Materials Today: Proceedings 54 (2022) 22–27

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Nanoparticles controlling self-healing properties in cement pastes

Maria Stefanidou *, Eirini-Chrysanthi Tsardaka, Aspasia Karozou

Laboratory of Building Materials, School of Civil Engineering, Aristotle University of Thessaloniki, Greece

ARTICLE INFO

Article history:
Received 1 September 2020
Received in revised form 28 June 2021
Accepted 1 July 2021
Available online 21 July 2021

Keywords:
Cement pastes
Nano-silica
Nano-calcium oxide
Self-healing

ABSTRACT

The ability to control self-healing of cement by using nanoparticles was investigated in the present work. The physico-mechanical properties, the mineralogical composition and the microstructure observation were tested before cracking at 28 days. After the formation of cracks the healing capability under water immersion was detected by optical observation. The self-healing was supported by porosity reduction, new formed materials' formation in micropores and cracks' width elimination in the pastes. The addition of 1.5%wt nano-calcium oxide (NC) healed the cracks by 100% on some areas and by 61% in other areas, based to the crack width measurement. The combination of NC and nanosilica (NS) by 1.5%wt respectively, led to crack width decrease, through the formation of efflorescence-like crystals. Overall, the use of nanoparticles in low proportions is proposed for self-healing properties promotion in cement pastes.

Selection and peer-review under responsibility of the scientific committee of the International Conferences & Exhibition on Nanotechnologies, Organic Electronics & Nanomedicine – NANOTEXNOLOGY 2020.

1. Introduction

Despite their many advantages, cement-based materials remain vulnerable to cracking. Ageing, ambient conditions, heat and humidity changes and volume changes are some of the destructive causes [1]. Oxidation of the reinforcement is one of the main issues that occur due to the cracking of concrete. Cracks not only limit the applicability of the cement-based materials but also, they restrain their durability. Thus, the need to prevent cracking arises. Intervention and repair that are subsequently required, increase the construction cost. Towards this direction, in recent years, there has been an ongoing effort to develop advanced materials with increased lifespan through the ability of materials to self-heal their deficiencies (cracking) mainly when these flaws are first formed.

Mineral admixtures that are added in the production step, can offer self-healing. The mechanism for self-healing is based on the interaction or bonding of water molecules when water enters the crack. An advantage of mineral admixtures' addition is that self-healing could start immediately, as they are added during production, and they are well dispersed in the matrix, and as a result, they stop cracks propagation [2]. Additionally, it has been found that mineral admixtures (like sodium carbonate and calcium sulfoaluminate) addition can contribute in calcite precipitation [3]. Water immersion is the most effective curing condition, although, in some cases, wet-dry cycles allowed healing too [4,5]. Nevertheless, it has been recently demonstrated that gas permeability can also have a very positive outcome on healing [3]. Calcium oxide, calcium hydroxide, and lime-based materials have been used for healing means [6–8], due to their ability to capture atmospheric carbon dioxide and form calcite [6,9]. The precipitation of calcite ensures the healing of the cracks.

In addition to the above, a possible beneficial approach to assist healing is the introduction of nano-sized admixtures into the material. NC has been proved to promote calcite precipitation. In the literature, there are not many reports suggesting the use of nanoparticles in order to offer self-healing properties in cement-based materials. The addition of 5%wt NC augmented the re-crystallization rate in the cracks' areas and pores of cement-based mortars [10]. Cracks were filled with newly formed material; portlandite that prevailed in the structure, and C-S-H crystals. The formation of these new materials has reduced the porosity of the mortars, thus supporting the healing process. Also, NC vitally and favourably worked in cement pastes healing and has been demonstrated by secondary calcite formations recording at the very early age of 7 days [10]. SEM pictures unveiled secondary crystals filling small and bridging larger cracks in lime-cement pastes with NC-NS incorporation.

