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Effect of self-healing additions on the development of mechanical strength of cement paste

G. Perez[1], I. Jimenez[1], E. Erkizia[2], J.J. Gaitero[2], I. Kaltzakorta[2] and A. Guerrero[1]
[1]Institute of Construction Science "Eduardo Torroja", CSIC, Madrid, Spain
[2]Tecnalia, Materials Business Unit, Sustainable Construction Division, Derio, Spain

Abstract. Important research efforts have been recently focused on the development of self-healing cement composites. The healing mechanism, implemented within the material, must be automatically initiated as soon as the first signs of damage appear at the micro-scale. For doing so, two different additions have been developed to incorporate them simultaneously into the cementitious matrix: silica microcapsules containing an epoxy sealing compound (CAP) and nanosilica particles functionalized with amine groups (NS). As a first step to the development of a self-healing concrete with these two additions, their pozzolanic activity has been measured by an accelerated test. The high values of fixed lime obtained at 28 days (85% for CAP, 93% for NS and 88% for a mix of them) suggest that they are suitable for construction materials' applications. Furthermore, the behaviour of the additions in an ordinary Portland cement paste with 20 wt.% of commercial micro-silica has been studied, considering the partial substitution of micro-silica by CAP, NS and their mix. High values of compressive strength (>60 MPa) have been obtained in all cases after 28 days of hydration. However, while the addition of CAP induces a reduction of the compressive strength of the 24% with respect to the reference material, the addition of NS gives rise to a slight enhancement of the strength (5%) due to a pozzolanic reaction confirmed by X-ray diffraction data. Finally, in the presence of both CAP and NS, the beneficial effect of the nanosilica is counteracted by the microcapsules and a reduction of 28% is obtained for the compressive strength.

1 Introduction

Due to their availability, outstanding performance and cost effectiveness cement-based materials are one of the most widely used materials. However, during the life-time of structures, cement composites are subjected to several actions, such as thermal changes, impact and corrosion which invariably give rise to the formation of cracks. These cracks often lead to durability problems which undermine structural performance and result in a shortened useful lifetime, and even failure, as well as causing an increase in maintenance and repair costs.

It is clear that improving the long-term durability of a material will improve its service-life and reduce maintenance and repair. Recently, in an attempt to mimic natural living systems, researchers are developing materials with self-healing properties as a way of improving their durability [1-3]. This research line is also very active in the cementitious materials field where a wide variety of self-healing mechanisms are being studied [4-11].

Within this context, our group is developing a self-healing cementitious material in which the self-healing mechanism is based in the combined action of two additions. On the one hand, an epoxy compound encapsulated in silica microcapsules, which acts as an adhesive and, on the other hand, a curing agent dispersed in the matrix by means of amine functionalized silica nanoparticles. Clearly, the self-healing additions should be chemically compatible with the cementitious matrix and should not deteriorate drastically the materials properties. In this paper we report the pozzolanic activity of the additions and compare it to a well known pozzolanic addition such as silica fume. Furthermore, the effect of the additions on the mechanical properties and the hydration of a cement paste that contains silica fume have been studied.

2 Experimental methods

Silica microcapsules containing the epoxy sealing compound (CAP) and amine-functionalized nanosilica particles (NS) were synthesized in our laboratory by a sol-gel method described elsewhere [12-13].

The pozzolanic activity of both additions was determined by an accelerated method in which the samples were placed in contact with a saturated lime solution at 40ºC for 1, 3, 7 and 28 days. After each period, the CaO concentration in the solution was analyzed and the combined lime in mmol/l was obtained by the difference between the concentration in a control saturated lime solution and that found in the solution in contact with the sample. A mix of the two additions in a proportion of 43% of CAP and 57% of NS has also been tested.

Cement paste prismatic specimens of 1x1x6 cm^3 were prepared. All the blends considered include 24 g of distilled water, 3.2 g of a superplatizicer additive (Structuro 351 from Fosroc) and 20 g of additions (CAP, NS and silica fume from Elkem Grade 940-U undensified) per 80 g of ordinary Portland cement type CEM I 52.5N. Table 1 collects the amount of each addition in the different cement pastes studied. In the case of the silica fume and CAP, the additions were mixed with the cement powder and stirred for 1min at 300 r.p.m. before pouring on them the water with the superplastizicer. On the contrary, NS was added to the water with the superplastizicer and ultrasonicated for 5 min prior to adding them to the cement powder. After mixing, the samples were cast in steel moulds where they stayed for 24 h in a chamber with 100% relative humidity and 20ºC. After this time they were unmolded and cured in a saturated lime solution until the moment of the test.

Table 1. Additions considered in the different cement pastes. (per 80 g of CEM I, 24 g of water, 3.2 g of superplatizicer)

Sample	Silica Fume (g)	CAP (g)	NS (g)
REF	20	0	0
CAP10	12	8	0
NS13	9.3	0	10.7
MIX10	1.3	8	10.7

The strength of the specimens was tested at different curing ages and based on the UNE-EN-196-1 standard. The loading speeds used were 100 N/s and 5 N/S for the compressive and flexural strength test respectively.

