

Pozzolanic reactivity of zeolitic rocks from two different Cuban deposits: Characterization of reaction products

S. Martínez-Ramírez^{a,*}, M.T. Blanco-Varela^a, I. Ereña^a, M. Gener^b

^a Instituto de Ciencias de la Construcción Eduardo Torroja (CSIC), C/Serrano Galvache 4, 28033 Madrid, Spain

^b Centro Técnico de Desarrollo de Materiales de Construcción, Carretera de Casablanca y Calle 70, La Havana, Cuba

Received 2 June 2005; received in revised form 16 December 2005; accepted 19 December 2005

Available online 30 January 2006

Abstract

Volcanic pozzolans are vitreous or poorly crystallized materials rich in SiO₂ and Al₂O₃ that react with the portlandite generated during cement hydration to yield hydrated calcium silicates and aluminates with low solubility and good cementitious properties (pozzolanic reaction).

The purpose of the present study was to analyze the reaction between calcium hydroxide and two natural, partially crystalline pozzolans found in Cuba, characterize the C–S–H gels produced and determine the relationship between pozzolan composition and structure and its capacity to fix calcium.

The findings of the XRD and FTIR analyses conducted with this aim included a gradual decline of the zeolite (heulandite and faujasite) peaks on the diffractograms with reaction time, and changes in the IR absorption bands attributed to the zeolites, along with the appearance of new bands indicative of the formation of the CSH gel.

Although the amount of Ca fixed by the two pozzolans after 90 days was similar, the reaction rate was faster in the Los Congos material. The gel forming in the Carolinas sample had Al in its composition, with Q³ (1Al) and Q² (1Al) units whose content increased with time.

The presence of Fe in the Los Congos sample hampered the analysis of the gel formed, although the presence of Al in its composition could be inferred from the ²⁷Al MAS NMR data. The thermodynamic data showed that C–S–H gel was formed in both cases.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Natural pozzolans; C–S–H gel; Zeolites; Spectroscopic techniques

1. Introduction

Today no one questions the economic, environmental and technical benefits of using pozzolans as a component of cement and all developed countries have legislation in place to regulate such use (Rahhal and

Talero, 2003, pp. 29–40). Many countries that lack the industrial by-products (fly ash, silica fume, and so on) most commonly used for this purpose do nonetheless have a stock of natural pozzolans.

Volcanic pozzolans are vitreous or poorly crystallized materials rich in SiO₂ and Al₂O₃ that react with the portlandite generated during cement hydration to yield hydrated calcium silicates and aluminates with low solubility and good cementitious properties (pozzolanic reaction). Weathering can transform

* Corresponding author. Fax: +34 913026047.

E-mail addresses: sagrario@ietcc.csic.es (S. Martínez-Ramírez), blancomt@ietcc.csic.es (M.T. Blanco-Varela).

volcanic glass into zeolites or clays. The zeolitization of glass is generally believed to improve, and argillation to detract from, its pozzolanic properties (Lea's, 1999, pp. 471).

The ability of zeolites to react as effectively as tuffs, disputed in the 1960s (Lea's, 1999, pp. 471), is no longer a matter of controversy, as zeolites are now known to be hydrated aluminosilicate minerals whose cage-like structure affords a large (internal and external) surface area, a property that determines high reactivity (Perraki et al., 2003, pp. 205–212).

Authors studying the pozzolanity of zeolitic rocks such as heulandite, clinoptilolite and mordenite (Drzaj et al., 1978, pp. 711–720; Perraki et al., 2003, pp. 205–212; Alcántara Ortega et al., 2000, pp. 1641–1643; Fragoulis et al., 1997, pp. 889–905) have shown that they are able to fix calcium and produce C–S–H gel within 7 days (Perraki et al., 2003, pp. 205–212); after 28 days, moreover, the Ca/Si ratio in the C–S–H gel forming at 50 °C in the reaction between clinoptilolite and portlandite has been determined to range from 0.8 to 1.2 (Alcántara Ortega et al., 2000, pp. 1641–1643;). Drzaj et al. (1978) concluded that the zeolite–portlandite reaction actually comprises a series of topochemical reactions controlled by diffusion, which in the early stages consists in the diffusive solution of zeolite and portlandite, and that the final product is the result of heterogeneous nucleation along the solid–liquid (C–S–H gel) interface.

The effect of the presence of zeolite on the physical properties of the material has been studied by a number of authors: in some cases, to analyze the pozzolanic reaction between the zeolite and the Ca(OH)₂ (Drzaj et al., 1978, pp. 711–720; Alcántara Ortega et al., 2000, pp. 1641–1643; Kitsopoulos and Dunham, 1996, pp. 576–583), and in others, to explore developments when the zeolite is included in blended cement pastes (Perraki et al., 2003, pp. 205–212; Fragoulis et al., 1997, pp. 889–905; Poon et al., 1999, pp. 427–432; Shi and Day, 2000b, pp. 607–613; Shi and Day, 2000a, pp. 51–58; Brough et al., 2001, pp. 1437–1447; Pekmezci and Akyüz, 2004, pp. 2175–2179; Janotka and Mojumdar, 2003, pp. 17–27).

Alcántara Ortega et al. (2000), who addressed the former issue by studying the properties of alkali-activated clinoptilolite, concluded that when curing conditions, clinoptilolite particle size and the amount of portlandite were optimized, the reaction product obtained was a compact material containing 20% Ca(OH)₂ (by wt) with an average compressive strength of 38.7 MPa (Alcántara Ortega et al., 2000, pp. 1641–1643). Fragoulis et al. (1997) found that due to their large specific surface, blended cements containing this type of zeolite require more water in the mix and consequently exhibit lower

strength values than cement without pozzolanic additions.

Some authors suggested that the optimum pozzolan/cement ratio for blended cement pastes, is about 0.28 (Pekmezci and Akyüz, 2004, pp. 2175–2179), calling for the lowest water/cementitious ratios (*w/cm*) (Poon et al., 1999, pp. 427–432). They also reported that pastes with high *w/cm* ratios and low substitution levels show high reactivity.

While the pozzolanic reactivity of volcanic glass containing plagioclase as the crystalline phase has also been explored by different researchers and its reaction products and mechanical behaviour identified (Poon et al., 1999, pp. 427–432, Shi and Day, 2000b, pp. 607–613;), natural faujasite-containing zeolites have not been studied. By the same token, although the changes in cement pastes prompted by zeolites have been addressed in the literature, nothing has been published on the nature of the C–S–H gel formed.

In an earlier paper (Blanco-Varela et al., *in press*) the authors characterized two zeolitic rocks from different deposits (Carolinas and Los Congos, Cuba), concluding that the most abundant crystalline phases in the hypocrySTALLINE (predominantly glass) Carolinas rock are heulandite–clinoptilolite type zeolites. The Los Congos sample was found to be a vitreous (holohyaline), perlitic rock containing andesine, quartz, calcite and faujasite as the majority minerals. The authors showed in that study that both rocks have pozzolanic properties, although the reaction products, namely the C–S–H gel, have not been adequately characterized.

The purpose of the present study is to analyze the reaction between calcium hydroxide and two natural, partially crystalline pozzolans found in Cuba, characterize the resulting C–S–H gels and relate pozzolan composition and structure to its capacity to fix calcium.

2. Experimental

The basic materials used in this study were samples of zeolitic rocks from the deposits at Carolinas and Los Congos, Cuba, whose chemical, mineralogical and microstructural characterization were reported in a previous paper (Blanco-Varela et al., *in press*). The grain size distribution of ground samples of the two rocks was determined with laser diffraction techniques. The specific area and pore structure of the solids was found by measuring gas adsorption by the solids as described by Brunauer, Emmet and Teller (B.E.T. method). The gas used for the trials was N₂ and the degasification was carried out at 140 °C for 12 h, and then at 350 °C for 6 h.