The present research work aims to study the use of nanoparticles for the control of cement paste healing phenomena. It was

* Corresponding author.
E-mail address: stefan@civil.auth.gr (M. Stefanidou).

https://doi.org/10.1016/j.matpr.2021.07.028
2214-7853/
Selection and peer-review under responsibility of the scientific committee of the International Conferences & Exhibition on Nanotechnologies, Organic Electronics & Nanomedicine – NANOTEXNOLOGY 2020.

decided to study the healing progress in pastes, in order to focus on the microstructure and exclude the interference of aggregates. When small cracks were formed, the influence of nanoparticles, NC 1.5%wt alone and NC combined with NS by 1.5%wt respectively, was determined. The controlled fracture (pre-cracking) was performed using the 3-point bending technique, according to previous experience [10,11] and literature [2,12]. The specimens were cured under water, while at the age of 28 days, the mechanical, mineralogical, and microstructure properties were recorded. The results indicated improved compressive strength and porosity, while the densification of the microstructure with new material formations was observed in nano-modifies samples. Added to that, significant crack width reduction was recorded in those samples. Smart materials that can heal their flaws due to the presence of a small percentage of nanoparticles is a promising advantage in the construction sector.

2. Materials and methods

Cement I42.5 was supplied from a local plant. Table 1 shows the chemical composition of cement given in oxides (X-Ray Fluorescence, S8 Tiger, Bruker Instruments), and Table 2 shows the granulometry (according to particle size analyzer Mastersizer 2000, Malvern Instruments) (Fig.1) and the density (ASTM-C188-95) of the cement. Nano-calcium oxide and nano-silica (0.007 μm) were supplied from Sigma-Aldrich, and their mineralogical response is given in Fig. 2.

Analytical balance AB204-S/FACT, Mettler Toledo (220,0 ± 0.0001 g) was used for the weight of the nanoparticles and a balance Kern PCB 4000–2 (max capacity 4000 ± 0.01 g) was used to weight cement.

Compressive strength (loading rate: 0.5KN/sec) was tested at 28 days (based on EN 196–3:2005), on (25x25x50)mm specimens, using a Technik ToniNorm device and the mean value of six measurements was calculated. Open porosity was tested at 28 days according to RILEM CPC 11.3 method, in water under vacuum [13]. The specimens were added in water tank and the water was forced to entry to the open pores by using negative pressure 1 bar. The specimens were weight and the calculations were made according to the respective standard. The observation of microstructure was performed at 28 days on dried specimens using Scanning Electron Microscopy, Jeol JSM-6390LV, Oxford Instruments. The mineralogical composition of raw materials and samples was determined by using X-Ray Diffractometer, at 30 kV and 10 mA, Cu(Ni), Brucker Instruments at 28 days.

The formation of the cracks was performed by using the "3-point bending method" with very low displacement rate (0.3 mm/min) until the crack was formed. Specimens (40x40x160)mm were marked and notched in the middle of their length and they were cracked at 28 days. The target of the cracking is to create controlled cracks of less than 0.5 mm width. The crack width, was observed by using a Dino-Lite2 microscope and was measured by using DinoCapture2.0 software. The captions of the cracks were taken before healing and seven days after the water immersion. The comparison of the captions and the crack width modification were used for the evaluation of healing at 7 days healing process.

3. Preparation of cement pastes

The composition of mixtures is given in Table 3. Low proportions of nanoparticles were added and the amount was selected according to previous studies [14,15]. Nano-particles were added in water and were subjected to ultrasonication for 30 min. The suspensions were directly added to the cement powder and stirred up to homogenization. Consistency was determined using a Vicat apparatus (EN 196–3:2005). Superplasticizer (SP) was used in nanomodified mixtures in order to maintain the consistency of the systems. Pastes were cast in (25x25x50)mm molds for the testing of mechanical properties and (40x40x160)mm molds for the three-point bending test. Specimens were cured under water until the conduction of the tests.