Finally, X-ray diffraction patterns of the samples were obtained with a Philips PW 1730 equipment, with a graphite monochromator and Cu K_{α} radiation.

3 Results and discussion

3.1. Pozzolanic activity of the additions

Figure1 shows the results of the pozzolanic activity test performed on the additions. The results obtained for a silica fume (SF) sample are included as a reference of the behaviour of effective pozzolanic additions currently used in construction materials.

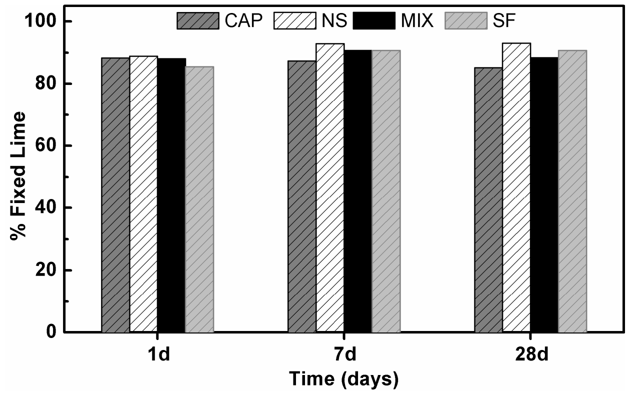

Fig. 1. Pozzolanic activity of the additions. Values of fixed lime corresponding to silica fume (SF) are included as a reference.

Values of fixed lime higher than 80% are obtained from the first day of reaction in all the samples considered. In the case of the microcapsules (CAP), a value of 88% fixed lime is obtained at 1 day, slightly decreasing to 85% at 28 days. For the nanosilica (NS), an opposite tendency is observed, with a slight increase from 89% at 1 day up to 93% at 28 days and values of fixed lime higher than those obtained for the SF sample at all the ages. Finally, the sample prepared with a mix of both additions shows a value of 88% of fixed lime both at 1 and 28 days of reaction. It is interesting to note that at 7 and 28 days the MIX sample shows a percentage of fixed lime in between the values corresponding to the constituents, in all cases lower than the values of the nanosilica sample. This behaviour indicates that the presence of microcapsules diminishes the pozzolanic activity of the amine-functionalized nanosilica.

The results shown in figure 1 indicate a very high pozzolanic activity of the two additions and their mix, similar or even better than that of silica fume. Consequently the additions should be compatible with the cement matrix.

3.2. Mechanical strength of cement pastes

The behaviour of the additions in an ordinary Portland cement paste with a 20 wt.% of commercial silica fume has been studied, considering the partial substitution of silica fume by CAP, NS and a mix of them with the proportion considered in the previous pozzolanic activity test (Table 1). Figure 2 shows the values of mechanical strength obtained in compressive (Figure 2.a)) and flexural (Figure 2.b) stress modes.

Different rates are observed in the development of mechanical strength between the samples in figure 2. In the reference sample, a low value of compressive strength (figure 2.a)) of 3.7 MPa is obtained at 1 day of hydration, significantly increasing up to 54.7 MPa for 3 days. A lower increase rate is observed at higher ages giving rise to a value of 90.1 MPa for 28 days. The sample CAP10, with the addition of microcapsules, shows a much better mechanical behaviour than the reference at 1 day, with a compressive strength of 24.3 MPa. However, strength development slows down and a value of 68.6 MPa, 24% lower than in the reference, is obtained at 28 days.

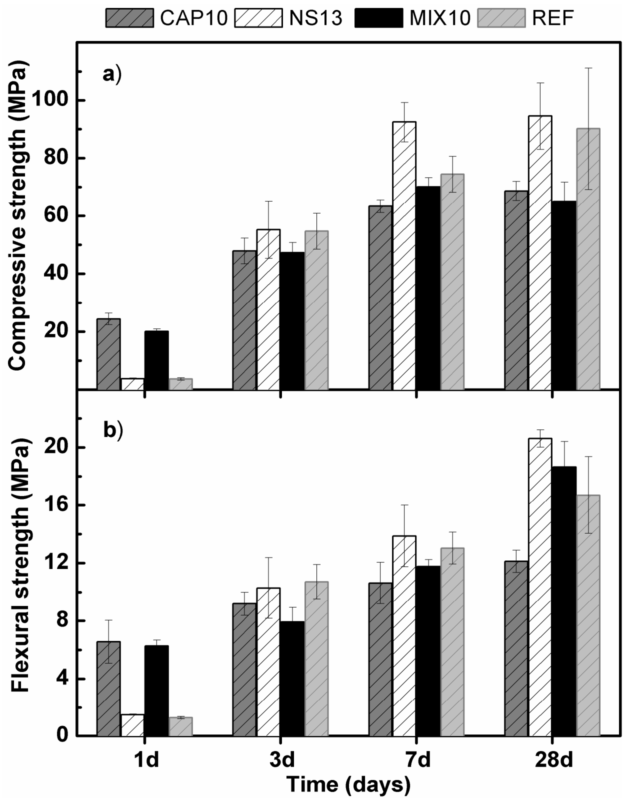

Fig. 2. Mechanical strength of the cement pastes.