Table 1
Chemical composition of the pozzolans (wt.%)

	L.I. ^a (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)	SO ₃ (%)	Na ₂ O (%)	K ₂ O (%)	MSR ^b (%)	Reactive SiO ₂ (%)
Carolinas	13	64.38	12.05	1.76	0.58	4.32	0.21	2.57	1.42	98.88	59.43
Congos	11.1	51.07	14.16	9.66	3.97	5.61	0.11	3.32	1.15	94.86	24.97

^aL.I.—Loss on ignition; ^bMSR—methanol-salicylic residue.

Pozzolan solubility in salicylic acid in a methanol medium was determined with a procedure described by Takashima (1958).

Five grams of ground pozzolan and 200 ml of saturated portlandite solution were placed in six polypropylene beakers, which were sealed and stored in an oven at 40 °C. The beakers also contained portlandite in semi-permeable bags to maintain saturated conditions while preventing any direct mixing between the pozzolan and the portlandite. The receptacles were removed from the oven at 7, 14, 28, 60 and 90 days and the contents immediately filtered into an Erlenmeyer flask.

The concentration of Ca²⁺, Si⁴⁺, Al³⁺, SO₄²⁻, Na⁺ and K⁺ and pH were determined on filtrate aliquots. Si⁴⁺ was determined by colorimetric procedure; Al³⁺ by atomic absorption and ions SO₄²⁻, Na⁺ and K⁺ by ionic chromatography. The calcium ion content was assessed by complexometric titration with EDTA and calcein as the indicator.

The concentration values for Ca, Na, K, Al, Si and pH were entered in the PhreeqC program, a software tool for speedy evaluation of the effects of compositional change on phase equilibrium, and the saturation indices of the minerals in the solution were calculated to determine which phases were in equilibrium with the solution at each age. The solids obtained after filtering were vacuum dried to a constant weight and characterized by XRD, FTIR and ²⁹Si and ²⁷Al MAS NMR; their Ca content was likewise determined. After 90 days, the solid obtained was analyzed for its methanol-salicylic acid solubility and the residua characterized by ²⁹Si MAS NMR.

3. Results

The chemical analysis of the pozzolans, their reactive silica and the residue in methanol-salicylic acid are given in Table 1.

The analysis showed that the SiO₂ content is much greater, while the Fe₂O₃ and MgO contents are much lower, in the Carolinas than the Los Congos pozzolan. The amount of reactive silica of Carolinas is two times the amount of Los Congos one so that a higher pozzolanic reactivity of Carolinas rock can be expected. Solubility in methanol-salicylic acid was found to be low for both pozzolans (1.12% in Carolinas and 5.12% in Los Congos) so that it would be possible to use selective solubilization in this medium to measure the degree of reaction in samples in contact with the calcium hydroxide ion. The results of laser diffraction grain size and BET specific surface area analyses are shown in Table 2.

The laser diffraction results showed that in the Carolina pozzolan, 90% of the particles were under 42 μm, and in the Los Congos material, the 90% were under 38.9 μm. The Los Congos pozzolan was also found to have a specific surface area 40% greater than the Carolinas rock.

The changes taking place in the crystalline phases in the Carolinas and Los Congos samples in contact with a saturated portlandite solution are reflected in the diffractograms, recorded at different test times, in Figs. 1 and 2. In a prior study the chief crystalline phases in the Carolinas pozzolan were found to be a heulandite-type zeolite closely resembling clinoptilolite and quartz, calcite and mullite (Blanco-Varela et al., in press).

The majority crystalline phases in the Los Congos rock were the zeolite faujasite, and andesine, an albite/anortite series plagioclase feldspar (Blanco-Varela et al., in press). In both series the XRD traces showed a time-dependent decline in the intensity of the peaks attributed to the crystalline phases, while no further peaks appeared that might be indicative of the formation of new crystalline phases.

The FTIR patterns for the samples in contact with the Ca(OH)₂ are given in Figs. 3 and 4. Band assignments for the initial spectra were determined in prior research (Blanco-Varela et al., in press).

The main changes observed in the IR spectra for Carolinas at the different test times were as follows:

- disappearance of the shoulder at 3620 cm⁻¹ in the initial spectrum, due to the stress from the OH groups bonding to the silicon (Fig. 3a), and decline in the intensity of the Si–O–Si, Si–O–

Table 2
Grain size distribution of the initial pozzolans determined by laser diffraction

Sample	Fraction (%)					
	<1.2	<9.8	<32	<42.1	<45	<90
Carolinas						
s.a.=24.06	μm	μm	μm	μm	μm	μm
m ² /g ^a	10%	50%	78.96%	90%	92.29%	100%
Los Congos						
s.a.=34.52	μm	μm	μm	μm	μm	μm
m ² /g ^a	10%	50%	85%	90%	93.63%	99.88%

^a s.a.=Specific surface area.

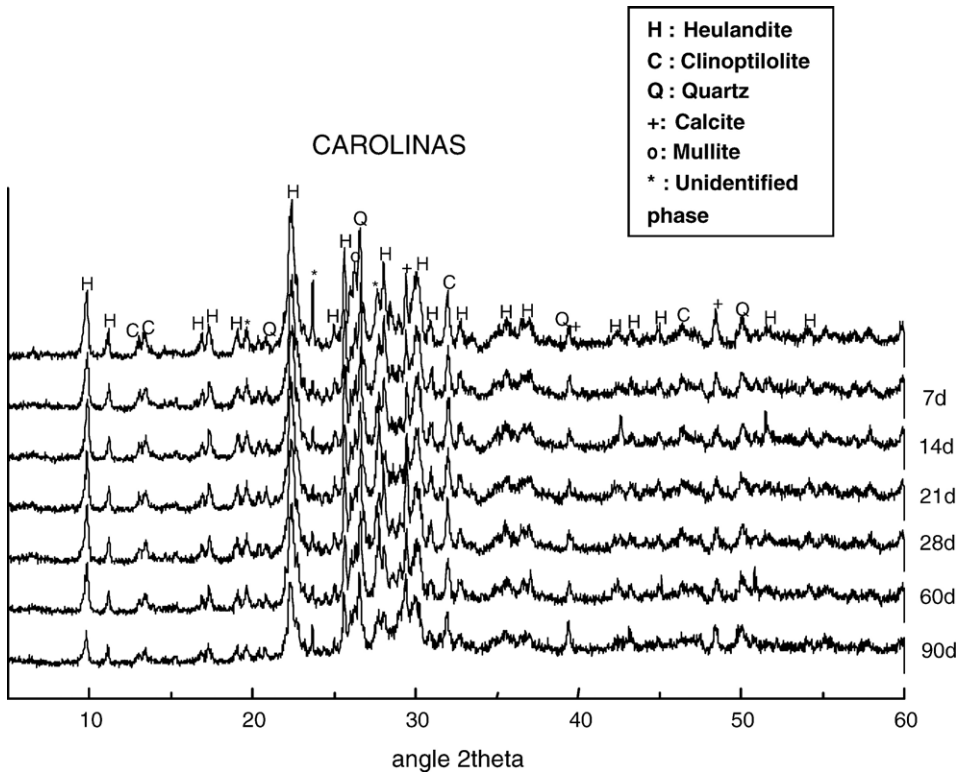


Fig. 1. XRD patterns of the crystalline phases in Carolinas rock in contact with $\text{Ca}(\text{OH})_2$, 0 to 90 days.

