Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 33 (2003) 2031–2036

CEMENT AND CONCRETE RESEARCH

Mechanical and durable behaviour of alkaline cement mortars reinforced with polypropylene fibres

F. Puertas*, T. Amat, A. Fernández-Jiménez, T. Vázquez

Eduardo Torroja Institute (CSIC), P.O. Box 19002, 28080, Madrid, Spain

Received 1 August 2002; accepted 27 June 2003

Abstract

The development of new binders, alternative to traditional cements and concretes obtained by the alkaline activation of different industrial by-products (blast furnace slags and/or fly ashes), is an ongoing study and research topic of the scientific community.

The mechanical and durable behaviour of alkaline cement mortars reinforced with polypropylene fibres has been the object of the present investigation. Three different alkaline matrices were used: (a) granulated blast furnace slag activated with waterglass (Na_2SiO_3+NaOH) with a concentration of 4% Na_2O by mass of slag and cured at room temperature, (b) aluminosilicate fly ash activated with 8M NaOH and cured at 85 °C during the first 24 h and (c) 50% fly ash+50% slag activated with 8M NaOH solution at room temperature. In the mechanical tests (flexural and compressive strengths), two different dosages of fibres were used: 0.5% and 1% by mortar volume. Shrinkage tests according to ASTM C 806-87 standard with (1%) and without fibres were also carried out. The durability tests carried out were freeze/thaw and wet/dry cycles. In these tests, the dosage of fibre was 0.5% by mortar volume. The results obtained show that the nature of the matrix is the most important factor to strength development, more than fibre presence and content amount.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Alkali-activated cements; Fibre reinforcement; Mechanical properties; Shrinkage; Durability

1. Introduction

Alkaline cements are new binders, alternative to traditional Portland cements, obtained through the alkaline activation of different industrial by-products (e.g., blast furnace slag and/or fly ash). These new building materials are characterised by high mechanical performance, low energy cost and low pollutant gas emissions (CO_2, SO_2, NO_x, etc.) generated during the manufacturing process of ordinary Portland cement (OPC).

Depending on the raw materials, blast furnace slag and/or fly ash, different reaction products and microstructures are developed, and these produce differences in the engineering behaviour and properties.

Cements and concretes resulting from the alkaline activation of a vitreous blast furnace slag are characterised by their advantages, compared with traditional cements and concretes, such as earlier and higher mechanical strengths (they can reach 100 MPa at 28 days), lower hydration heat and stronger resistance to chemical attack. They also present some disadvantages such as quick setting and high shrinkage rate with formation of microcracking [1]. The alkaline activation of blast furnace slag has been extensively studied [2–6]. Its main reaction product is a low-crystalline hydrated calcium silicate, like a CSH gel type. This gel phase is different from the one in the Portland cement pastes. It has a low CaO/SiO_2 ratio and some structural differences (higher Al content in its structure) [7]. The formation of other phases or hydrated compounds will depend on the activator nature and quantity, the structure and composition of the slag and the curing conditions.

The alkaline activation of aluminosilicate fly ashes also results in cohesive reaction products. In this activation process, the reaction temperature plays an important role. At room temperature, reaction rate is very low. However, if the process occurs at temperatures between 40 and 85 °C, the reaction rate increases noteworthy, producing mortars that develop flexural strength higher than 20 MPa at 2 h of curing. This activation has not been well studied yet. The reaction product obtained in this type of activation is an inorganic polymer of amorphous nature and 3D structure

* Corresponding author. Tel.: +34-913020440; fax: +34-913020700.
E-mail address: puertasf@ietcc.csic.es (F. Puertas).

0008-8846/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00222-9

formed by aluminosilicate hydrates, where negative charges are balanced by alkaline ions [8–10].

Alternative cements can also be obtained when the raw material is a mix of vitreous blast furnace slags and aluminosilicate fly ashes. These alkaline cements are less known, although recent studies [11] have demonstrated that in mixes of 50% fly ash/50% slag activated at room temperature, compressive strength higher than 50 MPa are developed at 28 curing days. The main hydration product in these mixes is a hydrated calcium silicate of the CSH gel type with Al and Na in its structure.

