Proceedings of the EUROCOALASH 2012 Conference,
Thessaloniki Greece, September 25-27 2012
http:// www.evipar.org/

Alkaline activation-induced conversion of fly ash into an effective binder

Part III. Reducing the clinker content

A. Fernández-Jiménez[1], I. Garcia-Lodeiro[1] and A. Palomo[1]

[1] Instituto de Ciencias de la Construcción Eduardo Torroja (IETcc – C.S.I.C.), Serrano Galvache Nº 4, 28033 Madrid, Spain; ' email anafj@ietcc.csic.es

Abstract

The present paper contains a discussion of the environmental issues surrounding binders used in construction in general and an introduction to fly ash activation technology and certain basic concepts about hybrid cements (binders with a very low clinker factor and high fly ash content). In the authors' opinion, such technology may soon become highly enough developed to bridge the gap between portland cement and the cements of the future.

A good deal of research is still required on low portland clinker, high aluminosilicate content binders, however. This paper reports on mechanical strength development in several such hybrids and on the mineralogical and microstructural development of the reaction products, which were observed to constitute a mix of C-A-S-H and (N,C)-A-S-H gels.

Keywords: fly ash, alkali activation, clinker factor, hybrid cements, geopolymer

1 Introduction

Concerns around the CO_2 emitted in portland cement manufacture constitute a standing invitation for the scientific community to seek sustainable alternatives.

The reduction of the portland cement content in construction binders via replacement with supplementary cementitious materials (SCMs) such as slag, natural pozzolans or fly ash is a successful practice that has been in place for many years [1-6]. The use of SCMs has, moreover, been acknowledged by legislation the world over as a way of generating different types of cement and consolidated by unanimous reports that the practice leads to significant improvements in cementitious systems while contributing to sustainability.

The inclusion of fly ash in binders as a partial replacement for portland cement, in addition to effectively reducing cement consumption, provides a solution for recycling this industrial by-product. Most standards limit the replacement ratio to under 55 % [7], however, primarily because at higher percentages the early age mechanical strength of the cement declines substantially (when used alone, fly ash exhibits no hydraulic behaviour). One proposal (and one of the principal aims of the present study) for raising the ash content in OPC blends to >70 wt% without compromising initial mechanical strength development and without having work at higher than ambient temperature is to alkali activate the blend. These alkali-activated binders are known as ***hybrid cements*** [8].

While the reaction products of the alkaline activation or hydration of aluminosilicates have been fully identified, sizeable knowledge gaps persist around the structure and composition of the main reaction product formed in hybrid cements. N-A-S-H gel ($Na_2O.Al_2O_3.SiO_2.nH_2O$), the main reaction product of the alkaline activation of aluminosilicates, is a substance in which tetrahedrally coordinated Si and Al units combine to form three-dimensional structures. The role played by the alkalis is to re-establish the charge balance [9-11]. During portland cement or Ca-rich aluminosilicate (such as blast furnace slag) hydration, the cementitious material formed is C-S-H gel ($CaO-SiO_2-H_2O$), whose linear structure may include small amounts of Al [12-15]. More recently, research has been undertaken [16-18] on the nature of the reaction products deriving from the alkaline activation of cement and fly ash blends.

The present study focused on alkaline activation as an excellent and effective procedure for reducing the clinker content in cements with good mechanical performance.

2 Mechanical strength

The materials considered here, namely portland cement, portland clinker, blast furnace slag and type F fly ash, are all common cement and concrete components and all have compositions that lie in the $CaO-SiO_2-Al_2O_3$ system. A series of binders were prepared by blending these materials in the proportions specified in Table 1. These binders were hydrated with water (**W**, reference system) or an alkaline solution (**N8**, 8-M NaOH solution: d=1 200 g/L; pH=13.3; or **SS**, a sodium silicate solution: SiO_2/Na_2O ratio=1.5; d=1 200 g/L; pH=13.3). The water/binder or alkaline solution/binder ratios used in each case are given in Table 1. These pastes were moulded into 1x1x6-cm prismatic specimens and cured for 24 hours in a curing chamber (22 ºC and 99 % relative humidity), after which the specimens were removed from the moulds and stored in the chamber until they reached the test age (2 and 28 days). The specimens were tested to failure on an Ibertest (Autotest –200/10-SW) test frame to determine their bending and compressive strength.