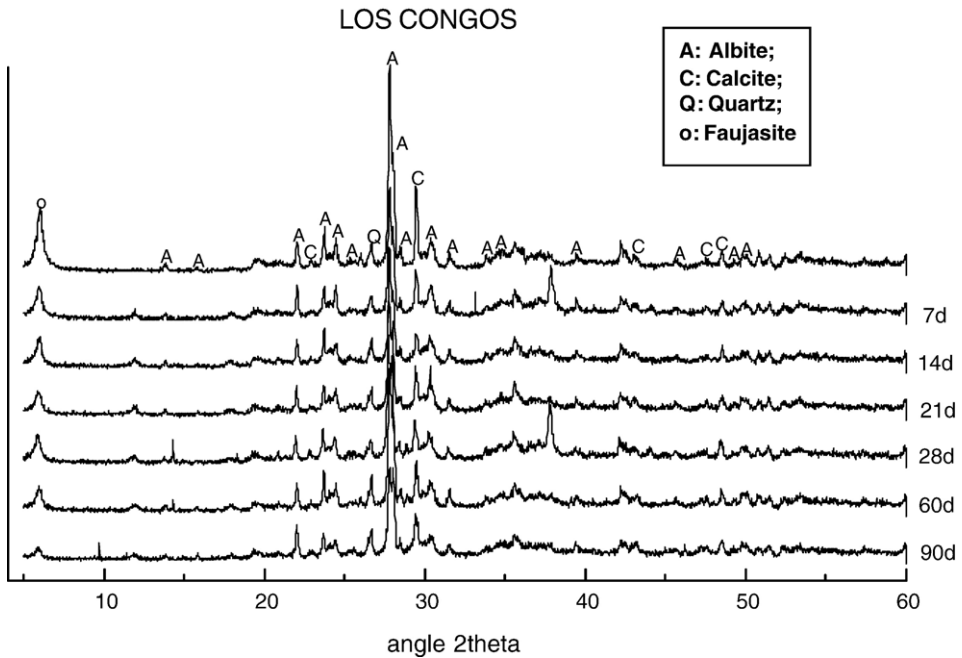


Fig. 2. XRD patterns of the crystalline phases in Los Congos rock in contact with $\text{Ca}(\text{OH})_2$, 0 to 90 days.

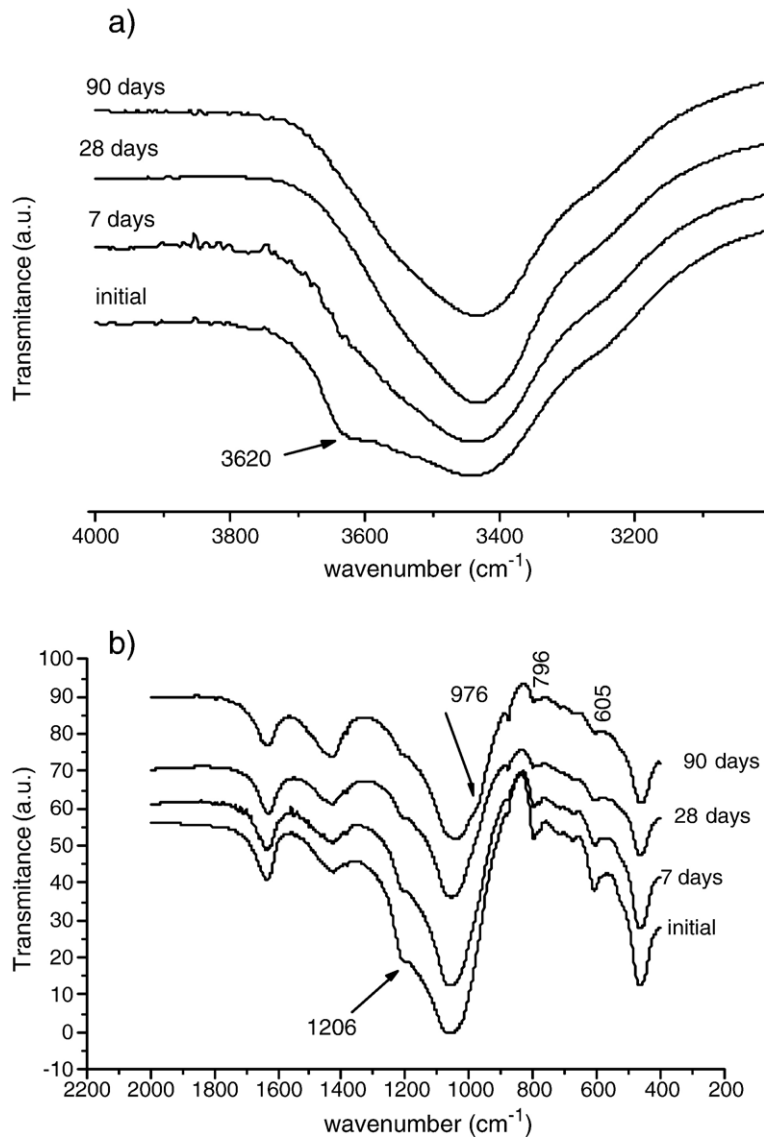


Fig. 3. FTIR spectra for the Carolinas sample: (a) 4000–3000 cm⁻¹ and (b) 2000–400 cm⁻¹.

Al stretching band corresponding to the heulandite-type zeolite at around 1206 cm⁻¹; these changes were observed as early as 7 days into the trial;

- (b) slight shift in the band at 1064 cm⁻¹ to lower vibration frequencies at around 1040 cm⁻¹, together with a gradual narrowing of this band, both indicative of a shorter range of lengths for the Si–O bond in the sample;
- (c) appearance of a shoulder at 976 cm⁻¹ that may be characteristic of the pozzolanic reaction product, the C–S–H gel; the changes described in (b) and (c) are gradual but can be seen most clearly in the spectrum for the 90-day sample (Fig. 3b);

- (d) steady decline in intensity of the band at 796 cm⁻¹, due to quartz and to amorphous silica stretching vibrations, and the band at around 605 cm⁻¹, assigned to vibrations owing to the zeolite pseudo-framework.

- (e) increase in the bands at 1420, 877, 713 cm⁻¹ (especially in the 90-day sample), evincing slight carbonation of the solids or precipitation of CaCO₃ during the test period.

In the Los Congos sample (Fig. 4a and b), the band at 1020 cm⁻¹ shifted slightly to 1012 cm⁻¹. These minor changes can be interpreted as the incipient formation of the C–S–H gel as a result of the reaction between the

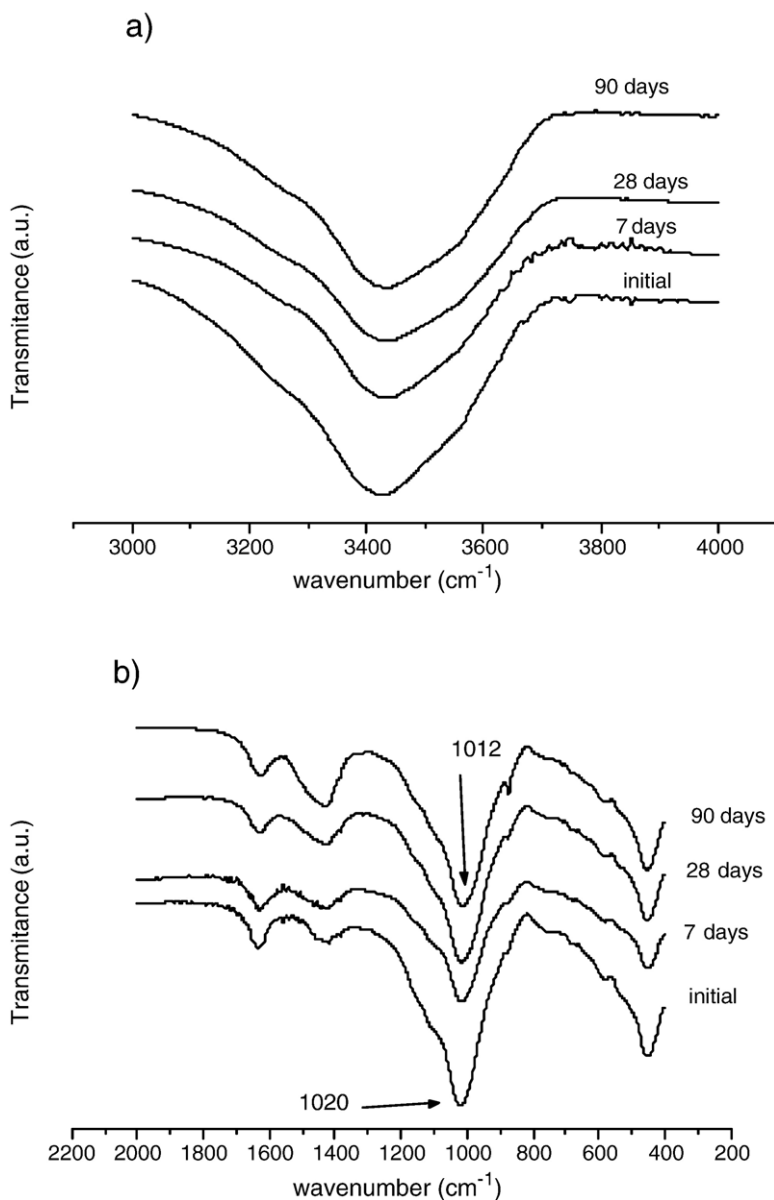


Fig. 4. FTIR spectra for the Los Congos sample: (a) 4000–3000 cm⁻¹ and (b) 2000–400 cm⁻¹.

zeolite and the Ca(OH)₂ in the solution. The most striking changes were found in the carbonate vibration bands at 877 and 713 cm⁻¹, an indication of substantial carbonation in the samples.