A possible technological solution to (a) the drying, shrinkage and formation of microcracks in mortars and concretes of activated blast furnace slag and (b) the apparent brittleness of the alkaline-activated fly ashes is the incorporation of reinforcement fibres to the mix. In a previous work [12], the toughness and impact resistance of different alkaline cements reinforced with fibres of different nature (acrylic and polypropylene) has been studied. The main conclusions obtained were the following: (a) with low fibre content (0.2% in volume), toughness and toughness index of these mortars are not affected, (b) with higher content (1%), these values increase, (c) in the different matrices studied, the polypropylene fibres increase the impact strength more than the acrylic fibres and (d) the microstructural study carried out on these mortars proved that acrylic fibres show signs of being altered and have a large amount of deposits on their surface, whereas polypropylene fibres remain more or less intact.

Following on these studies, in the present paper, the mechanical strength, volume stability and durability behaviour of alkaline cement mortars reinforced with polypropylene fibres are studied further.

2. Experimental

2.1. Raw materials and cement mortar preparations

The raw materials used in the alkaline cement mortar preparations were:

- Granulated blast furnace slag (from Ensidesa, Avilés, Spain)
- Fly ash (from Aboño Thermal Central, Spain)
- Mix of 50% of Aboño fly ash and 50% of granulated slag from Ensidesa
- Portland cement type I (as reference material)

The chemical analysis of fly ash, blast furnace slag and Portland cement used is shown in Table 1.

Table 1
Chemical composition (% mass)

	Fly ash	Slag	Cement
CaO	5.51	41.45	63.83
SiO_2	51.49	35.50	18.95
Al_2O_3	29.03	12.15	5.89
Fe_2O_3	7.67	1.01	4.50
MgO	2.35	8.34	2.21
SO_3	–	0.18	2.85
S^{2-}	–	0.92	–
Na_2O	0.66	0.58	0.29
K_2O	2.83	0.64	0.75
Blaine (m^2/kg)	398	460	404

X-ray diffraction analysis indicated that the slag consisted mainly of a glassy phase, and no crystalline phases were detected. Through FTIR, it was classified as a melilite with a mineralogical composition close to A_5G_5 (A=akermanite and G=gehlenite). XRD confirmed that fly ash consisted of a glass phase, quartz and mullite.

Three different alkaline matrices were prepared:

- Granulated blast furnace slag activated with a mixture of Na_2SiO_3 and NaOH solutions (waterglass) with 4% concentration of Na_2O by mass of slag. The concentration of NaOH solution was 2.8 M. This activation is performed at room temperature (22 °C).
- Fly ash activated with 8M NaOH solutions. Curing the specimens at 85 °C during the first 24 h accelerates the activation.
- 50% Fly ash+50% slag activated with 8M NaOH solution activated at room temperature.

These matrices were chosen according to previous investigations [8,11,13]. Portland cement was used in this study as reference material.

A polypropylene fibre (Crackstop) manufactured by Cemfiber was used, with a density of 0.9 g/ml, a diameter of 18 μm and a length of 12 mm. Fibre percentage was varied 0–1% by volume of mortar.

Considering these variables, mortars of different sizes were manufactured depending on the test to be carried out. Mortars were manufactured in accordance with the Spanish Standard UNE 83-821-92. Sand/binder ratio was 3:1. Siliceous standardised sand with 99.9% quartz content was used. The mixing liquid/cementitious material ratio was kept constant at 0.5. In all the tests, specimens without fibres were considered reference materials.

2.2. Tests carried out

2.2.1. Mechanical strengths and modulus of elasticity

The fibre percentages in these mortars were 0%, 0.5% and 1% by mortar volume. Series of three 4×4×16-cm prismatic specimens of each mortar and for each testing time were prepared. The flexural and compressive strengths were determined at 2 and 28 days of curing.

Other series of 4×4×16-cm prismatic specimens were used to determine flexural strength at 28 days and the elastic modulus of the mortars. The fibre percentages used in theses mortars were between 0% and 1% by mortar volume.

