Assessment of autonomous and autogenous healing on cementitious grouts promoted by additions of microcapsules and crystalline admixtures

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Abstract. The demand for more sustainable building materials has led to the development of systems with self-repairing properties. The self-healing technology has been shown to be effective in concrete and mortars, however, this technology is not often studied in grouts. Cementitious systems can show an autogenous healing, i.e., an intrinsic ability to repair microcracks by themselves. This type of healing can be improved by the addition of crystalline admixtures. In addition, the crack healing can also be enhanced by adding other materials, e.g., through the incorporation of polymeric microcapsules into the cementitious matrix that will promote a healing effect but, in this case, an autonomous healing. Thus, the main objective of this work is to assess the effect of the addition of microcapsules and crystalline admixture on viscosity and water capillary absorption of cementitious grouts. Cementitious grouts (w/b = 0.46 and w/b = 0.39) were prepared containing microcapsules (3% by weight of binder) and crystalline admixture (3% by weight of binder). Rheological measurements and water sorptivity tests were made. Viscosity measurements were taken at 3, 20 and 60 minutes. Sorptivity tests were performed on cracked specimens in order to quantify the healing efficiency. Cracks were created 7 and 28 days after casting and the water absorption was measured for 7, 14 and 28 days after cracking. The results showed that the viscosity changed considerably depending on the w/b ratio and the healing agent type. Among all grouts, reference grout presented the highest viscosity and grout with microcapsules and crystalline admixture the lowest. The water absorption of the grouts with microcapsules was the lowest regardless of curing age and w/b ratio. Regarding crystalline admixture, at both curing ages the water absorption was quite high.

1 Introduction

Although concrete is the most used material in civil construction, cementitious grouts are also an option to perform or speed up some processes during the construction work. Grout is a material used in several applications such as soil reinforcement, masonry, tunnelling, among others. The selection of grout components/type depends on several factors such as raw material, geological characteristics of the site to be grouted, purpose of grouting, desired performance/strength, budget and project execution time [1].

Widely known as a fluid mixture composed by water, cement, fine aggregates and chemical additives, cementitious grouts have fluidity as a critical property, as this directly affects the injectability of the grout which will be successful when the rheology (among other properties) is well known/optimized. Normally, the rheological parameters of the grout are measured experimentally and then the results can be interpreted according to different analytical models [2,3]. The grout is commonly considered a non-newtonian fluid. In this study, the Bingham model was used to calculate viscosity from the flow curve (shear stress vs. shear rate) through the Equation (1) where τ is the measured shear stress (Pa) at a shear rate (s^{-1}) of $\dot{\gamma}$, τ_0 is the yield stress (Pa) and μ_p is the plastic viscosity (Pa.s).

$$\tau = \tau_0 + \mu_p * \dot{\gamma} \qquad (1)$$

Plastic viscosity indicates how easily the grout flows during injection. It is important to have viscosity well controlled as it shows the possibility of segregation of the mixture.

Although the grout has numerous advantages for a work, it is always important to be aware of the composition due to the negative impact caused by civil construction on the environment. It is important that these materials exhibit higher efficiencies, especially in terms of durability and, hence they become much more attractive to consumers and manufacturers. In this sense, self-repairing technology brings a competitive advantage to the construction sector, such as increasing the service life, reducing maintenance costs and contributing to the regeneration and conservation of nature [4–7].

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Several self-healing approaches can be explored in cementitious materials as they present two types of healing: autonomous and autogenous. The most suitable healing method will depend on several factors such as compatibility cement matrix/healing agent, crack width, environmental conditions. Autogenous healing is an inherent phenomenon of cement materials that involves physical, mechanical and chemical mechanisms [5,8]. Crystalline admixtures (CA) can be used to promote autogenous healing because when the CA reacts with water and cement, different compounds (calcium silicate [9] and/or calcium carbonate [10] hydrates) are produced, blocking the microcracks [11,12]. As cracks can also be closed by autonomous healing, the incorporation of microcapsules (MC) will promote this type of healing mechanism, as the core material is released at the time of cracking, healing the area without depending on environmental conditions [13–15].

Although self-healing technologies are widely applied in concrete and mortar, they are rarely applied in grouts. Thus, the main objective of this work is to evaluate whether plastic viscosity and water absorption change by additions of polyurethane microcapsules containing a waterproofing resin and CA in cementitious grouts.