The bending and compressive strength values for the specimens are also given in Table 1. According to these findings, blends with low cement or clinker contents can yield materials with good cementitious properties provided a suitable alkaline activator is used. In all the cases studied, solution N8 (commonly used to alkali activate fly ash) failed to deliver the mechanical strength values sought. This was attributed to an excess of alkalis in the system, which retarded portland cement clinker hydration [19]. In highly alkaline media, C_3S hydration is known to be delayed substantially due to the common ion effect (the increase in OH^- ion concentration in the system), and to the fact that the C-S-H gel may decompose in these media [19]. The use of portland cement in the blends studied was nonetheless beneficial because in the presence of alkalis the heat released during cement hydration hastened fly ash dissolution.

When the SS solution (which contained a certain percentage of soluble sodium silica) was used, however, mechanical strength rose considerably in all cases. The addition of soluble silica yielded denser matrices and a gel richer in Si. Moreover, in these cases, the binder set and hardened at ambient temperature. The material obtained with this activator (solution SS) exhibited mechanical properties comparable to or better than type 32.5 CEM portland cement, even though the cement or clinker content in these blends was 30 % or under (see cements B3-SS and B4-SS, Table 1).

3 Reaction products

Exhaustive studies were conducted to determine the nature of the reaction products formed in cementitious systems B3 and B4, whose portland cement clinker content was no higher than 30% or 15 %, respectively.

More specifically, they were studied by XRD *(BRUKER AXS D8 ADVANCE)*, SEM/EDX (JEOL 5400 electron microscope fitted with an OXFORD ISIS energy-dispersive X-ray spectrometer) and ^{29}Si MAS-NMR (BRUKER AVANCE-400 spectrometer).

3.1 Mineralogical characterisation

The XRD patterns for anhydrous blends B3 (30 % clinker/70 % FA) and B4 (15 % clinker/15 % slag/ 70 % FA) as well as for the 28-day water- (reference system) and SS-hydrated materials are reproduced in Figure 1. The diffraction lines for the clinker and ash (and in blend B4, slag) constituents overlapped in the patterns for the two anhydrous materials. Both traces exhibited a halo attributed to the ash and the slag as well as lines associated with the crystalline phases of the clinker (alite, belite), ash (quartz, mullite, hematite) and slag (gehlenite, merwinite). A certain amount of calcite was likewise present in the starting blend, a result of the partial weathering of the initial clinker.

The small amount of portlandite detected on the traces for both water-hydrated binders (B3-W and B4-W) confirmed that the clinker reacted. The portlandite signal was more visible in sample B3-W than in B4-W because the latter contained less clinker. The presence of a substantial amount of calcite was also observed, perhaps because part of the portlandite in the specimens carbonated during handling. Some of the carbonation detected in the pastes affected may have been induced by cement carbonation prior to mixing. That process would have distorted actual paste carbonation during hydration, which would have been less intense than inferred by the XRD findings.

In the alkali-activated systems (B3-SS and B4-SS), hydration was retarded in the anhydrous silicate present in the clinker, for substantial amounts of alite were detected in the 28-day material. The absence of peaks associated with crystalline calcium hydroxide (portlandite) on the XRD spectrum did not, however, rule out the formation of the amorphous form of that compound. The formation of hydroxysodalite, a zeolite, was detected in system B4-SS. The presence of zeolites (generally detected in alkali-activated fly ash systems [20-21]) in these pastes confirmed the acceleration of the initial fly ash reaction in these alkali-activated systems.

In light of the scant information provided by XRD on the composition and structure of the gel primarily responsible for the mechanical strength of these hybrid cements, other techniques such as scanning electron microscopy (SEM/EDX) and MAS-NMR were required to acquire a deeper understanding of their nature.