4. Results and discussion

4.1. Compressive strength and open porosity

Fig. 3 displays the compressive strength and open porosity values of cement paste at 28 days. The addition of calcium oxide nanoparticles(NC) benefited the compressive strength and contributed positively to the open porosity, in agreement to previous studies of cement pastes modified with NC [10]. Consequently, it could be claimed that the mechanical properties of cement pastes are positively affected due to the formation of a denser structure, when NC is incorporated. On the other hand, the combination of NC and NS did not significantly modify compressive strength. It has been displayed that NC-NS addition in air lime pastes hindered the compressive strength evolution at 28 and 90 days [16]. Also, in this case, the addition of NC-NS in cement-lime pastes hampered compressive strength at 28 and 90 days.

Open porosity of C-NC-NS was reduced to a higher degree comparing C and C-NC. In the previous work [10], NC-NS combination offered alike behaviour of open porosity. The nanoparticles contribute to the open porosity reduction. Specifically, the open porosity was changed by −18.58% in NC and by −55.75% in C-NC-NS. Specifically, it has been displayed before that NC addition has reduced the open porosity of lime-pozzolan pastes at 7 and 28 days, by 37% and 22% [17] and that of cement pastes by 55% and 42% at 7 and 28 days [10].

Table 1
Chemical composition of cement powder (mg/L) and Loss of Ignition.

Binder	Na_2O	K_2O	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	SO_3	L.I.%
Cement I42.5N	0.02	1.10	61.70	1.20	3.07	3.14	15.01	3.34	2.81

Table 2
Granulometry and density (g/m3).

Binder	d(0.1) (μm)	d(0.5) (μm)	d(0.9) (μm)	Density (g/m^3)
Cement I42.5 N	1.275	4.667	222.03	3.105

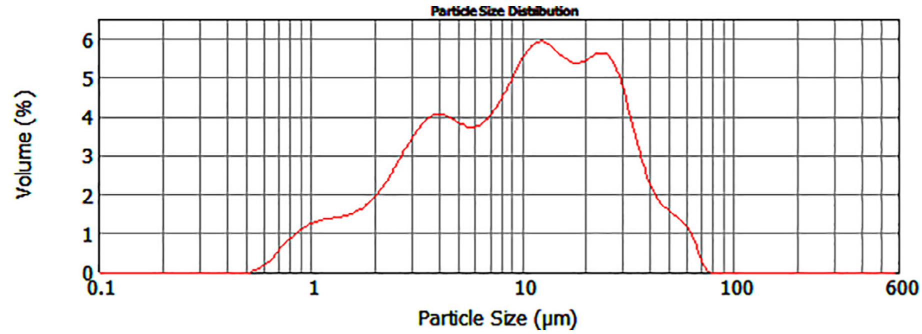

Fig. 1. Particle size distribution of cement I42.5 N.

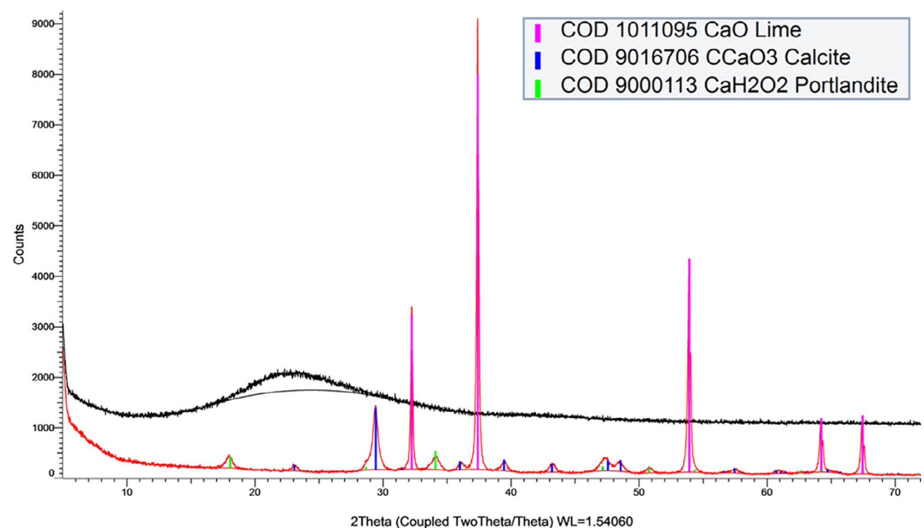

Fig. 2. Diffractograms of NC (red line) and NS particles (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Composition of cement pastes.