2.2.2. Shrinkage

Shrinkage tests were carried out according to the ASTM C 806-87 standard. The first measurement was taken after 24 h of mixing, while the rest of measurements were taken every 3 or 4 days up to 35–45 days. The fibre content in these tests was 1%.

Two different exposure conditions were explored in the present study. The prismatic mortar specimens of 2.55× 2.5×23 cm were placed in a curing chamber with a RH higher than 95%. In the other, the specimens were placed in laboratory at 21 °C and ~50% RH.

2.2.3. Durability tests

2.2.3.1. Wet/dry cycles. Mortar specimens of 16×16×2.5 cm were prepared. The tests were performed after 28 days. At this time, the specimens were submitted to 50 wet/dry cycles. Each cycle was 6 h at 70±5 °C and 18 h immersed in water at 21 °C. After 50 cycles, the impact strength of the mortars was tested. Mortars that were not submitted to wet/dry cycles were tested as reference materials.

The impact test was carried out dropping a sphere of 540 g from 100-cm height on the upper surface of the specimen. With this system, the number of impacts to produce the first crack and the total fracture of the specimens was measured.

2.2.3.2. Freezing/thawing cycles. Series of three prismatic mortar specimens of 4×4×16 cm were prepared with each mortar. Tests were carried out after 28 days. At this time, mortars were submitted to 50 freezing/thawing cycles. Each day, two cycles were carried out: 3 h at −20 °C, 0.5 h immersed in water, 3 h at −20 °C, and again another 0.5 h immersed in water, and for the rest of the time (17 h), the specimens were kept immersed in water. After 50 cycles, the mortars were tested, and their flexural and compressive strengths were determined.

3. Results and discussion

3.1. Mechanical strengths

Flexural and compressive strength values obtained at 2 and 28 curing days are presented in Table 2. The alkaline-activated slag mortars (AAS) show higher strength at early and longer ages than cement and the other activated mortars (especially in compressive strengths). Alkaline slag mortar activated with waterglass is a material with a very low total porosity. In previous studies [7], it has been shown that the total porosity of AAS mortars is lower than 10% and that porosity decreases as the reaction time increases. In addition, because of the alkaline activation of slag, a CSH is formed with composition and structural differences from those of OPC pastes [7]. Semicrystalline CSH presents a high proportion of Al in the tetrahedral bridges of the silicate lineal chain and a lower Ca/Si ratio than the CSH gel formed in OPC pastes [7,13]. The low porosity together with the structure of the main reaction product (microstructure) explains the high mechanical strength of these mortars.

Table 2
Mechanical strength results

Mortars	Fibre (%)	2 days		28 days	
		Flexural (MPa)	Compression (MPa)	Flexural (MPa)	Compression (MPa)
Slag	0	7.2	59.5	7.8	89.5
	0.5	6.5	60.1	7.6	90.0
	1	6.4	59.0	6.7	79.0
Fly ash	0	3.9	24.5	6.8	39.4
	0.5	4.5	33.9	6.1	35.8
	1	4.9	34.3	5.5	26.9
Fly ash/slag	0	3.6	11.8	4.6	30.0
	0.5	3.4	13.5	4.8	31.2
	1	2.9	13.6	4.8	30.1
Cement	0	6.3	39.1	7.8	53.0
	0.5	5.8	35.5	7.5	48.2
	1	5.4	38.9	7.4	47.6

In fly ash activated mortars, the main reaction product is an amorphous alkaline aluminosilicate hydrate with a 3D structure [8]. This material has cohesive properties and it can be considered a precursor of a zeolitic-type product. The formation rate of that reaction product increases with the curing temperature.

Finally, in the activated fly ash/slag system, the mechanical strengths are explained by the microstructure resulting from the formation of a CSH as a consequence of the alkaline activation of the slag [11]. Another compound can also be formed due to the alkaline activation of the fly ash (an alkaline aluminosilicate with 3D structure). However, the proportion of this is very low compared with that formed in the slag activation. The most important factor in the strength development of the slag activation is the activator nature [6]; the waterglass solution generates high-strength materials, while the NaOH solution generates materials with lower strengths.