3.2 Microstructural characterisation

Figure 2 shows a series of SEM micrographs of 28-day B3-W and B3-NS pastes. The cement matrix observed to form in both contained some unreacted clinker amd fly ash (point 1). Paste B3-W appeared to be much less compact than B3-SS. Microanalysis revealed the formation in B3-W of a C-S-H gel, the majority reaction product in normal cement hydration. This gel took up small amounts of aluminium (point 2, C-(A)-S-H gel), in all likelihood a product of the pozzolanic reaction between the fly ash and portlandite.

The formation of a more compact solid mass was observed in material B3-SS (Figure 2(b)), which was primarily in contact with the unreacted or only partially reacted ash particles. The precipitation of a denser, more compact and more continuous product may partially explain the higher mechanical strength developed by this material. The morphological analysis alone was insufficient to clearly distinguish whether a single gel or a mix of gels was forming, however. The microanalytical findings (points 3 and 4) showed that this cementitious mass was formed entirely of Na, Ca, Si, and Al, although the percentage composition, especially of Ca and Si, varied widely. Gels richer in Ca formed where a C_3S or C_2S particle was once located (see point 3), whereas the Si and Al contents were higher in places formerly occupied by an ash particle (point 4). In other words, at least two types of gels can be distinguished: a C-A-S-H gel (point 3) and a (N,C)-A-S-H gel (point 4). Na formed part of the composition of both gels, balancing the charge created when an Al tetrahedron replaced a Si tetrahedron.

Material B4 was studied with BSEM to enhance the precision of the microanalytical findings. The micrographs and EDX analyses in Figure 3 show the composition of the cementitious gel precipitating in the 28-day water-hydrated and SS-solution-activated materials. Unreacted clinker (K), slag (s) and fly ash (f) were clearly visible in both. The main reaction product in cement B4-W was a C-S-H-type gel with a Ca/Si ratio of ~0.8/0.9 (point 5).

The changes in the composition of the precipitate depending on its location in the vicinity of a clinker, fly ash or, in this case, a slag particle, are readily observable in Figure 3(b). The particle in point 6 comprised C_3S present in the clinker. The lighter colour, Ca-rich ring surrounding it was associated with the formation of microcrystalline portlandite, which would be difficult to detect with XRD. The greater the distance from that grain, the higher the Si content in the gel and the lower its calcium content (points 8 and 9). This gel contained a certain amount of Al and even some Na. The Al content was greater than detected in the water-hydrated materials (see point 5). Since the main source of Al in these cements was fly ash, these findings confirmed the substantially higher degree of reaction in early age fly ash in the presence of an alkaline activator.

The rise in the Al content in the gel was associated with a decline in the Ca/Si ratio (point 8, atomic ratios: $Ca/Si \cong 0.7/0.8$ and $Si/Al \cong 3$), which denoted the formation of C-A-S-H-type gels. Given the higher degree of fly ash reaction in these systems, the presence of (N,C)-A-S-H gels was also detected, i.e., gels with higher Si and Al contents (point 9, with atomic ratios: $Ca/Si<0.4$; $Si/Al \cong 2.0/2.5$ and $Na/Al \cong 0.5$-0.6). In this specific case, because the cementitious material contained slag, the presence of Mg was detected in the areas around this type of grains (point 10).

Figure 4 shows the ^{29}Si MAS NMR spectra for the 28-day systems. These spectra cannot be readily interpreted because the signals emitted by the different gels overlapped among themselves and with the unreacted prime materials.

The ^{29}Si MAS NMR spectrum for the clinker contained a narrow, symmetrical signal with a bandwidth of around 15 ppm. This signal had a peak centred at -71.38 ppm and a shoulder at -73.99 ppm, which respectively reflected the Q^0 monomers or Si tetrahedra present in C_3S_{ss} (alite) and C_2S_{ss} (belite), the two main constituents of portland cement [22-23]. The fly ash spectrum exhibited a wide signal centred at around -108 ppm. This signal was characterised by a series of shoulders associated with the various forms in which the silicate appeared in the fly ash (mullite, vitreous phase, quartz, Q^4(nAl) and Q^3(nAl) units [9-10]). The wider and more asymmetrical signal centred at -76.5 ppm (Q^1 units) on the BFS spectrum was associated with the akermanite-type vitreous phase of this material [13].