Acronym	Cement I42.5 (%)	NC %wt	NS %wt	Vicat (mm)	W/B	SP %wt
C	100	–	–	6	0.23	1.5
C-NC	100	1.5	–	6	0.23	1.5
C-NC-NS	100	1.5	1.5	18	0.30	1.5

4.2. Mineralogical composition

Fig. 4 shows the mineralogical composition of cement pastes at 28 days. Portlandite, calcite, alite, ettringite, and quartz responses, were detected in all systems. The differences in mineralogical composition that were observed are related to the intensity of the peaks of the minerals. In C-NC, ettringite diffraction is reduced, and instead, AFM compounds formation is favored, as depicted between 10 and 13°. The high specific surface of NC, which allows greater interactivity could be connected to the latter outcome.

Furthermore, the effect of nanoparticles in cement hydration and calcite proportion were recorded. The promotion of cement hydration due to NS addition has been denoted in many reports [18–20]. As it is shown in Fig. 5, the presence of NC increased the calcite response, and both nanomodified systems presented lower intensity of alite peaks, comparing to the reference. This phenomenon could be an indication of the contribution of nanoparticles to cement hydration.

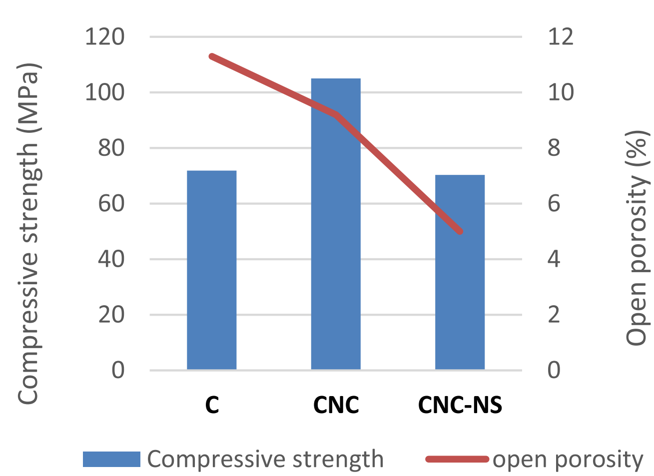

Fig. 3. Compressive strength and open porosity values of reference cement pastes (C) and nanomodified systems with 1.5%wt NC (C-NC) and combination of 1.5%wt NC and 1.5%wt NS (C-NC-NS), at 28 days.