Fig. 5 contains the ²⁹Si MAS NMR spectra for the initial Carolinas sample and the same sample after 7, 21 and 90 days in saturated solution of portlandite, as well as for the residue left in the 90-day sample after methanol-salicylic attack. Table 3 lists the chemical shifts in the bands, their assignment and the area of each obtained after spectrum deconvolution.

The four signals on the ²⁹Si MAS NMR spectrum for the Carolinas sample were assigned to zeolites in previous research (Blanco-Varela et al., in press). New signals appeared at -96, -91, -86 and -82 ppm when the sample came into contact with the portlandite solution, due to the presence of Q³ and Q² units. The first two signals are due to the Q³ units resulting from the division of the Q⁴ units in the pozzolan; the signal at -91 ppm, assigned to silicon atoms surrounded, through oxygen atoms, by one aluminium and two silicon atoms, i.e., Q³ (1Al) units, is due to the calcium-poor C-S-H gel formed; and the signals due to Q² units are the signals

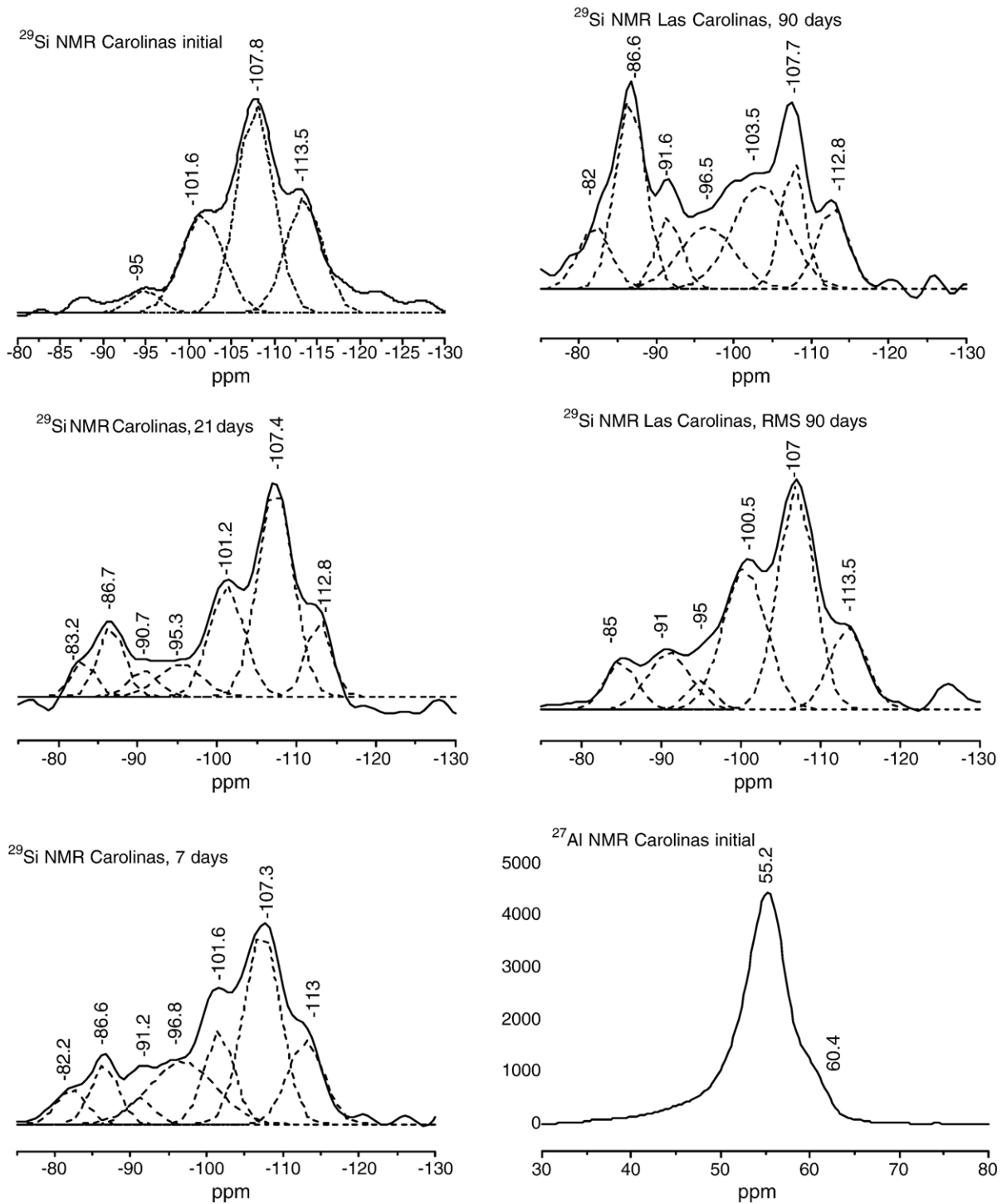


Fig. 5. ^{29}Si MAS NMR for the Carolinas material: (a) initial; and after (b) 7, (c) 21 and (d) 90 days of immersion in a $\text{Ca}(\text{OH})_2$ solution. ^{27}Al MAS NMR of the sample after 90 days.

characteristic of the C–S–H gel. The area of the Q^4 units without Al or with 1Al (–113 and –107 ppm) was found to decline sharply, whereas the area of the signal due to

Q^4 units with one or two Al remained practically unchanged after 90 days of test. As a result of the formation of two-dimensional structures and the C–S–H

Table 3

²⁹Si NMR bands of Carolinas sample before and after to be in contact with a Ca(OH)₂ saturated solution for 7, 21 and 90 days and of the residue of Takashima attack of the 90-day sample

Carolinas	Bands assigned to pozzolan				WB ^a	Bands assigned to C–S–H gel		
ppm/area%	Q ⁴ (0Al)	Q ⁴ (0 or 1Al)	Q ⁴ (1 or 2Al)	Q ⁴ (or 3Al)	Q ³ (0Al)	Q ³ (1Al)	Q ² (0Al)	Q ² (1Al)
Initial	–113.5 25.1	–107.8 45.7	–101.6 25.0	–95.0 4.2				
7 days	–113.0 15.0	–107.3 34.7	–101.6 13.7		–96.8 19.9	–91.2 3.6	–86.6 8.0	–82.2 5.1
21 days	–112.8 10.7	–107.4 41.2	–101.2 21.2		–95.3 7.9	–90.7 4.1	–86.7 10.2	–83.2 4.6
90 days	–112.8 10.3	–107.7 12.5	–103.5 24.0		–96.5 13.9	–91.6 7.6	–86.6 23.4	–82.0 8.2
90-day MSR	–113.5 13.7	–107.0 37.7	–100.5 28	–95.0 3.5		–91.0 10.9	–85.0 6.9	

^a WB: amorphous band.

gel chains, the area of the Q³ (1Al) and Q² units rose with the time the sample was in contact with the Ca(OH)₂ solution. The absence of the band at –79 ppm, related to Q¹ units, may be attributed to the long chains formed: the outcome would be such a small number of Q¹ units that the respective band would be too small to visualize.