The signal at -72 ppm (attributed to the anhydrous silicates in the clinker) nearly disappeared in the spectra for the water-hydrated materials (B3-W and B4-W). The peak at -74 ppm, generated by unreacted slag, was still visible on the spectrum for B4-W. Another prominent component observed on these spectra, at around -108 ppm, was attributed to the unreacted ash. (The pozzolanic reaction between the fly ash and the portlandite released during clinker hydration, took place slowly, if at all). The large amount of unreacted ash remaining in these materials would explain their lower mechanical strength. A new signal was observed in both B3-W and B4-W spectra at around -85/-86 ppm, which may have been associated with the presence of the Q^2 units in C-S-H gel [23].

The B4-W spectrum also exhibited shoulders at around -86 and -99 ppm whose presence was attributed to the formation of a more polymerised gel, and possibly to the Q^3(nAl) units in the C-A-S-H-type gel resulting from the reaction of the slag present in this system (15 %).

When alkaline activators were used (materials B3-SS and B4-SS), a peak appeared at -73/-74 ppm, confirming the lower degree of clinker reaction in these highly alkaline media. The component initially associated with the unreacted fly ash was altered considerably in both systems. A series of new signals was detected on these spectra, at -86/-87 ppm, -95 ppm and -99 ppm. The signal at -86/-87 ppm could not be readily attributed to the presence of Q^2 units only for several reasons: i) the Q^2 signals in C-S-H gels normally appear at -85 ppm: ii) these systems contained unreacted clinker; iii) the intensity of this signal was much higher here than in the water-hydrated systems (B3-W and B4-W). That, together with the presence of the aforementioned signals at -95 ppm and -99 ppm, suggested that a more polymerised gel or mix of gels was forming in these materials and that these signals were generated by the Q^3(nAl) or Q^4(nAl) units [8, 16,24,25] that give rise to C-A-S-H and (N,C)-A-S-H gels.

4- Summary

The results of this study showed that a material with good cementitious properties and low portland cement or clinker content (30 %) can be obtained at ambient temperature using alkaline activators. The presence of soluble silica in the activator played a decisive role in the development of mechanical strength. The addition of silica yielded denser matrices and a gel or gels richer in Si. That produced hybrid cements with 28-day compressive strength values upward of 32 MPa despite the low clinker contents.

In the absence of alkalis, these materials failed to develop suitable mechanical strength. In these systems the clinker hydrated normally and subsequently the ash (pozzolanic reaction) reacted with the $Ca(OH)_2$ produced during clinker hydration. Due to the low clinker and high ash content, this process was observed to be slow. As a result, the material exhibited a long setting time, which would explain the low early age strength values observed.

By contrast, the presence of alkalis and the heat released in initial cement hydration expedited the fly ash reaction substantially. That in turn raised the initial strength of these hybrid cements and induced the formation of two types of gels: i) a C-S-H gel taking aluminium into its structure (C-A-S-H gel) as a result of clinker hydration; ii) a N-A-S-H gel taking Ca into its structure ((N,C)-A-S-H gel) as a result of the alkaline activation of the ash. Judging from the behaviour of synthetic gel blends, with time these gels would be expected to interact and evolve into a new single (and more thermodynamically stable) gel that could be denominated (N,C)-A-S-H [25]. These results provided further evidence that alkaline activators enhance the fly ash reaction, inducing the formation of greater amounts of the cementitious gel from which these hybrid cements derive their mechanical strength.

4 Acknowledgements

This research project was funded under Spanish Ministry of Science and Innovation project BIA2010-17530. And thanks to Alfredo Gil Maroto for their co-operation in the mechanical tests.

References

[1] Naik T.R., Kraus R.N. and Siddique R. Controlled Low Strength Materials Containing Mixtures of Coal Ash and New Pozzolanic Material, *ACI Materials Journal*, Vol.100, No 3, 2003, pp 208-215.