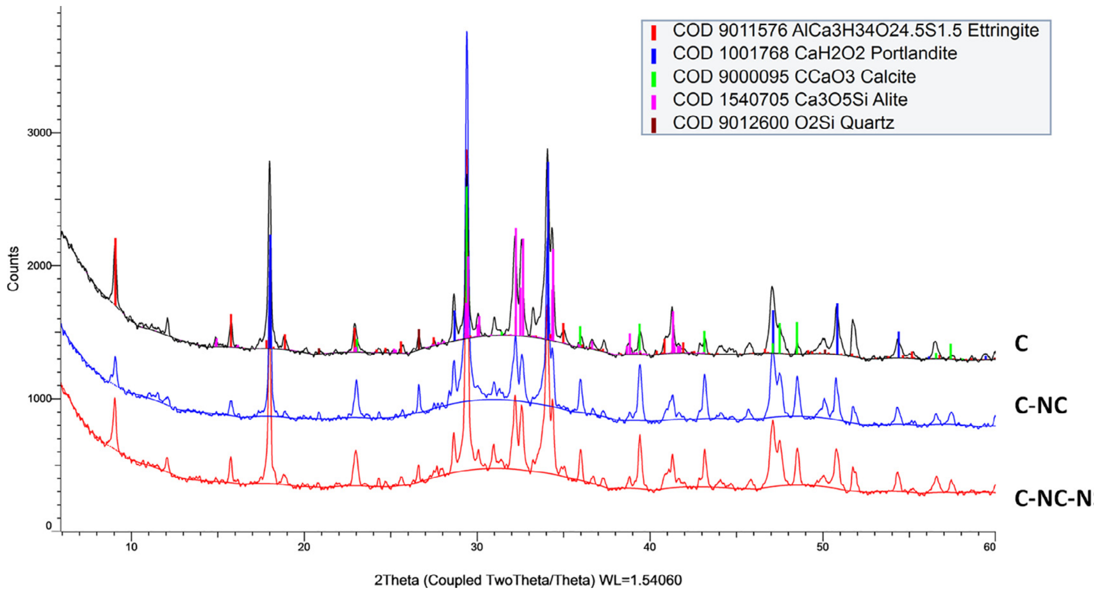

Fig. 4. Mineralogical composition of nanomodified cement pastes at 28 days.

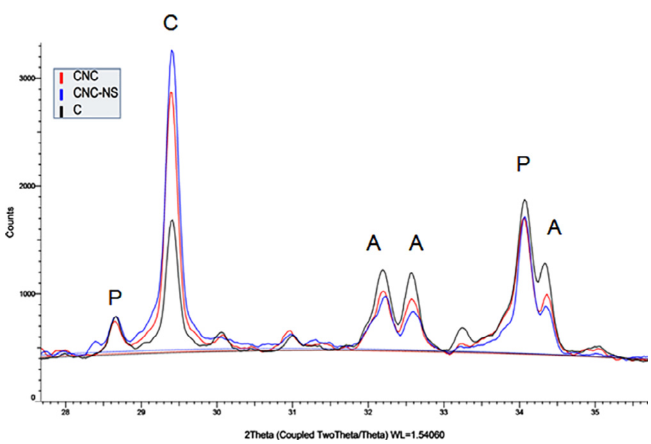

Fig. 5. X-ray diffractograms of nanomodified cement pastes at 28 days.

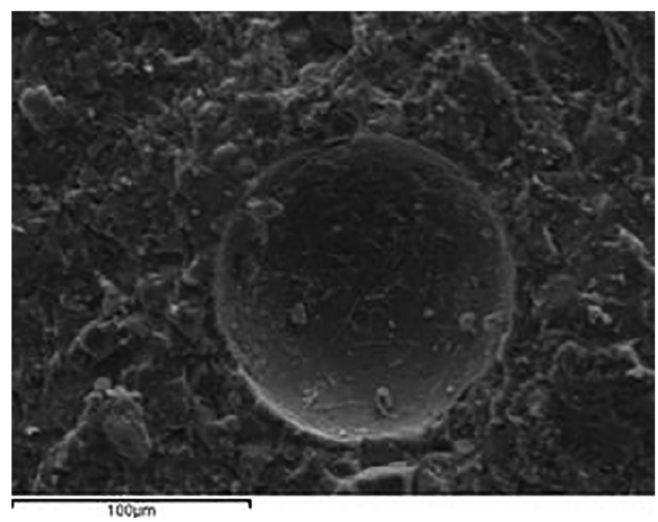

Fig. 6. SEM-micrograph of cement paste at 28 days.

4.3. Microstructure observation

The microstructure of neat cement pastes is given in Fig. 6. The typical cement structure was found dense, and large pores attributed to open porosity were observed. These pores were found free of material, despite the fact that the specimens were cured in water. Also, micro-cracks and discontinuities were absent.