2 Methodology

To assess the effects on the rheology and water absorption by adding CA (Penetron Admix®) and MC (polyurethane microcapsules containing a water repellent agent), in this study four grouts mixtures containing CEM I/42.5R, class C fly ash, sand, limestone and superplasticizer (MasterCast 228) were prepared. The dry materials were added into the mixer according to the proportions presented in Table 1 and mixed for 40 s. Then, water was added and the mixture was mixed for 2 more minutes. All the materials were mixed in a rotary mixer with a flat beater. For mixtures containing CA, the additive was mixed with the dry materials. In turn, MC was first manually mixed with water and then added to the dry materials. Fly ash replaced 20 wt% of cement. Therefore, the binder was considered as a mixture of 80% of cement and 20% of fly ash (weight percentage). Sand and limestone were fixed at 80% and 20% of binder weight, respectively. MasterCast 228 (% with respect by cement weight) was added to G1 and G2 grouts to obtain a flow time of 80 seconds. From mixtures G1 and G2, mixtures G3 and G4 were prepared maintaining the same w/b ratio, respectively. The grout named as G3 was prepared adding into the mixture G1, 3% (by weight of cement) of microcapsules. Mixture G4 corresponds to same formulation of the G2 containing 3% wt of microcapsules and 3 wt% of crystalline admixture (% with respect to cement weight). The dosage of 3% CA and MC was recommended by the manufacturers. Mixtures G3 and G4 were not re-adjusted with superplasticizer because it would also be important to assess how the flow time would change with these additions.

For rheological measurement a rotational viscometer (Brookfield DV3T Rheometer) was used, equipped with a SC4-21 spindle. The measurements were taken 3, 20 and 60 min after the addition of water into the grout.

Table 1. Mix proportions of grouts.

Mix ID, Grout components (% by weight)		G1	G2	G3	G4
w/b ratio		0.39	0.46	0.39	0.46
Binder	CEM I/42.5R	80	80	80	80
	Fly ash	20	20	20	20
Limestone		20	20	20	20
Sand 0/2 mm		80	80	80	80
Superplasticizer		2.8	2.5	2.8	2.5
Crystalline Admixture		0	3	0	3
Microcapsules		0	0	3	3

The grout was poured into the cup after 3 minutes and settled for 10 s. Then, a pre-sheared of 60 s at 254 s^{-1} was performed. After this time, the mixture was left for 30 s to stabilize. The ascending and the descending curves were measured for 285 s. The shear rate increased from 25 to 232 s^{-1} over a period of 150 s and then decreased from 232 to 25 s^{-1} over another 135 s. Each shear rate was maintained for the duration of 15 s and the measurements were performed in duplicate. The average of tests was considered to determine the shear stress (measured as a function of the shear rate). Values were obtained from the ramp down curve through linear regression and the Bingham model. Shear stresses were measured at the shear rates of 232, 225, 200, 175, 150, 125, 100, 75, 50 and 25 s^{-1}. Between each measured time (3, 20 and 60 min), the grout was kept in the cup and, before measuring, the grout was mixed for 5s with a spatula.

For sorptivity tests, the grout mixture was poured into 40x40x160 mm steel moulds. After 24 h of curing, each specimen was cut in 3 pieces of 40x40x50 mm which were then placed in a standard curing chamber for 7 and 28 days. Then the specimens were cracked through a three-point bending test. A high load speed (300 KN/s) was applied to generate different crack openings. The crack opening was not controlled. The average crack width was 250 ± 50 µm (measured with a crack width ruler). After cracking, the specimens were not placed under a specific healing condition, their lateral surfaces were sealed and only the cracked surface (40 mm x 40 mm) was directly exposed to a 3 mm water level. Mass measurements were taken at 7, 14 and 28 days, after removing the excess of water from the bottom. To quantify the water absorption, it was considered the Equation (2) where Q_n is the weight (g) of the specimen at time n (t = t_n), Q_0 is the weight (g) of the specimen before starting the test and A is the exposed area of the specimen (mm^2). The water absorption test was performed in triplicate for each of the mixtures presented in Table 1.

$$W = \frac{Q_n - Q_0}{A} \tag{2}$$

3 Experimental results: analysis and discussion

3.1 Rheological measurements

The rheological behaviour of one of the grouts (G2) are given for the shear stress versus shear rate curves in Fig. 1. As can be seen, G2 presented a Bingham behaviour. The same response was obtained by the other grouts. Therefore, viscosity was calculated by Equation 1 from the Bingham model and the curves are shown in Fig. 2. Although the grouts G1 and G2 had the same flow time, it is noticed how the amount of water changes the viscosity. The viscosity of the grout with w/b = 0.46 (G2 and G4) is lower than the grout with w/b = 0.39 (G1 and G3). As expected, the increase of water reduces the viscosity due to the reduction of interparticle forces [16,17].