[2] Papayianni I. An investigation on the pozzolanicity and hydraulic reactivity of a High Calcium Fly Ash, *Magazine of Concrete Research*, Vol. 39, No 138, 1987, pp 19-28.

[3] Papayianni I. Performance of a High Calcium Fly Ash in Roller Compacted Concrete, *ACI SP-132*, V.M. Malhotra Ed., Vol. 1, Detroit, 1992, pp 367-386.

[4] ECOBA Draft Status Report. *Calcareous Fly Ash in Europe*, June 2007.

[5] Hellenic Technical Specification. Greek Fly Ashes, *Journal of the Government of Hellenic Democracy*, Bulletin 2, No 551, 2007.

[6] Naik T.R., Ramme B.R. and Kolbeck H.J. Controlled Low Strength Materials (CLSM) produced with High Lime Fly Ash, *Proc. of 9th Int. Ash Use Symposium ACAA, Vol.1, Concrete and related products*, Electric Power Research Institute, EPRI ES-7162, 1991, pp 9-1 to 9-18.

[7] EN-197-1:2011:E. Cement. Composition, specifications and conformity criteria for common cements (2011).

[8] Shi C., Fernández Jiménez A., Palomo A., New Cements for the 21st Century, The pursuit of an alternative to Portland cement" Cement and Concrete Research 41 (2011) 750–763.

[9] Palomo A., Alonso S., Fernández-Jiménez A., Sobrados I., Sanz J. 2004. Alkali activated of fly ashes. A NMR study of the reaction products, J. Am. Ceramic. Soc., 87, 1141-1145.

[10] Fernández-Jiménez A., Palomo A., Sobrados I., and Sanz J,, 2006. The role played by the reactive

alumina content in the alkaline activation of fly ashes, Microporous and Mesoporous Materials, 91, 111-119.

[11] Duxon P, Fernández-Jiménez A, Provis J.L, Lukey G.C, Palomo A., van Deventer J.S.J. 2007. Geopolymer technology: The current state of the art. Journal Material Science 42, 2917-2933

[12] Richardson I.G. and Groves G.W. 1997. The structure of calcium silicate hydrate phases present in hardened pastes of white Portland cement/blast furnace salg blends. Jounal of Materials Sciencce 32 4793-4802

[13] Fernández-Jiménez A., Puertas F., Sanz J.and Sobrados I., 2003. Structure of calcium silicate hydrated formed in alkali-activated slag pastes. Influence of the type of alkaline-activator, J. Am. Ceramic Soc. 86, [8], 1389-1394.

[14] Puertas F., Palacios M., Manzano H. Dolado J.S., Rico A. Rodríguez J., A model for the C-A-S-H gel formed in alkali-activated slag cements, J. Eur. Ceram.Soc. 31 (2011) 2043–2056.

[15] Andersen M.D. Jakobsen H.J. and Skibsted J. 2003. Incorporation of aluminum in the calcium silicate hydrate (C-S-H) of hydrated Portland cements: a high-field 27Al and 29Si MAS NMR study. Inorganic Chemistry 42,2280-2287.

[16] Palomo A., Fernández-Jiménez A, Kovalchuk G, Ordoñez L.M, Naranjo M.C. 2007. Opc-fly ash cementitious systems: study of gel binders produced during alkaline hydration. Journal Material Science 42, 2958–2966.

[17] Garcia-Lodeiro I, Fernandez-Jimenez A, Palomo A. 2012, Variation in hybrid cements over time. Alkaline activation of fly ash-Portland cement blends, Cement and Concrete Research (Submitted)

[18] Garcia-Lodeiro I, Fernandez-Jimenez A, Palomo A (2012) Kinetics of hydration in hybrid cements: First reaction stages, Journal of European Ceramic Society (Submitted)

[19] Martinez-Ramirez S., and Palomo A. 2001. OPC hydration with highly alkaline solution. Advanced Cement Research 13 (3) 123-129.

[20] Palomo A.,.Grutzeck M.W and Blanco M.T., 1999, Alkali-activated fly ashes. A cement for the future, Cem. Concr. Res., 29, 1323-1329.