In SEM-micrograph of C-NC a denser structure with few large pores was obtained, compared to the reference. The pores contained newly formed crystallized material that was probably deposited and formed due to the humid environment. Fig. 7 displays this new formed crystallized material that has its own micro-porosity and is marked in red cycles. It can be distinguished that the new materials' microstructure is not alike cements' microstructure. It seems that it has smaller density and looks more porous than cement. The cohesion between the new material and cement pore edge is strong. All these, indicate the filling of the structure attributed to NC. In combination with calcite precipitation increase given in diffraction patterns of C-NC (Fig. 5), the new formed material could be connected to the calcite precipita-

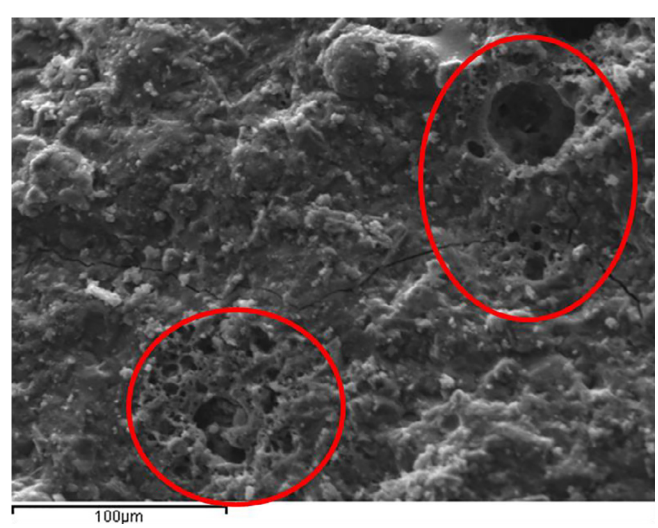

Fig. 7. SEM-micrograph of NC-modified cement paste at 28 days.

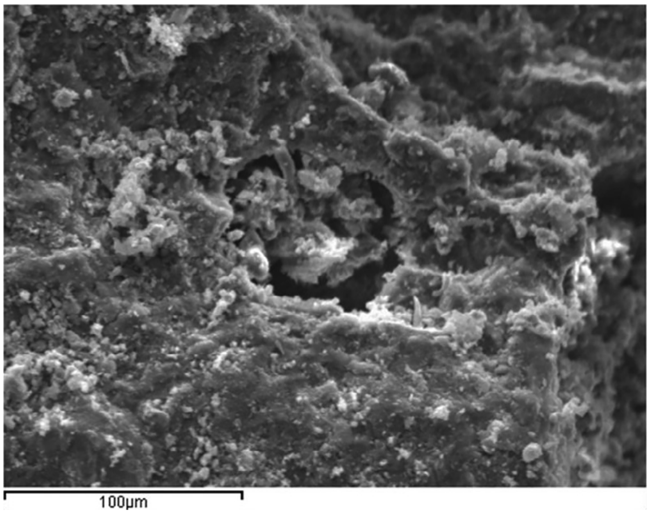

Fig. 8. SEM-micrograph of NC-NS- modified cement paste at 28 days.

tion [15]. Added to that, the dense and compact microstructure explains also the increased compressive strength mentioned earlier.

Fig. 8, shows the filled pore of the C-NC-NS sample. The round shape pores have been modified, due to crystallized deposits in them. The pore edges have lost the round shape due to the recrystallized deposits. The new formed material looks more compact than that of C-NC, but it is not cohesively attached to the inner surface of the pore.

4.4. Observation of healing

At the age of 28 days, the cracked specimens were subjected to water immersion in order to trigger the healing according to previous findings [4,5]. The pictures captured at 28 days right after cracking and the pictures captured at 7 days immersion (C', C-NC', C-NC-NS'), are given in Fig. 9.

