initially coming, concerning C-S-H and portlandite. The C-S-H is formed as a consequence of rehydration of the new nesosilicate. Larnite remains unchanged. The CaO would participate in C-S-H rehydration process but it mainly reacts to the formation of portlandite. Ettringite is rehydrated. Calcite formed

by carbonation during dehydration processes coexists with rehydrated solid phases.

A progressive damage is developed with coarser cracking due to rehydration, as noticed in Fig. 11 that has to be addressed together with addition of microstructural evolution.

5. Conclusions

1. In this paper, a ^{29}Si MAS-NMR spectroscopy, complemented by XRD, and TG analysis, show the full picture of compositional changes occurring in cement paste due to high temperature action. Results confirm the loss of free and hydration water, the transformation of portlandite and calcite into lime, and dehydration of ettringite. The initial crystalline C_2S and brownmillerite remain not transformed independently of the temperature.

3023

But in particular it has been concluded that:

- The heating process induces a continuous dehydration of C-S-H gel with the increasing of temperature. The maximum transformation is at $450°C$ where the C-S-H chains are only formed by Q^1 tetrahedra, silicate dimers, "modified C-S-H". Two Q^1 resonances are observed by NMR.
- Below $200°C$, possible evolution of hydration of anhydrous is pointed out.
- Above $T_c = 200°C$ a new phase formation from C-S-H is noticed, dehydrated C-S-H identified as a "new nesosilicate", with $CaO/SiO_2 \approx 2$, assimilated to a structure of C_2S but with less crystalline structure.
- At $750°C$, the C-S-H gel has completely disappeared and is mainly replaced by the new nesosilicate phase.

2. The rehydration of a heated cement paste shows that the process is reversible and new formation of a C-S-H gel from the new nesosilicate is confirmed with a CaO/SiO_2 ratio close to the initial C-S-H gel and recovering its initial stoichiometry. Also crystalline phases, which were transformed to lime at $750°C$, are newly formed such as portlandite and calcite from carbonation. Ettringite is rehydrated and anhydrous cement remains practically unaltered.