The most intense aluminium signal on the ²⁷Al MAS NMR spectrum for the Carolinas sample, located at 55.2 ppm, was assigned (Blanco-Varela et al., in press) to tetrahedrally co-ordinated Al (Fig. 5). This sample also exhibited a shoulder at 60.4 ppm. The intensity of the peak at 55.2 ppm dropped with time of exposure to the Ca(OH)₂-saturated solution as a result of the pozzolanic reaction. The shoulder at 60.4 ppm, on the contrary, grew with time (Fig. 6). There was no evidence whatsoever of octahedrally co-ordinated aluminium in either the initial or the 90-day Carolinas sample spectra.

The ²⁹Si NMR spectrum for the Los Congos zeolitic rock showed resonance lines in the –70- to –110-ppm interval, with three peaks (Fig. 7): a first very small peak at –84.5 ppm, a second fairly intense peak at –93 ppm and a third at –108.2 ppm. In prior research (Blanco-Varela et al., in press), these signals were

assigned to the Q⁴ units in faujasite and albite-andesine. The poor resolution of the ²⁹Si MAS NMR spectrum may be partly attributed to the relatively high iron content. The highest peak in these relatively wide spectra (Fig. 7), at –93 ppm in the initial sample, shifted to –89.6 ppm after the sample had been in contact with the portlandite solution for 90 days. The hydroxyl ion in the saturated solution broke the Si–O or Al–O bonds in the pozzolan breaking the three dimensional structure of andesine and faujasite giving rise to less condensed structures which justify the shift of the signal.

Such finding can also be inferred from the XRD data, which showed that the peak at 2θ = 27.8° and 6.5° corresponding to andesine and faujasite, respectively, while increases the amorphous halo from C–S–H gel.

The ²⁷Al MAS NMR spectrum for Los Congos exhibited a large signal at 57.2 ppm, with two shoulders, at 46.6 and 38 ppm (Fig. 7). The large 57.2-ppm signal was assigned to the Al(IV) present in faujasite and albite (Kubicki and Sykes, 2004, pp. 3909–3918). The smaller peaks in the 30–50-ppm range could be attributed to penta-co-ordinated aluminium atoms, distorted, tetrahedrally co-ordinated aluminium or a non-framework tetrahedrally co-ordinated aluminium species (Mozgawa et al., 2002, p. 281; Meneze et al., 2001, pp. 367–377). A very small signal was also observed at 2 ppm due to the Al(VI) present in the zeolite (Meneze et al., 2001, pp. 367–377). The intensity of the 57.7-ppm band declined with exposure to a Ca(OH)₂ medium, while the time-dependent growth of the small band appearing at 61 ppm was interpreted as an indication that the pozzolanic reaction was taking place (Fig. 8).

The chemical analysis of the calcium oxide content in the solid samples is given in Table 4. The rise in the percentage of calcium oxide in the solid samples provided proof that both natural pozzolans are reactive

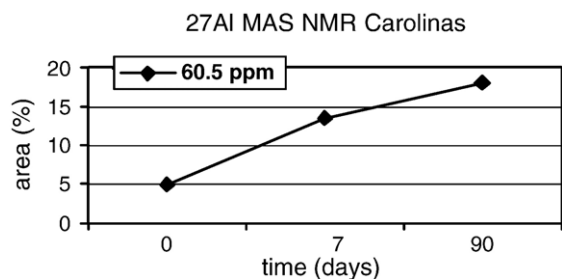


Fig. 6. ²⁷Al NMR signal for the Carolinas sample, 0 to 90 days.

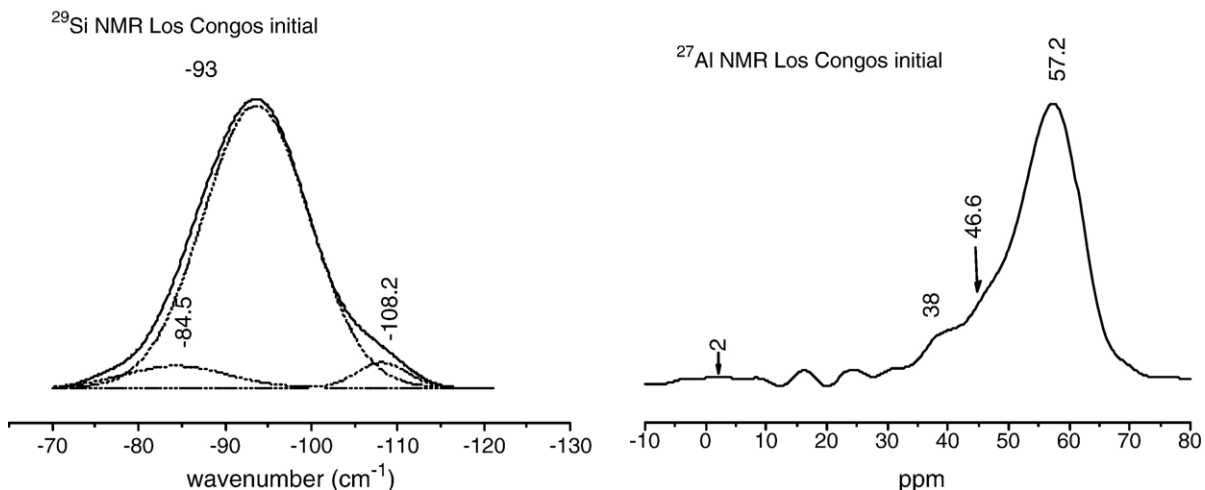


Fig. 7. ²⁹Si and ²⁷Al MAS NMR for Los Congos initial sample.

and can form C–S–H gels or hydrated calcium aluminates; another possible source of this calcium is the precipitation of CaCO₃ due to the reaction of the calcium ion in the solution with atmospheric CO₂. The amount of water fixed in cement hydration products is usually determined with DTA/TG techniques, assuming as a general rule that the loss up to 450 °C is due to water fixed in the C–S–H gel, ettringite, hydrated calcium monosulphoaluminate or C₂ASH₈, etc.; water loss in the 450 to 550 °C range is from portlandite and any loss over these temperatures is regarded to be due to CO₂ (Puertas et al., 1997, pp. 232–239). Table 5 gives the weight loss in the different temperature ranges for the two natural pozzolans and the two 90-day samples as measured by their TGA curves. The 90-day Carolinas and Los Congos samples showed 450 °C weight losses of 12.8% and 9%, respectively. These cannot be interpreted to be due entirely to dehydration of the C–S–H gel or other pozzolanic reaction products, however,

since the zeolite rocks themselves lost 11% and 4%, respectively, of their weight in that same temperature range and the degree of reaction of each was unknown. It may nonetheless be concluded that both 90-day samples contained more calcium carbonate (around 4.4% and 7.4%, respectively) than the original material.

The methanol-salicylic acid residue is also shown in Table 5. The greater solubility of the samples after 90 days of attack by the Takashima (1958) procedure confirmed the existence of pozzolanic reaction products in those samples.

The chemical analysis of the solutions in contact with the samples at different test times is given in Table 6. The higher Na content (Table 6) in the solutions in contact with the Carolinas pozzolan compared to the Los Congos pozzolan solutions may indicate that heulandite-type zeolite is more soluble than faujasite and andesine.

Calcium concentration was high because the samples were in a saturated Ca(OH)₂ solution. The Al and Si concentrations were very low due to the formation of pozzolanic reaction products such as the C–S–H gel. However, Al concentration is increasing while Si concentration is decreasing along the time. The concentration of Al is higher in Carolinas than in Los Congos solutions. Solutions are oversaturated in C–S–H

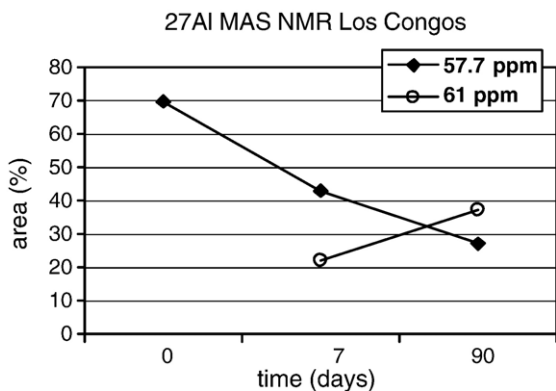


Fig. 8. ²⁷Al NMR signals at 57.7 and 61 ppm, 0 to 90 days.