Analysing the effect caused by adding MC for grouts with w/b = 0.39, a reduction in the viscosity in both mixtures is observed up to 20 minutes. The viscosities of G1 and G3, from 3 to 20 min, ranged from 540.8 to 515.9 Pa.s and from 518 to 487.9 Pa.s, respectively. However, after 20 minutes each mixture behaves differently. The viscosity of the sample containing only MC decreases to 445.8 Pa.s after 1 hour since preparation. In contrast, the G1 increases its flowability and, in 60 min, the viscosity reaches 609.6 Pa.s. Comparing the mixtures with higher w/b, G2 and G4, the addition of MC in the mixture containing CA (G4) also caused a decrease in viscosity in the first 20 min. The opposite of what was measured with G2, which showed an increase in viscosity. From 20 to 60 min, the viscosity of G2 remained practically constant while the flowability of the mixture G4 decreased and viscosity changed from 316.7 to 353.4 Pa.s.
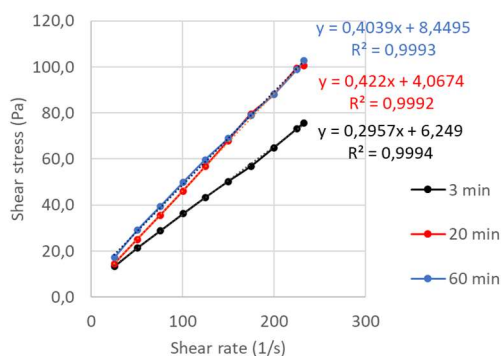

Fig. 1. Shear stress versus shear rate curves of a cement-based grout with 3% of crystalline admixture (G2 mixture). For each time measured, equation and R-square value obtained by linear regression are presented.
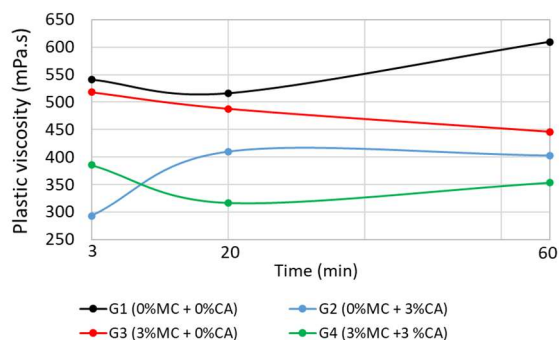

Fig. 2. Evolution of the viscosity over time of grouts

A decrease in viscosity was also observed by Oh *et al.* [18] when studying additions of microcapsules containing a silicate-based inorganic materials as a healing agent. The authors concluded that the decrease is due to a "ball bearing effect" (as microcapsules are spherical this reduces the interparticle friction between large and small particles). The reduction in viscosity could also be caused by particle agglomeration. Although the addition of microcapsules in G3 and G4 slightly increased the bleeding (the increase was less than 0.3%), sedimentation and segregation were not observed visually during the period evaluated. Another hypothesis is that the microcapsules broke in the mixing process and the healing agent could have condensed and formed a silicone oil. To confirm the previously suggested explanations, other tests are needed, such as microstructure images by SEM, water permeability measurements, surface wettability by contact angle measurement, porosity measurements and agglomeration and dispersion measurements.

3.2 Sorptivity

As the sorptivity shows the tendency of the porous material to absorb water, it is expected that the measurements indicate the occurrence of the healing effect. When the cracks are filled, the water uptake is prevented and the sorptivity decreases. Fig. 3 shows the increase in the average mass of the specimens after 28 days in contact with water. Results of sorptivity tests for 28 days are reported in Table 2. Fig. 4 shows the water absorbed at 7 days of curing and Fig. 5, at 28 days of curing.
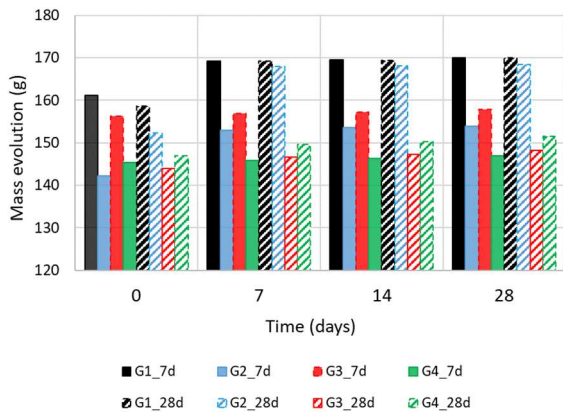
Fig. 3. Evolution of the mass average by water absorption over 28 days.