Acknowledgement

References

1. J. PIASTA, Z. SAWICZ and L. RUDZINSKI, *Mater. Struct.* **17** (1984) 291.
2. W. M. LIN, T. D. LIN and L. J. POWERS COUCHE, *ACI Mater. J.* **93** (1996) 199.
3. S. K. HANDOO, S. AGARWAL and S. K. AGARWAL, *Cem. Concr. Res.* **32** (2002) 1009.
4. S. K. DEB, M. H. MANGHNANI, K. ROSS, R. A. LIVINGSTON and P. J. M. MONTEIRO, *Phys. Chem. Minerals* **30** (2003) 31.
5. Y. SHIMADA and J. F. YOUNG, *Adv. Cem. Res.* **13** (2001) 77.
6. N. N. SKOBLINSKAYA and K. G. KRASILNIKOV, *Cem. Concr. Res.* **5** (1975) 381.
7. *Idem.*, *ibid.* **5** (1975) 419.
8. K. KIRA, Y. MAKINO and Y. MURATA, *Gypsum Lime* **170** (1981) 7.
9. C. K. PARK, B. K. KIM, S. Y. HONG, G. Y. SHIN and H. K. OH, in Proceedings of Int. Congr. Chem. Cem., 10th, 1997, edited by H. Justnes (Amarkai AB, Goeteborg, Swed., 1997) Vol. 4, p. 4iv068.
10. S. SHAW, C. M. B. HENDERSON and B. U. KOMANSCHEK, *Chem. Geol.* **167** (2000) 141.
11. S. SHAW, S. M. CLARK and C. M. B. HENDERSON, *ibid.* **167** (2000) 129.
12. M. CASTELLOTE, X. TURRILLAS, C. ALONSO, C. ANDRADE and J. CAMPO, *Accepted Cem. Concr. Res.*
13. M. CASTELLOTE, X. TURRILLAS, C. ALONSO, C. ANDRADE, I. LLORENTE and J. CAMPO, in Proceedings of Reunion de usuarios de síncroton, San sebastían (Spain), edited by U.F.M. (Donostia International Physics Center, 2002).
14. M. HEIKAL, *Cem. Concr. Res.* **30** (2000) 1835.
15. M. S. MORSY, A. F. GALAL and S. A. ABO-EL-ENEIN, *ibid.* **28** (1998) 1157.
16. Y. XU, Y. L. WONG, C. S. POON and M. ANSON, *ibid.* **31** (2000) 1065.
17. C. ALONSO, C. ANDRADE, E. MENENDEZ and E. GAYO, *Hormigón y acero* **221** (2001) 97.
18. X. CONG and R. J. KIRKPATRICK, *Cem. Concr. Res.* **25** (1995) 1237.
19. H. F. W. TAYLOR, "Cement Chemistry" (Academic Press, London, UK, 1990).
20. S. N. GHOSH, S. L. SARKAR and S. HARSH, in "Mineral Admixtures in Cement and Concrete," edited by S. Rehsi (ABI Books, New Delhi, 1993) p. 158.
21. D. MASSIOT, H. THIELE and A. GERMANUS, *Bruker Report* **140** (1994) 43.
22. G. ENGELHARDT and D. MICHEL, in "High-Resolution Solid-State NMR of Silicates and Zeolites" (John Wiley & Sons, Chichester, 1987).
23. M. MÄGI, E. LIPPMAA, A. SAMOSON, G. ENGELHARDT and A. R. GRIMMER, *J. Phys. Chem.* **88** (1984) 1518.
24. N. J. CLAYDEN, C. M. DOBSON, G. W. GROVES and S. A. RODGER, in Proceedings of Congr. Int. Quim. Cimento, 8th, edited by (Geral 8o CIQC, Rio de Janeiro Brazil., 1986) Vol. 3, p. 51.
25. C. M. DOBSON, D. G. C. GOBERDHAN, J. D. F. RAMSAY and S. A. RODGER, *J. Mater. Sci.* **23** (1988) 4108.
26. M. GRUTZECK, A. BENESI and B. FANNING, *J. Amer. Ceram. Soc.* **72** (1989) 665.
27. R. RASSEM, H. ZANNI-THEVENEAU, I. SCHNEID and M. REGOURD, *J. Chim. Phys. Phys.-Chim. Biol.* **86** (1989) 1253.
28. Z. P. BAZANT and M. F. KAPLAN, in "Concrete at High Temperature: Material Properties and Mathematical Models" (Longman Group Limited, Burnt Mill, Harlow (Essex), England, 1996).
29. P. BERASTEGUI, S. G. ERIKSSON and S. HULL, *Mater. Res. Bull.* **34** (1999) 303.
30. S. MINDESS and J. YOUNG, "Concrete" (Prentice-Hall, Englewood Cliffs, NJ, 1981).
31. M. GRUTZECK, J. LAROSA-THOMPSON and S. KWAN, in Proceedings of Int. Congr. Chem. Cem., 10th, 1997, edited by H. Justnes (Amarkai AB, Goeteborg, Swed, 1997) Vol. 2, p. 2ii067.
32. I. KLUR, Etude par RMN de la structure des silicates de calcium hydratés, Université Paris 6 (Thesis) (1996).
33. R. J. KIRKPATRICK and X. D. CONG, in "An Introduction to 27Al and 29Si NMR Spectroscopy of the Cements and Concretes," edited by P. Colombet and A. R. Grimmer (Gordon and Breach Science Publishers, 1994) p. 55.
34. J. HJORTH, J. SKIBSTED and H. J. JAKOBSEN, *Cem. Concr. Res.* **18** (1988) 789.
35. R. YUAN and Z. WANG, *Wuhan Gongye Daxue Xuebao* **10** (1988) 7.