[21] Arjunan, P., Silsbee, M.R., Roy, D.M. 1997. Quantitative determination of the cristalline and amorphous phases in low calcium fly ash. 10th International Congress on the Chemistry of Cements, Gotteborg (Sweden).

[22] G. Engelhardt, D. Michel, “High Resolution solid-state NMR of silicates and zeolites”, Ed. Wiley & Sons, New Delhi, India (1987)

[23] X. Cong, R. J. Kirkpartrick, “^{29}Si NMR study of the structure of calcium silicate hydrate”, Adv. Cem. Based Mater. 3, 144-156 (1996)

[24] Garcia-Lodeiro I, Fernández-Jiménez A, Macphee D.E, Palomo A. 2010.Effects of calcium addition on N-A-S-H cementitious gels. Journal American Ceramic Society, 1-7

[25] I. Garcia-Lodeiro, A. Palomo, A. Fernández-Jiménez, D.E Macphee, Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na_2O-CaO-Al_2O_3-SiO_2-H_2O, Cem. Con. Res. 41 (2011) 923-931

Table 1. Hybrid cement composition and mechanical strength

Paste			Mechanical strength			
Binder denomination (content)	**L=hydration liquid**	**L/s ratio**	**Bending (MPa)**		**Compressive (MPa)**	
			2-day	**28-day**	**2-day**	**28-day**
B1 (50 % OPC +50 % FA)	Water (W)	0.35	5.40	8.19	13.43	38.23
	SS	0.35	1.23	4.88	12.05	**41.72**
B2 (30 % OPC +70 % FA)	Water (W)	0.35	2.64	4.99	7.32	18.46
	SS	0.35	1.65	1.59	13.90	23.29
B3 (30 % portland clinker +70 % FA)	Water (W)	0.33	2.65	5.78	11.23	28.91
	N8	0.40	1.29	6.51	4.83	24.72
	SS	0.49	3.17	6.23	12.91	**36.94**
B4 (15 % portland clinker +15 % slag + 70 % FA)	Water (W)	0.33	1.8	5.51	5.21	25.69
	N8	0.40	2.73	6.03	7.03	21.09
	SS	0.49	2.78	4.46	13.04	**41.97**

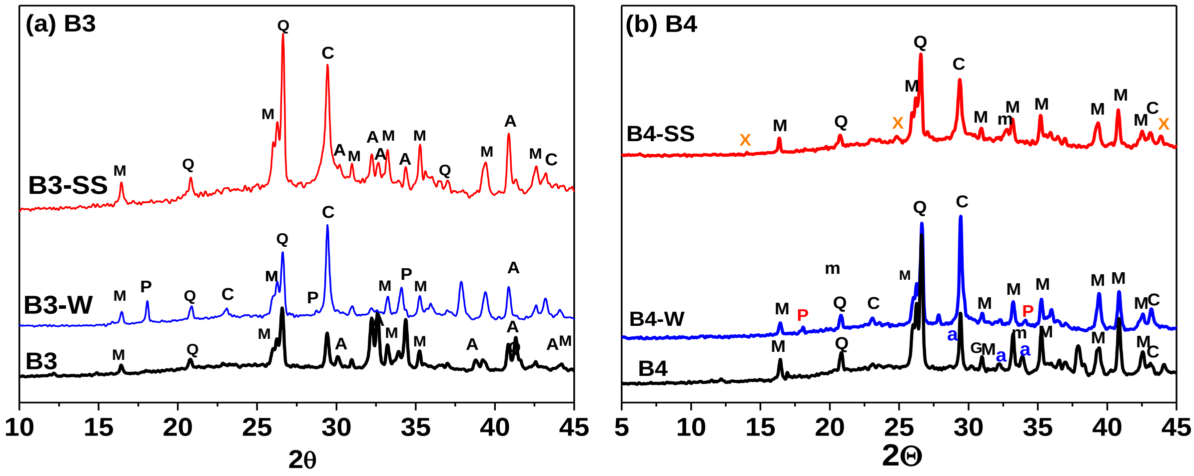

Fig. 1. XRD patterns for anhydrous and 28-day water-hydrated (W) and SS-activated (a) B3 and (b) B4 cementitious systems *(Q=quartz; M=mullite; A=akermanite; G=gehlenite; m=merwinite; C=calcite; a=alite; P=portlandite; SX=hydroxysodalite)*