Table 2. Water absorption measurements (g/mm^2) of grouts specimens cracked at 7 and 28 days.

Curing age	Mix ID	Healing time (days)		
		7	14	28
7d	G1	0.005269	0.005575	0.005871
	G2	0.021444	0.022063	0.022981
	G3	0.000265	0.000392	0.000662
	G4	0.00028	0.000566	0.000871
28d	G1	0.006733	0.007121	0.00744
	G2	0.0099	0.010094	0.010356
	G3	0.00206	0.002733	0.003456
	G4	0.002092	0.002885	0.003713

From Table 2, it is noted that water uptake of the grouts containing MC were lower at 7 and 28 days of curing age for both w/b ratio and the absorption was quite linear and similar. It is noted that at 7 days (Fig. 4) G3 and G4 registered less absorption over time than at 28 days (Fig. 5). In both curing ages, is also noted that G4 absorbed slightly more than grout G3. Regarding the specimens with CA, G2 absorbed less water at 28 days than at 7 days. Analysing Fig.3 and 4, the absorption of grout G2 slightly increased over 28 days. G1 also showed a slight increase in water intake in both curing ages. In general, the water uptake of G3 and G4 was lower than G1 and G2. Mixing CA with MC (grout G4) promoted a good decrease in water absorption.

Although healing is dependent on water/moisture for both healing agents [9,19] it is not clear if the differences in water absorption results are due to the crack healing (as the specimens were not previously exposed to any healing conditions) or due to a breakage of the microcapsules during the mixing step (after the curing period, the condensed healing agent favoured the production of a "water-repellent grout"). In addition, as the opening value is an average value, there is the possibility of non-uniformity in widths, that is, the specimens may have different crack opening along the entire length of the sample as well as different sizes between them (impairing the comparison), which also influences the water absorption.

4 Conclusion

The objective of this study was to evaluate the influence of crystalline admixture (Penetron Admix®) and microcapsules (polyurethane microcapsules containing waterproofing resin) on viscosity and water absorption of cementitious grouts.
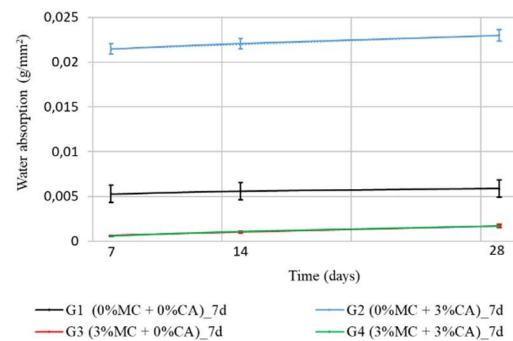

Fig. 4. Sorptivity analysis of grouts (with and without microcapsules and crystalline admixture) cracked at 7 days of curing age.
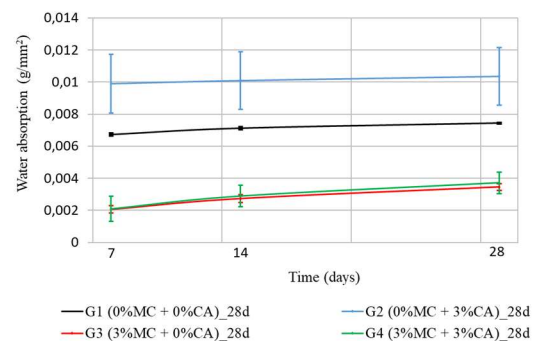

Fig. 5. Sorptivity analysis of grouts (with and without microcapsules and crystalline admixture) cracked at 28 days of curing age

– For grout containing only 3% MC (G3), a reduction in the viscosity over time was observed. For the grout prepared with 3% MC and 3% CA (G4), the viscosity decreased in the first 20 minutes and then increased.

– The viscosity of the grout with w/b ratio of 0.46 containing only crystalline admixture increased up to 20 min and thereafter remained constant.

– The reference grout (0% MC + 0% CA) showed a decrease in viscosity from 3 to 20 min and then, an increase. Among all grouts, reference grout presented the highest viscosity over time and the grout with both additives (3% MC + 3% CA) the lowest.