Cement are capable of autogenous healing. According to the literature some unhydrated cement particles can hydrate on the cracks' area surface and aid to the width reduction, but also the produced portlandite from cement hydration interaction is adding to this effort [12,21]. The hydration of cement particles is the main mechanism of healing at early age and narrow cracks are more likely to be healed [22]. Additionally it has been demonstrated that the addition of NC in cement pastes, even in low proportions could result to aragonite or calcite precipitation and crack width elimination, under the respective curing regime [15]. As a result, the diameter decrease that was detected in some areas of the crack and approaches 37.5%, is ought to the autogenous healing. On the other hand, some areas of the crack remained unaffected in C'.

The crack width elimination in the case of C-NC' approaches 100% on healed areas and 61% on other measured areas. It is clear that the new formed material is oriented to the internal surface of the crack, so as the addition of NC worked favorably on the 7 days self-healing effort. The bridge like crystals that merge the cracks edges may service extra formation of crystals, in the case of time extended water immersion. Taking into account the calcite precipitation that the NC-cement paste presented, the system is favored due to NC addition.

In C-NC-NS', the crack diameter decrease reached 75% at some points, which is encouraging for the results of the combination of NC and NS in cement pastes. Though, the formed crystals were

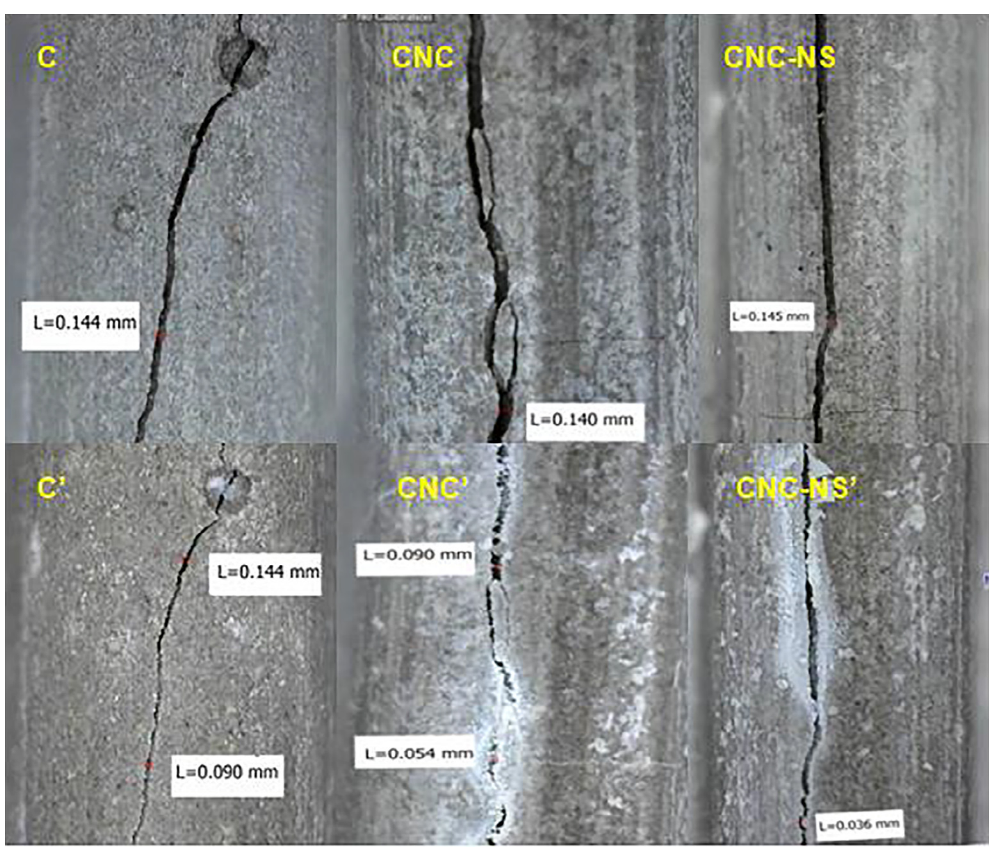

Fig. 9. Microscope pictures of cement pastes after 7 days subjected to water.

not developed indefinitely in the crack filling and they spread out towards the external surface of the specimen like "efflorescence". As a result, NC-NS combination has a potential to favor healing under water immersion.