The strength behaviour of fibre-reinforced mortars is shown in Table 2. Results appearing in this table indicate that polypropylene fibres induce only slight modifications (in some cases, a slight decrease) in the mechanical strengths. The presence of the fibre reduces the workability, which affects the compaction of the mortar; this could explain the flexion and compression decreases observed.

3.2. Modulus of elasticity

In Table 3, the elastic modulus determinations are presented. The activated mortars (with and without fibre) have lower modulus of elasticity than cement mortars. Activated slag mortars have high strength and relatively high deflection. On the contrary, fly ash/slag mortars have low strength and low deflection. For the same strength, activated slag mortars have slightly more deformability than cement mortars.

Table 3
Modulus of elasticity

Mortars	Fibres (%)	Flexural strength (MPa)	Elastic modulus (MPa)	Deflection (mm)
Slag	0	7.36	4860	0.1277
	1	5.91	3896	0.1361
Fly ash	0	5.79	4441	0.1071
	1	4.79	3660	0.1084
Fly ash/slag	0	4.80	4906	0.0852
	1	4.66	3810	0.1068
Cement	0	7.76	5679	0.1136
	1	7.61	6137	0.1051

The flexural strength in fibre-reinforced mortars is slightly lower than in mortars without fibres. In activated mortars, the presence of polypropylene fibres reduces the elastic modulus. The polypropylene fibres have a low modulus of elasticity; they are easily deformed and reduce the compatibility of the material.

3.3. Shrinkage tests

The shrinkage behaviour of alkali-activated slag mortars in the testing conditions studied is presented in Fig. 1. When mortar specimens are stored at a high humid environment, a high shrinkage takes place at early ages. Fibre content increases this effect, and more investigations are needed to explain this fact. From 10 to 15 days after storage, the shrinkage values remain practically constant until the end of the test (0.08–0.12%). When the test specimens are under high humidity conditions (>95% RH), the shrinkage should be related to the matrix characteristics and mostly to the nature and structure of the main reaction products formed (basically, a CSH that contains Al in its structure [7]), which means that the shrinkage is of chemical type. Under those high humidity conditions, the activation process is favoured and a large amount of reaction products is formed.

When mortar specimens are stored under laboratory environment (21 °C and 50% RH), they experience a continuous shrinkage, and at the end of the test (45 days), constant values have not been reached. Under these conditions, the shrinkage is mainly due to the drying of the water absorbed in the pore mortar system. The presence of the fibre reduces slightly that shrinkage. When the shrinkage takes place in a more continuous way, the polypropylene fibres could contribute positively to moderate the dimensional alterations of the mortars, acting as a link between the matrix and the particles of aggregate.

In Fig. 2, the shrinkage behaviour of cement mortars is shown. When the test specimens were stored under high humidity conditions, the shrinkage is relatively low (stable values around 0.04%) as expected. When they are stored under laboratory environment, mortars show a substantial shrinkage due basically to the drying and elimination of the free water inside the mortar, reaching final values around 0.10%. In this case, fibres contribute positively to the reduction, in a small percentage, of the final shrinkage.

Behaviour of alkaline-activated fly ash mortars is shown in Fig. 3. Under conditions of high humidity, a very slight expansion takes place initially. This is accentuated in test specimens that contain fibres (final value of expansion of 0.0075%). In absence of fibres, mortars also experience initially a very slight expansion; the shrinkage takes place after 20 days, reaching at the end of the test a value of 0.015%. Under laboratory environment, a slight shrinkage takes place at early ages, reaching at the end of the test a shrinkage of around 0.02% (in mortars with and without fibre). Comparing these results with those from activated slag mortars and even from those of Portland cement, the conclusion is that alkali-activated fly ash mortars are largely stable with very few dimensional variations under the two studied conditions. This is mainly due to the stability of the main reaction product, a 3D structure formed by alumino-silicate hydrates.