Table 4
Percentage by weight of CaO in solid samples

	Initial	7 days	14 days	21 days	28 days	60 days	90 days
Carolinas	4.32	13.87	13.9	13.95	17.98	17.32	21.27
Los Congos	5.61	17.41	18.18	17.46	21.24	21.25	21.08

Table 5
Weight loss (%) by temperature range

		25– 100 °C	100– 200 °C	200– 450 °C	450– 650 °C	650– 850 °C	MSR
Carolinas	Initial	3	4.42	3.68	1.14	0.89	98.88
	90 days	2.78	5.53	4.54	1.87	1.96	74.77
Congos	Initial	2.24	1.11	0.69	0.82	0.75	94.88
	90 days	2.45	2.85	3.56	2.39	3.28	86.86

gel (except for 90-day solution) and in different calcium hydrate aluminates.

4. Discussion

4.1. Carolinas

The 59.43% reactive silica in the Carolinas sample, primarily from the zeolite, was the species that reacted with the Ca(OH)₂ solution to produce the C–S–H gel. This fact was confirmed by the drop in the intensity of the diffraction bands characteristic of zeolite (Fig. 1) and the appearance of a band at 976 cm⁻¹ in the FTIR spectrum (Fig. 3) characteristic of C–S–H gel (Bensted and Varma, 1974, pp. 440–450). The disappearance of the band at 3620 cm⁻¹ on that spectrum was interpreted to indicate the severance of the bond between the OH groups and the Si. Since the sample was fixing Ca in the solution, it could be assumed that the calcium was bonding to the Si that had lost their OH groups.

Thermodynamic data indicates that at different ages the samples are oversaturated in C–S–H gel confirming its formation in the samples. According to saturation index values the solutions are slightly oversaturated in several calcium hydrate aluminates, however, those

phases have not been identified through any of the experimental techniques used. Even Al octahedrally co-ordinated, characteristic of calcium hydrate aluminates, has not been observed in the NMR spectra. So that it can be concluded that those phases are not present in the samples or their concentration is under detection limit of the techniques. Then Al is fixed in the C–S–H gel.

The reaction mechanism for the formation of the C–S–H gel from pozzolan is the reverse of the mechanism involved in cement hydration. Whereas the latter entails an increase in the degree of condensation, as monomeric species with isolated silicate units (Q^0) polymerize into dimeric (Q^1) units and chains (Q^2), in the pozzolanic reaction three-dimensional structures are broken down into flat or linear units.

One consequence of this difference in mechanism is that in general, the low carbonate content C–S–H gel in cement paste with no pozzolanic additions comprises primarily linear silicate chains (Q^1 and Q^2 units) (Lippmaa et al., 1982, pp. 597–602; Grimmer, 1994, p.77; Cong and Kirkpatrick, 1995, pp. 103–111; Cong and Kirkpatrick, 1996a, pp. 144–156; Cong and Kirkpatrick, 1996b, pp. 1585–1592) of variable length (Cong and Kirkpatrick, 1996a, pp. 144–156; Richardson, 2004, pp. 1733–1777), in which a few aluminium ions take the place of the silicon atoms as framework constituents (Q^2 (1Al) (Richardson, 2004, pp. 1733–1777; Faucon et al., 1999, pp.7796–7802; Richardson et al., 1994, pp.813–829). As the Ca/Si ratio in the CSH gel declines, the relative intensity of the Q^2 signal compared to the Q^1 signal rises, i.e., chain length grows (Richardson, 2004, pp. 1733–1777).

However ²⁹Si MAS NMR studies conducted on gels with a low calcium content, formed from blast furnace slag hydration (Puertas et al., 2004, pp. 139–148;

Table 6
Analysis of solutions in contact with the samples (mM/kg)

Sample	Days	Ca	Na	K	Al	Si	pH	Oversaturated phases
Carolinas	7	15.3	3.45	0.27	0.018	0.013	12.19	A, C
	14	17.125	3.18	0.10	0.018	0.012	12.21	A, B, C
	21	17.32	2.89	0.13	0.015	0.012	12.24	A, B, C
	28	17.92	2.99	0.08	0.018	0.008	12.67	A, B, C, D, E
	60	18.75	3.13	0.13	0.026	0.007	12.26	A, B, C, D, E
	90	21.05	3.37	0.08	0.029	0.005	12.08	C
Los Congos	7	16.27	1.09	0.13	0.003	0.013	12.07	A
	14	16.95	1.06	0.36	0.004	0.011	12.15	A
	21	17.8	0.98	0.16	0.022	0.011	12.25	A, B, C, D
	28	18.25	0.88	0.18	0.018	0.009	12.57	A, B, C, D, E
	60	19.72	1.08	0.21	0.018	0.008	12.24	A, B, C, D
	90	20.92	1.13	0.21	0.022	0.005	12.07	C

A = C–S–H(1.1); B = C–S–H(1.8); C = C₃ASH₄; D = hydrogrossular; E = C₃AH₆.

Fernandez-Jimenez et al., 2003, pp. 1389–1394; Brough and Atkinson, 2002, pp. 865–879; Fernandez-Jimenez et al., 2002, pp. 29–41; Wieker et al., 1997, pp. 24) or pozzolanic reactions—in an alkaline medium—between silica fume and lime, highly reactive $\beta\text{C}_2\text{S}$ (Cong and Kirkpatrick, 1996a, pp. 144–156) or silica with C_3S (Brough et al., 1996, pp. 3365–3373), reveal the presence of Q^3 units in addition to the Q^2 and Q^1 units described above, an indication of the existence of tetrahedral silicates in cross-linked type structures.

The ^{29}Si MAS NMR spectrum for the Carolinas pozzolan prior to the test only had bands attributable to Q^4 ; as the test proceeded, bands attributed to Q^3 and Q^2 appeared on the reaction product spectra. The hydroxyl ion in the saturated portlandite solution broke the Si–O or Al–O bonds in the pozzolan, disrupting the three-dimensional structure formed by the Q^4 units to give rise to the flat Q^3 or linear Q^1 and Q^2 units that comprise the C–S–H gel.

No Q^1 signal was observed in the ^{29}Si MAS NMR spectra for the Carolinas pozzolan after immersion in a saturated portlandite solution for 7, 21 or 90 days, perhaps because the signal was very small due to the length of the chains in the C–S–H gel formed (low Ca/Si ratio). Another possible explanation is that background noise in the spectra may have concealed the signal. In a structural study of C–S–H gels synthesized from chemical reagents, Grutzeck et al. (1989) (pp. 665–668) suggested that gels with long chains and a low Ca/Si ratio may emit small Q^1 signals, not visible on the ^{29}Si MAS NMR spectrum.

As Fig. 5 and Table 3 show, the C–S–H gel formed at all ages comprised primarily Q^2 silicate units forming long chains, in which some of the silicon atoms were replaced by Al; a certain fraction of the silicon atoms was also found in flat structures (–91-ppm band, from Si Q^3 (1Al)), however. The presence of Al as part of the C–S–H gel structural skeleton was further confirmed by the evolution of the 60.5-ppm band on the ^{27}Al MAS NMR spectrum. The curve in Fig. 7, representing the area of the band throughout the test, shows that it increased with time. The replacement of silicon by aluminium in the silicate framework of the gel reflected in this signal (Faucon et al., 1999, pp. 7796–7802) explains the increase in the Q^2 (1Al) and Q^3 (1Al) units with time (Table 3).