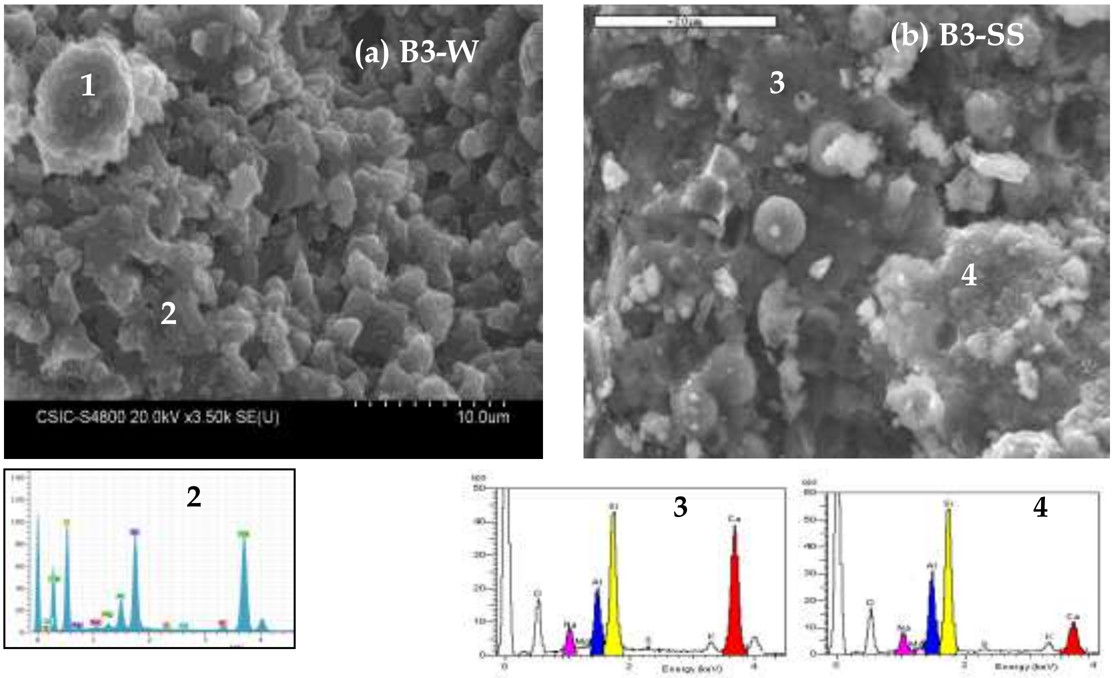

Figure 2. SEM micrographs of 28-day (a) B3-W and (b) B3-SS pastes

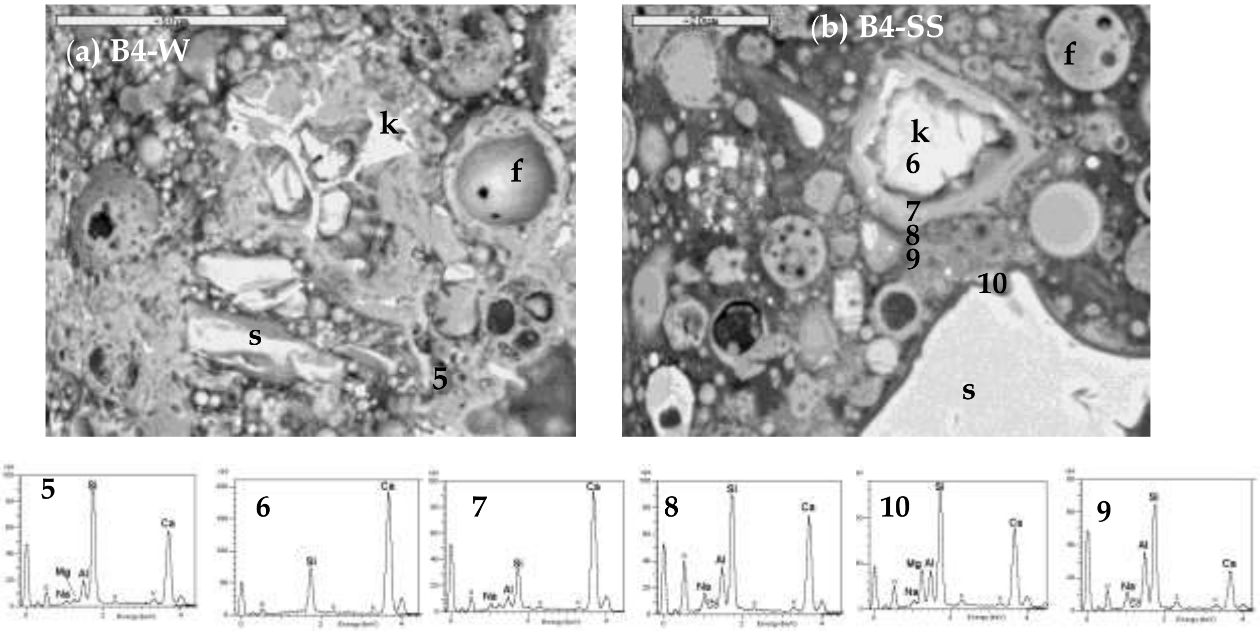

Figure 3. BSEM micrographs and EDX analysis of