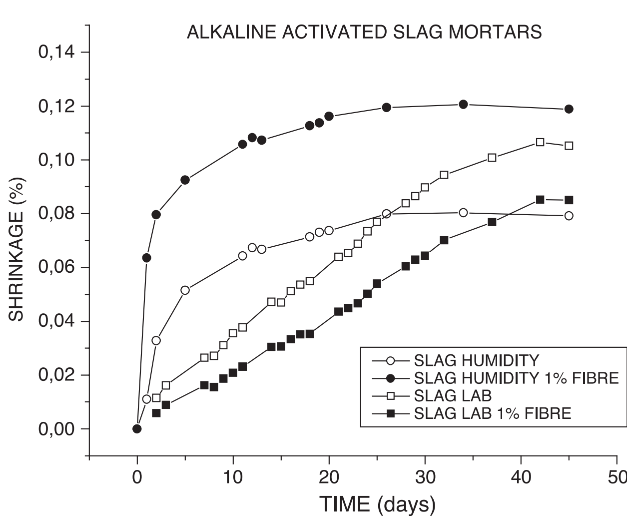

Fig. 1. Shrinkage versus time. Influence of curing conditions.

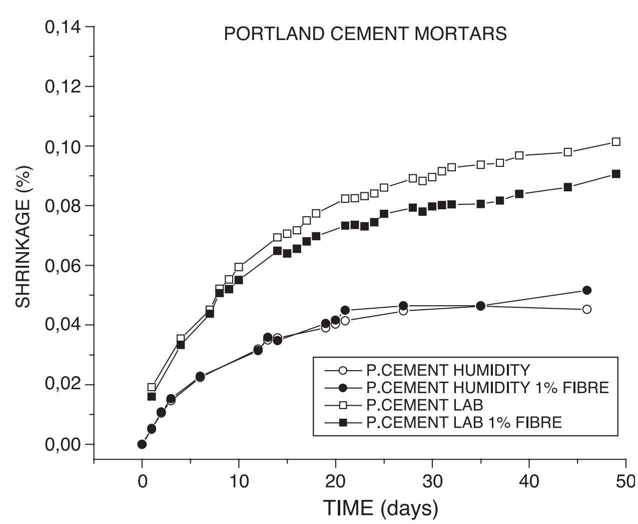

Fig. 2. Shrinkage versus time. Influence of curing conditions.

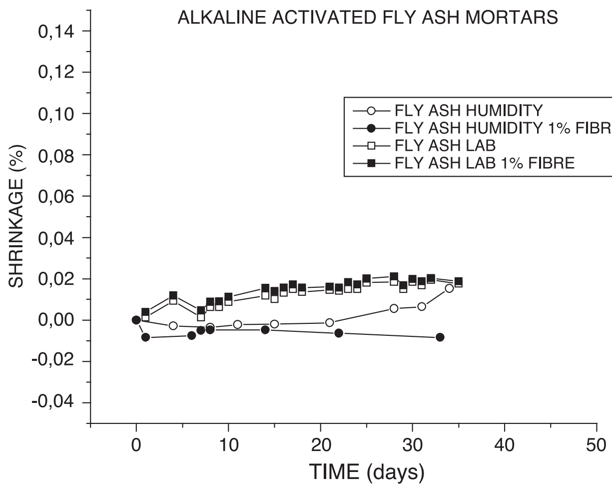

Fig. 3. Shrinkage versus time. Influence of curing conditions.

The shrinkage behaviour of the activated fly ash/slag mix mortars is presented in Fig. 4. Test specimens stored in high humidity undergo a slight expansion (0.05%). Similar behaviour is observed in mortars with activated fly ash. Mortars containing fibres do not show alterations in their dimensional stability. Under laboratory conditions, mortars show a shrinkage comparable with that observed in activated slag mortars. A practically linear increment of the shrinkage takes place with time (until shrinkage at the end of the test of about 0.10%). Therefore, fibres reduce the shrinkage.