– The water absorption of G3 and G4 was lower than G1 and G2 during the 28 days in contact with the 3-mm water level and for both curing age. The addition of CA to the grout increases absorption and a greater absorption was expected, as CA is a hydrophilic material. The lowest water absorption occurred for grouts containing microcapsules (G3 and G4). Both grouts absorbed similar amounts of water at both curing age and the absorption trend was similar.

– Merely observing the capillary water absorption does not indicate the crack has healed. As

mentioned before, it is unclear if differences in water absorption results are due to crack healing, breakage of microcapsules during the mixing step or non-uniformity in crack widths. As future works, it is necessary to have different healing conditions (e.g., total immersion of samples in water for a long period before measuring sorptivity) and, concomitantly, evaluate the evolution of the crack healing by other techniques, as microscopy. In addition, other tests are needed to better understand the effects of these additives on the grout, such as microstructure evaluation by SEM and X-ray tomography, water permeability measurements, surface wettability by contact angle measurement, porosity measurements, and agglomeration and dispersion measurements.

– In the future, it will also be necessary to investigate the trend of absorption rate change through the expansion of other parameters of crystalline admixtures and microcapsules, for example, better control of crack widths and different dosages.

References

[1] D.M. Harrison, Cement Grouts, in: The Grouting Handbook - A Step-by-Step Guide for Foundation Design and Machinery Installation, 57–68 (2013)

[2] K. Vance, G. Sant, N. Neithalath, Cem. Concr. Compos. **59**, 38–48 (2015)

[3] V.H. Nguyen, S. Remond, J.L. Gallias, Cem Concr Res. **41**, 292–300 (2011)

[4] S.H. Jakhrani, A. Qudoos, H.G. Kim, I.K. Jeon, J.S. Ryou, J. Ceram. Process. Res. **20**, 1–18 (2019)

[5] N. de Belie, E. Gruyaert, A. Al-Tabbaa, P. Antonaci, C. Baera, D. Bajare, A. Darquennes, R. Davies, L. Ferrara, T. Jefferson, C. Litina, B. Miljevic, A. Otlewska, J. Ranogajec, M. Roig-Flores, K. Paine, P. Lukowski, P. Serna, J.M. Tulliani, S. Vucetic, J. Wang, H.M. Jonkers, Adv. Mater. Interfaces **5**, 1–28(2018)

[6] M. Wu, B. Johannesson, M. Geiker, Constr. Build. Mater. **28**, 571–583 (2012)

[7] W. Zhang, Q. Zheng, A. Ashour, B. Han, Compos. B : Eng. **189**, 107892 (2020)

[8] M.S.S. Zabanoot, WIT Transactions on the Built Environment **196**, 31–38 (2020).

[9] American Concrete Institute Committee 212, ACI 212.3R-10 Report on Chemical Admixtures for concrete_Chapter **15**, (2017)

[10] K. Sisomphon, O. Copuroglu, E.A.B. Koenders, Cem. Concr. Compos. **34**, 566–574 (2012)

[11] A. S. Oliveira, J. Dweck, E.M.R. Fairbain, O.R.D.T. Filho, J. Therm. Anal. Calorim. **139**, 3361–3375 (2020)

[12] L. Ferrara, V. Krelani, F. Moretti, Smart. Mater. Struct. **25**, 1–17 (2016)

[13] N.J. Kanu, E. Gupta, U.K. Vates, G.K. Singh, Compos. Part A Appl. Sci. Manuf. **121**, 474–486 (2019)

[14] A. Kanellopoulos, P. Giannaros, A. Al-Tabbaa, Constr. Build. Mater. **122**, 577–593 (2016)

[15] B. Hilloulin, K. van Tittelboom, E. Gruyaert, N. de Belie, A. Loukili, Cem. Concr. Compos. **55**, 298–307 (2015).

[16] M. Sonebi, A. Abdalqader, T. Fayyad, A. Perrot, Y. Bai, Constr. Build. Mater. **262**, (2020)

[17] F. Rosquoët, A. Alexis, A. Khelidj, A. Phelipot, Cem. Concr. Res. **33**, 713–722 (2003)

[18] C.-G. Kim, Y.-W. Choi, S. Choi, S.-R. Oh, Materials **15**, 18 (2022).

[19] H. Feng, H.T.N. Le, S. Wang, M.H. Zhang, Constr. Build. Mater. **129**, 48–60 (2016)