materials present in (a) B4-W and (b) B4-SS pastes (c=OPC clinker; s=slag; f=fly ash)

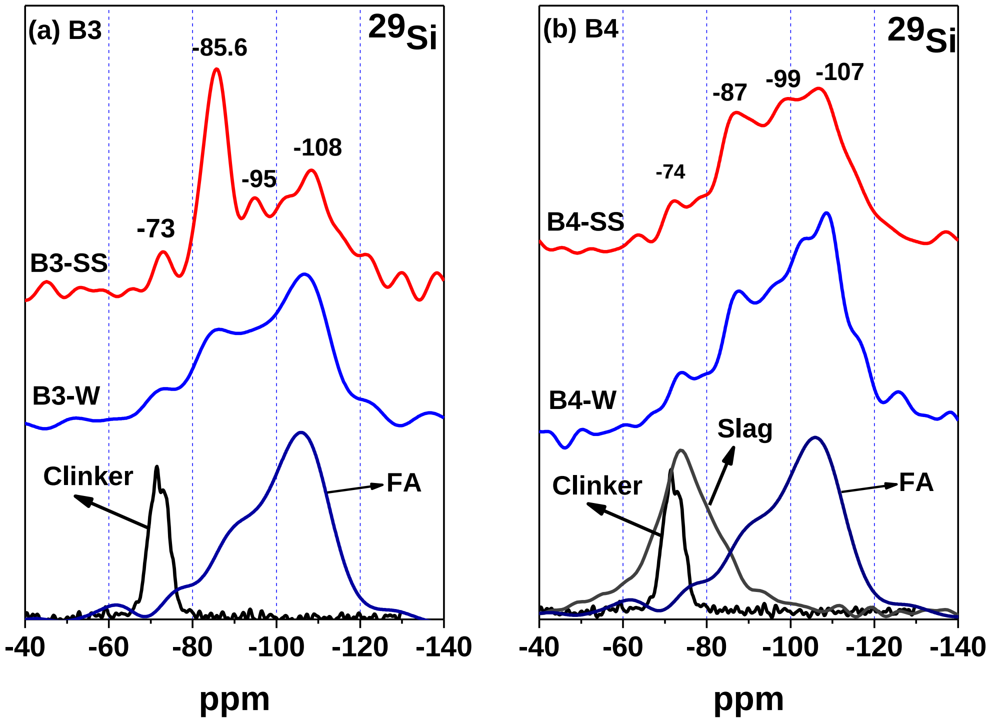

Figure 4. ^{29}Si MAS NMR spectra for (a) cement B3 and (b) cement B4