3.4. Durability test

The impact strength of mortars before and after they have been submitted to a test of 50 wet/dry cycles is presented in Table 4. In activated slag mortars, the content of 0.5% polypropylene fibres increases slightly the strength to fracture and to the formation of the first crack. However, behaviour in the cement mortars is different. The incorporation of fibre increases remarkably the resistance to fracture from 3 to 23 impacts. However, when these mortars with fibre are submitted to the wet/dry cycle, this treatment affects negatively. The resistance to fracture goes down from 23 to 9 impacts (see Table 4).

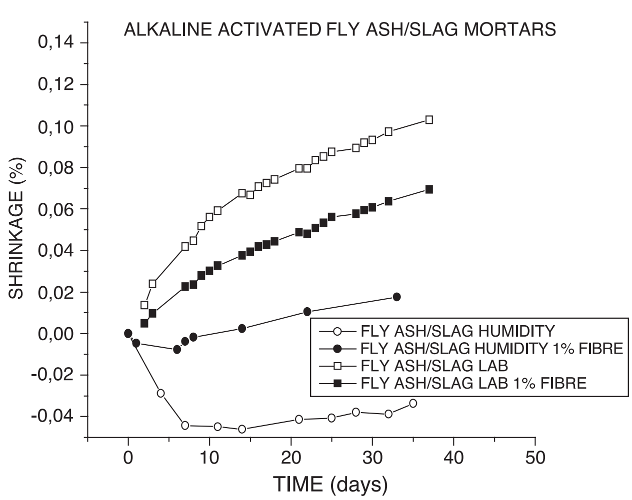

Fig. 4. Shrinkage versus time. Influence of curing conditions.

Table 4
Wet/dry tests: number of impacts

	Without fibre		0.5% fibre		Without fibre		0.5% fibre	
	No cycles	50 cycles	No cycles	50 cycles	No cycles	50 cycles	No cycles	50 cycles
	Slag mortars				Fly ash mortars			
First crack	1	1	2	3	1	1	1	3
Fracture	4	2	9	7	3	2	12	9
	Fly ash/slag mortars				Cement mortars			
First crack	–	1	1	1	1	1	2	1
Fracture	1	3	7	6	3	3	23	9

In activated fly ash/slag mortars, the presence of fibres with the studied percentage increases the resistance to the impact. After the wet/dry tests, mortars behaviour is not altered.

The effect of fibre reinforcement is more intense in Portland mortars than in alkaline ones. The aqueous phase of these mortars show a high alkalinity. In previous studies [12], it has been proved that polypropylene fibres experience superficial alterations within alkaline media, especially if the process happens at high temperature. These alterations can affect the adherence to the matrix and justify the lower reinforcement effect in alkaline mortars.

The mechanical behaviour of mortars after freezing/thawing cycles is shown in Table 5. The most significant result is the rise of strengths (flexural and compression) observed in test specimens of alkali-activated slag after exposure. These results confirm that under conditions of high humidity, the activation of the slag continues, producing a large quantity of reaction products and increasing the final strengths. This positive effect is also observed in mortars of activated fly ash/slag. In these mortars, the strength characteristics are closely related to the activation of the slag. The activated slag cement and concrete show a

Table 5
Freezing/thawing cycles: mechanical results

Mortars	Fibre (%)	Without cycles		50 cycles	
		Flexural (MPa)	Compression (MPa)	Flexural (MPa)	Compression (MPa)
Slag	0	8.8	91.4	10.7	108.2
	0.5	8.2	89.2	10.5	104.6
Fly ash	0	6.6	38.1	3.3	29.1
	0.5	6.7	44.5	3.9	35.4
Fly ash/slag	0	4.7	30.9	6.9	33.8
	0.5	4.9	31.2	6.6	34.7
Cement	0	8.2	50.2	6.9	52.9
	0.5	8.2	48.4	6.9	47.2

high resistance to low temperature, because freezing temperatures of alkaline metal solutions are below 0 °C (of about −15 to −20 °C). The fibres do not alter the described behaviour.

In cement mortars (with and without fibres) after the freezing/thawing cycles, a decrease of flexural strengths is observed. The values of compressive strength are not altered. It could be due to the increment of the microcracking resulting from tensions originated as a consequence of these cycles. The presence of fibres does not modify the described behaviour.