There was no Al signal in the octahedral zone of the ^{27}Al MAS NMR spectrum for the 90-day sample, indicating that all the dissolved aluminium was fixed into the C–S–H gel and no other pozzolanic reaction products with octahedrally co-ordinated Al, such as hydrated gellenite, C_4AH_{13} , or similar, were formed.

The wide band on the ^{29}Si MAS NMR spectrum, denominated WB in Table 3, which might include a small Q^4 band with two or three Al from the original pozzolan, was interpreted to correspond to an amorphous product with a Q^3 (0Al) structure, perhaps a C–S–H gel with a very low calcium content or an intermediate phase in zeolite hydrolysis. The near disappearance of that band in the ^{29}Si MAS NMR spectrum for the methanol-salicylic residue in the 90-day Carolinas sample is an indication that the species dissolved. The solubility of this phase in methanol-salicylic acid would support the hypothesis that it was a C–S–H gel with a low calcium content.

The percentage of Q^4 units in the samples declined with time. The steepest decrease was observed in the Q^4 signals with a lower percentage of Al, which seems to suggest selective dissolution of zeolite towards the areas richer in Si.

The rise in the percentage of Q^2 and Q^3 units over time, in turn, is a clear indication of the formation of more C–S–H gel as a result of the pozzolanic reaction. Table 3 shows that after 7 days 16.7% of the Si was in the form of C–S–H gel, and that this value rose to 39.2% after 90 days (these calculus disregard any contribution by the so-called WB band, whose assignment is uncertain).

Since C–S–H gel is highly soluble in methanol and salicylic acid, whereas the solubility of the Carolinas pozzolan in that medium is very low, it may be inferred from the data in Table 3 that the Carolinas 90-day sample contained 25.41% CSH gel. This value is clearly smaller than would be expected from the quantitative data obtained by deconvoluting the bands on the ^{29}Si MAS NMR spectrum. The ^{29}Si MAS NMR spectrum for the methanol-salicylic residue after 90 days should be the same as the spectrum for the initial sample (Fig. 5); and yet it had two new peaks, at –85 and –91 ppm, attributed to the C–S–H gel formed. This suggests that the methanol-salicylic attack was not complete and that not all the C–S–H gel formed was dissolved. According to the data in Table 3, 17.8% of the Si remained in the sample in the form of C–S–H.

4.2. Los Congos

The Los Congos sample contained 24.97% of reactive silica, less than in the Carolinas sample, providing initial evidence of the lower reactivity of the former material. The Los Congos XRD pattern shows two diffraction lines, at $2\theta=27.8^\circ$ and 28.04° , assigned to the albite-type feldspar. The line at 27.8° was observed to decline with time of exposure to the $\text{Ca}(\text{OH})_2$ solution, whereas the other line decreased much less

significantly. The intensity of the peak at $2\theta=6.5^\circ$, most likely due to faujasite, also waned over time when in contact with the portlandite solution. All these changes were interpreted to be due to the reaction between albite/andesine and faujasite and calcium hydroxide reaction.

The substantial width of the ^{29}Si MAS NMR spectrum for Los Congos due to the presence of Fe in the sample prevents any clear determination of the shifts due to the appearance and disappearance of the various phases (albite/andesine, faujasite and so on). Nonetheless, the shift observed in the peak from -93 ppm in the initial sample to -89.6 ppm after 90 days in contact with the $\text{Ca}(\text{OH})_2$ solution may be an indication that some of the phases reacted, and that the resulting structure is less condensed than the original one.

The higher intensity band on the FTIR spectrum shifted from 1020 to 1012 cm^{-1} , perhaps due to the formation of the C–S–H gel but also perhaps to the selective solution of the feldspar phase. As noted earlier, the sample contains an albite/andesine solid solution; the phase richest in Si peaked at 1035 cm^{-1} and the one with the highest Al content at 932 cm^{-1} , while the intermediate areas peaked at 1000 cm^{-1} (Van der Marel and Beutelspacher, 1976). The reaction between the phase richest in Si and the $\text{Ca}(\text{OH})_2$ may shift the band towards values closer to 1000 cm^{-1} . The thermodynamic data obtained with the PhreeqC program indicated that the solution was over-saturated with C–S–H gel.

Kubicki and Sykes, 2004 assigned the ^{27}Al MAS NMR signal appearing at 57.7 ppm to the Al(IV) present in faujasite and albite. Fig. 8 shows the evolution of that signal and the one appearing at 61 ppm. The former was observed to decrease with time of exposure to the $\text{Ca}(\text{OH})_2$ solution, an indication of its involvement in a pozzolanic reaction. The band due to pentahedral Al (38 ppm), in turn, disappeared in even the very earliest spectra.

The area of the signal appearing after 7 days of exposure to the $\text{Ca}(\text{OH})_2$ medium was observed to grow in the 90-day sample. According to the literature (Kubicki and Sykes, 2004, pp. 3909–3918; Richardson et al., 1993, pp. 2285–2288; Richardson et al., 1994, pp. 813–829), this band is due to the Al [IV] in the C–S–H gel formed during cement hydration. The Al [IV] positions in the C–S–H gel could not be determined because of the width of the band, an effect of the presence of Fe.

No significant increases were observed in the small band attributed to octahedral Al (2 ppm), an indication that no reaction products other than C–S–H gels were formed. Table 4 shows that both pozzolans fix Ca, since C–S–H gel was formed in both; while greater amounts were fixed in the Los Congos rock in the early stages, the values reached after 90 days were similar. Nonetheless,

the calcium carbonate in the Los Congos samples after 90 days had a higher proportion of CaCO_3 .

5. Conclusions

The chief conclusions to be drawn from the present study are as follows:

- (a) The zeolitic rocks from Carolinas and Los Congos reacted with $\text{Ca}(\text{OH})_2$ to form C–S–H gel as the sole pozzolanic reaction product. There was no indication of the formation of hydrated calcium aluminates in the results of any of the analyses conducted.
- (b) After 90 days the Carolinas sample fixed 17% of the CaO, mostly as C–S–H gel, although 1.4% was found to be in the form of carbonates. The ^{29}Si MAS NMR data suggest that 39% of the silicon in the sample formed a part of the C–S–H structure.
- (c) The gel in the Carolinas sample was formed from the 59.43% of reactive silica coming primarily from the zeolite. The steep decrease observed in the Q^4 signals with a lower percentage of Al seems to suggest selective dissolution of the zeolite.
- (d) The C–S–H gel in the 90-day Carolinas sample primarily comprised long silicate chains in which part of the silicon ions were replaced by Al. The presence of Si in Q^3 units indicates a laminar structure for the gel, in addition to its chain-like configuration. The amount of Al substituting Si in samples (in Q^3 (1Al) and Q^2 (1Al) units) is observed to increase with time.
- (e) The Los Congos pozzolan had a lower percentage of reactive silica (24.97%), which would explain the lower percentage of gel formed.
- (f) The presence of Fe in the Los Congos sample hampered the ^{29}Si MAS NMR analysis of the gel formed, although the presence of Al in its composition could be inferred from the ^{27}Al MAS NMR data.
- (g) Although the amount of Ca fixed by the two pozzolans after 90 days was similar in the two samples, it was fixed more rapidly in the more intensely carbonated Los Congos sample.

Acknowledgements

This paper has been funded by project No. 2003CU0005 from the convenio 01CU002 CSIC/CIT MA and the project MAT2003-08343 of the Spanish Plan Nacional de Investigación Científica e Innovación Tecnológica. Dr. Sagrario Martínez-Ramírez participated in this

research under a Ramon y Cajal contract awarded by the Ministry of Science and Technology and co-funded by the European Social Fund.