The effect of substituting silica fume by amine-functionalized nanosilica (NS13) is very significant in the compressive strength values at 7 and 28 days of hydration, when an increase of a 24 and 5% respectively is observed with respect to the reference paste.

Finally, the development of mechanical strength in the sample with the two additions (MIX10) shows a similar rate to the sample CAP10 and a value of compressive strength of 65.0 MPa is obtained at 28 days, a 28% lower than in the reference paste.

The behaviour of the flexural strength shown in figure 2.b) is in general consistent with that described for the compressive strength values.

In order to understand the differences in the hydration process that give rise to the differences observed in the mechanical resistances between the samples, the X-ray diffraction data of the cement pastes at 1 and 28 days of hydration are shown in figure 3. The axes have been configured so as to properly show the most significant changes.

As expected, a clear decrease of the signal corresponding to the anhydrous phases of the cement, namely alite, belite and calcium aluminate, is observed in the x-ray diffratograms of all the four samples analyzed between 1 and 28 days of hydration. More interesting is the analysis of the diffraction peaks corresponding to the portlandite phase, located at 18.0º and 34.1º. In a normal hydration process, the reaction of the anhydrous calcium silicates of cement with water gives place to the formation of C-S-H gel and portlandite ($Ca(OH)_2$) as mayor compounds. Since the C-S-H gel is mainly amorphous, the hydration process results in an increase in the intensity of the diffraction peaks of portlandite at the same time that those corresponding to anhydrous phases recede. This is in fact the case of the diffractograms of the reference paste in figure 3. For the case of sample NS13, a decrease is observed in the peaks at 18.0º and 34.1º, thus indicating a decrease in the portlandite contribution, that must be consumed in a pozzolanic reaction between the $Ca(OH)_2$ and the nanosilica to produce C-S-H gel. In fact, an increase in the broad halo around the peak at 29.4º suggests the efficient formation of this amorphous phase between 1 and 28 days. The enhancement of the C-S-H formation through this pozzolanic reaction must be responsible for the better mechanical behaviour of this sample.

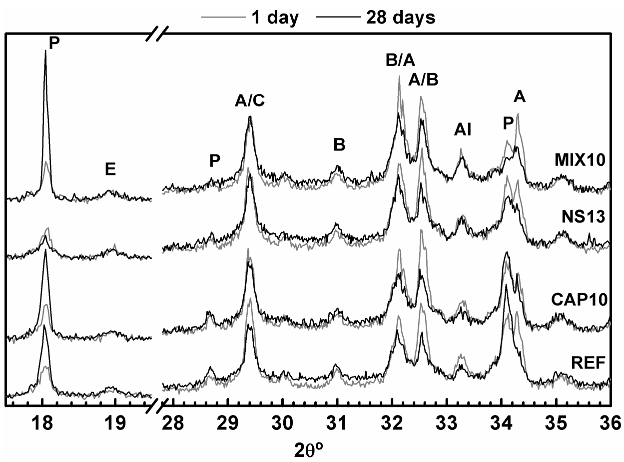

Fig. 3. X-ray diffractograms of cement pastes at 1 and 28 days. A-alite; B-belite; Al-calcium aluminate; E-ettringite; P-portlandite; C-calcite

Considering the sample with the addition of microcapsules (CAP10) the difractograms show a slight increase in the signal at 34.1º and, more interestingly, a clear increase in the signal at 18.0º. This result must be interpreted as the formation of portlandite with a preferential orientation in the crystalline planes corresponding to this diffraction angle, [001], instead of the usual orientation in the [101] planes of portlandite phase. Probably the formation of these crystals is related to the slowdown of the mechanical strength development observed for this sample.

A similar behaviour is observed in figure 3 for the MIX10 sample, where a slight decrease in the diffraction peak at 34º is observed between 1 and 28 days suggesting the presence of pozzolanic reaction. However, the clear increase in the peak at 18.0º indicates the efficient formation of portlandite in the corresponding orientation.

The results show that the pozzolanic reaction induced by the addition of amine-functionalized nanosilica to the cement paste and, consequently, the related enhancement of the mechanical strength, is counteracted by the negative effect induced by the presence of epoxy-containing silica microcapsules.

Nevertheless, it is important to note that all the cement pastes analyzed in this work, more specifically the MIX 10 sample, show a compressive strength higher than 60 MPa at 28 days that make them suitable for usual construction applications.

4 Conclusions

A preliminary analysis of epoxy-containing silica microcapsules and amine-functionalized nanosilica has been presented with view to consider them as complementary additions in the development of a self-healing concrete. The high pozzolanic activity and the high mechanical strength of cement pastes prepared with the two additions and their mix indicate that the additions may be considered as suitable for the intended application.

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