The most negative effect in the freezing/thawing cycles is observed on mortars of alkali-activated fly ash. This behaviour is similar when the material contains polypropylene fibres.

4. Conclusions

The main conclusions extracted from the present study are the following:

1. The nature of the matrix is the main factor influencing the development of mechanical strengths in alkaline cement mortars. Activated slag mortars show the highest strengths, with values higher than those developed by Portland cement mortars in equal conditions. Incorporation of polypropylene fibres, until 1% in volume, does not affect positively the mechanical behaviour of the studied mortars.
2. The alkaline mortars show a modulus of elasticity, determined through flexural test, inferior to those shown by Portland mortars. The polypropylene fibres do not improve the values of modulus of elasticity.
3. The activated slag mortars show the highest shrinkage. The activated fly ash mortars are those that evidence the highest volume stability, with practically null shrinkage. The effect of the fibres is different depending on the nature of the matrix.
4. Activation of slag mortars shows high stability cycles against freezing/thawing and increases their mechanical strengths. The presence of fibre does not modify this behaviour. Alkaline cement mortars going through wet/dry cycles have a similar behaviour as those corresponding of Portland cement. Fibres provide an improvement of the resistance to fracture in all mortars.

Acknowledgements

The authors thank the CICYT for funding this research through MAT98-0792 project and the Ministerio de Ciencia y Tecnología (Spain) for supporting the project MAT2001-1490. The authors also thank J.L. García and A. Gil for the elaboration and testing of the mortars.

References

[1] S.D. Wang, X.C. Pu, K.L. Scrivener, P.L. Pratt, Alkali-activated cement and concrete. A review of properties and problems, Adv. Cem. Res. 7 (27) (1995) 93–102.

[2] V. Glukhovskij, Y. Zaitsev, V. Pakhomow, Slag-alkaline cements and concretes—Structures, properties, technological and economical aspects of the use, Silic. Ind. 10 (1983) 197–200.

[3] B. Talling, J. Brandstetr, Present state and future of alkali-activated slag concretes. Fly ash, silica fume, slag and natural pozzolans in concrete, Proc. 3rd Int. Conf. Trondheim, Norway SP114-74 (1989) 1519–1545.

[4] F. Puertas, Cementos de escorias activadas. Situación actual y perspectivas de futuro, Mater. Construcc. 239 (45) (1995) 53–64.

[5] C. Shi, R.L. Day, A calorimetry study of early hydration of alkali-slag cements, Cem. Concr. Res. 25 (1995) 1333–1346.

[6] A. Fernández-Jiménez, J.G. Palomo, F. Puertas, Alkali-activated slag mortars. Mechanical strength behaviour, Cem. Concr. Res. 29 (1999) 1313–1321.

[7] A. Fernández-Jiménez, Cementos de escorias activadas alcalinamente: influencia de las variables y modelización del proceso, Doctoral Thesis, UAM, 2000.

[8] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes: a cement for the future, Cem. Concr. Res. 29 (1999) 1323–1329.

[9] A. Palomo, S. Alonso, Recycling fly ashes for making precast components, 2nd Int. Symp. on Prefabrication, Concrete Association of Finland, Helsinki, Finland, 2000, pp. 50–61.

[10] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, Effect of alkali metal activator on the properties of fly ash based geopolymers, Ind. Eng. Chem. Res. 38 (1999) 3932–3941.

[11] F. Puertas, S. Martínez-Ramírez, S. Alonso, T. Vázquez, Alkali-activated fly ash/slag cements. Strength behaviour and hydration products, Cem. Concr. Res. 30 (10) (2000) 1625–1632.

[12] F. Puertas, T. Amat, T. Vázquez, Behaviour of alkaline cement mortars reinforced with acrylic and polypropylene fibres, Mater. Construcc. 259 (2000) 69–84.

[13] I.G. Richardson, J.G. Cabrera, The nature of C-S-H in model slag-cements, Cem. Concr. Compos. 22 (2000) 259–266.