References

- Alcantara Ortega, E., Cheeseman, C., Knight, J., Loizidou, M., 2000. Properties of alkali-activated clinoptilolite. *Cem. Concr. Res.* 30, 1641–1643.
- Bensted, J., Varma, S.P., 1974. Some applications of infrared and Raman spectroscopy in cement chemistry. *Cem. Technol.* 4 (5), 440–450.
- Blanco-Varela, M.T., Martínez-Ramírez, S., Ereña, I., Gener, M., Carmona, P., in press. Characterization and pozzolanicity of zeolitic rocks from two Cuban deposits. *Applied Clay Sciences*.
- Brough, A.R., Atkinson, A., 2002. Sodium silicate-based, alkali-activated slag mortars: Part I. Strength, hydration and microstructure. *Cem. Concr. Res.* 32, 865–879.
- Brough, A.R., Dobson, C.M., Richardson, I.G., Groves, G.W., 1996. Alkali activation of reactive silicas in cements: in situ ^{29}Si MAS NMR studies of the kinetics of silicate polymerisation. *J. Mater. Sci.* 31, 3365–3373.
- Brough, A.R., Katz, A., Sun, G.-K., Struble, L.J., Kirkpatrick, R.J., Young, J.F., 2001. Adiabatically cured, alkaline-activated cement-based wasteforms containing high levels of fly ash. Formation of zeolites and Al-substituted C–S–H. *Cem. Concr. Res.* 31, 1437–1447.
- Cong, X.D., Kirkpatrick, R.J., 1995. ^1H - ^{29}Si CPMAS NMR study of the structure of calcium silicate hydrate. *Adv. Cem. Res.* 7, 103–111.
- Cong, X.D., Kirkpatrick, R.J., 1996a. Si-29 MAS NMR study of the structure of calcium silicate hydrate. *Adv. Cem Based Mater.* 3 (3–4), 144–156.
- Cong, X.D., Kirkpatrick, R.J., 1996b. O-17 MAS NMR investigation of the structure of calcium silicate hydrate gel. *J. Am. Ceram. Soc.* 79, 1585–1592.
- Drzaj, B., Hocevar, S., Slokan, M., Zajc, A., 1978. Kinetics and mechanism of reaction in the zeolitic tuff-CaO–H₂O system at increased temperature. *Cem. Concr. Res.* 8, 711–720.
- Faucou, P., Delagrave, A., Petit, J.C., Richet, C., Marchand, J.M., Zanni, H., 1999. Aluminium incorporation in calcium silicate hydrates (C–S–H) depending on their Ca/Si ratio. *J. Phys. Chem. B.* 103, 7796–7802.
- Fernandez-Jimenez, A., Puertas, F., Sobrados, I., Sanz, J., 2002. Structure of calcium silicate hydrate formed in alkali activated slag cement pates. In: Býlek, V., Kersner, Z. (Eds.), *Non-traditional Cement and Concrete*, pp. 29–41.
- Fernandez-Jimenez, A., Puertas, F., Sobrados, I., Sanz, J., 2003. Structure of calcium silicate hydrate formed in alkaline activated slag: influence of the alkaline activator nature. *J. Am. Ceram. Soc.* 86 (8), 1389–1394.
- Fragoulis, D., Chaniotakis, E., Stamatakis, M.G., 1997. Zeolitic tuffs of Kimolos Island, Aegean Sea, Greece and their industrial potential. *Cem. Concr. Res.* 27, 889–905.
- Grimmer, A.R., 1994. In: Colombet, P., Grimmer, A.R. (Eds.), *Application of NMR Spectroscopy to Cement Science*. Gordon and Breach, London, p. 77.
- Grutzeck, M., Benesi, A., Fanning, B., 1989. Silicon-29 magic angle spinning nuclear magnetic resonance study of calcium silicate hydrates. *J. Am. Ceram. Soc.* 72 (4), 665–668.
- Janotka, I., Mojumdar, S.C., 2003. Hydration of portland cement, natural zeolite mortar in water and sulphate solution. *Mater. Constr.* 53 (269), 17–27.
- Kitsopoulos, K.P., Dunham, A.C., 1996. Heulandite and mordenite-rich tuffs from Greece: a potential source for pozzolanic materials. *Miner. Depos.* 31, 576–583.
- Kubicki, J.D., Sykes, D.G., 2004. Ab initio calculation of H-1, O-17, Al-27 and Si-29 NMR parameters, vibrational frequencies and bonding energetics in hydrous silica and Na-aluminosilicate glasses. *Geochim. Cosmochim. Acta* 68, 3909–3918.
- Lea's, 1999. *Chemistry of Cement and Concrete*, Peter C. Hewlett, Arnold.
- Lippmaa, E., Mägi, M., Tarmak, M., Wieker, W., Grimmer, A.R., 1982. A high-resolution ^{29}Si NMR-study of the hydration of tricalcium silicate. *Cem. Concr. Res.* 12, 597–602.
- Meneze, S.M.C., Camorin, V.L., Lam, Y.L., San Gil, R.A.S., Bailly, A., Amoureux, J.P., 2001. Characterization of extra-framework species of steamed and acid washed faujasite by MQMAS NMR and IR measurements. *Appl. Catal. A* 207, 367–377.
- Mozgawa, W., Fojud, Z., Handke, M., Jurga, S., 2002. MAS NMR and FTIR spectra of framework aluminosilicates. *J. Mol. Struct.* 614, 281–287.
- Pekmezci, B.Y., Akyüz, S., 2004. Optimum usage of a natural pozzolan for the maximum compressive strength of concrete. *Cem. Concr. Res.* 34, 2175–2179.
- Perraki, Th., Kakali, G., Kontoleon, F., 2003. The effect of natural zeolites on the early hydration of portland cement. *Microporous Mesoporous Mater.* 61, 205–212.
- Poon, C.S., Lam, L., Kou, S.C., Lin, Z.S., 1999. A study on the hydration rate of natural zeolite blended cement pastes. *Constr. Build. Mater.* 13, 427–432.
- Puertas, F., Blanco-Varela, M.T., Palomo, A., Vázquez, T., 1997. Behaviour of a new cement fabricated with raw materials containing CaF₂ and CaSO₄·2H₂O: Part I. Hydration processes. *Zem.-Kalk-Gips* 4, 232–239.
- Puertas, F., Fernández-Jiménez, A., Blanco-Varela, M.T., 2004. Pore solution in alkali-activated slag cement pastes. Relation to the composition and structure of calcium silicate hydrate. *Cem. Concr. Res.* 34, 139–148.
- Rahhal, V., Talero, R., 2003. Effect of three natural pozzolans in portland cement hydration. *Mater. Constr.* 53 (269), 29–40.
- Richardson, I.G., 2004. Tobermorite/jennite- and tobermorite/calcium hydroxide-based models for the structure of C–S–H: applicability to hardened pastes of tricalcium silicate, dicalcium silicate, portland cement, and blends of portland cement with blast-furnace slag, metakaolin, or silica fume. *Cem. Concr. Res.* 34, 1733–1777.
- Richardson, I.G., Brough, A.R., Brydson, R., Groves, G.W., Dobson, C.M., 1993. Location of aluminium in substituted calcium silicate hydrated (C–S–H) gels as determined by ^{29}Si and ^{27}Al NMR and EELS. *J. Am. Ceram. Soc.* 76, 2285–2288.
- Richardson, I.G., Brough, A.R., Groves, G.W., Dobson, C.M., 1994. The characterization of hardened alkali-activated blast-furnace slag pastes and the nature of the calcium silicate hydrated (C–S–H) phase. *Cem. Concr. Res.* 24, 813–829.
- Shi, C., Day, R.L., 2000a. Pozzolanic reaction in the presence of chemical activators: Part I. Reaction kinetics. *Cem. Concr. Res.* 30, 51–58.
- Shi, C., Day, R.L., 2000b. Pozzolanic reaction in the presence of chemical activators: Part II. Reaction products and mechanism. *Cem. Concr. Res.* 30, 607–613.
- Takashima, S., 1958. *Semento Gijutzu Nenpo XII*, 12–13.
- Van der Marel, H.W., Beutelspacher, H., 1976. *Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures*. Elsevier Scientific Publishing Company, Amsterdam.
- Wieker, W., Hubert, C., Heidemann, D., 1997. Recent results of solid-state NMR investigations and their possibilities of use in cement chemistry. 10th ICCG (Goterborg) vol. 1, H. Justness, Trondheim, Norway, p. 24.