5. Conclusions

The present research work studied the potential of triggering self-healing properties to cement pastes by using nanoparticles. As it was illustrated in the results, the modified micro-properties improved the macro-properties and assisted the cracks' healing. Nevertheless, the kind of nanoparticle had specific influences on the healing of each mixture.

Nano-calcium oxide addition triggered the healing of the cracks in just seven days due to crystals' precipitation. This new formed material mainly developed in micro-pores according to SEM findings and on the surface of the cracks, according to optical microscopy findings. Bridge-like and oriented in the crack crystals verified the healing under water immersion. Most importantly, the observation of completely healed areas on the crack ensured the potential of nano-calcium oxide action.

The combination of NC and NS behaved differently. Denser material than in NC cement paste, was formed in the micro-pores and showed filling of the structure. Though, the crystals were formed indefinitely and partially healed the cracks after 7 days water immersion.

Withal, the open porosity reduction, the filled microstructure pores, and the cracks width elimination in nanomodified systems were crucial evidences, indicating that nanoparticles can be used in low proportions for self-healing purposes. However, the chemical composition of the formed crystals to ensure the precipitation origin and the influence of other curing conditions are vital for the comprehension of the mechanism.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» in the context of the project "Use of nanoparticles and inorganic admixtures in producing self-healing cement products" MIS 5047560.

References

[1] G. Yıldırım, Ö.K. Keskin, S.B. Keskin, M. Şahmaran, M. Lachemi, A review of intrinsic self-healing capability of engineered cementitious composites: Recovery of transport and mechanical properties, Constr. Build. Mater. 101 (2015) 10–21.
[2] H. Huang, G. Ye, C. Qian, E. Schlangen, Self-healing in cementitious materials: materials, methods and service conditions, Mater. Des. 92 (2016) 499–511.
[3] X. Wang, C. Fang, D. Li, N. Han, F. Xing, A self-healing cementitious composite with mineral admixtures and built-in carbonate, Cem. Concr. Compos. 92 (2018) 216–229.
[4] Y. Yang, M.D. Lepech, E.H. Yang, V.C. Li, Autogenous healing of engineered cementitious composites under wet-dry cycles, Cem. Concr. Res. 39 (2009) 382–390.
[5] M. Roig-Flores, F. Pirritano, P. Serna, L. Ferrara, Effect of crystalline admixtures on the self-healing capability of early-age concrete studied by means of permeability and crack closing tests, Constr. Build. Mater. 114 (2016) 447–457.
[6] K. Sisomphon, O. Copuroglu, E.A.B. Koenders, Self-healing of surface cracks in mortars with expansive additive and crystalline additive, Cem. Concr. Compos. 34 (4) (2012) 566–574.
[7] T.-H. Ahn, T. Kishi, Crack self-healing behavior of cementitious composites incorporating various mineral admixtures, J. Adv. Concr. Technol. 8 (2) (2010) 171–186.
[8] R. Polat, R. Demirboğa, W.H. Khushefati, Effects of nano and micro size of CaO and MgO, nano-clay and expanded perlite aggregate on the autogenous shrinkage of mortar, Constr. Build. Mater. 81 (2015) 268–275.
[9] C. Edvardsen, Water permeability and autogenous healing of cracks in concrete, ACI Mater. J. 96 (1999) 448–454.
[10] M. Stefanidou, E. Tsardaka, E. Tsampali, The role of nano-particles in Self-healing process of cementitious materials, Syner Crete'18, International Conference on Interdisciplinary Approaches for Cement-Based Materials and Structural Concrete, 2018.
[11] M. Stefanidou, E. Tsampali, G. Karagiannis, S. Amanatiadis, A. Ioakim, S. Kassavetis, Techniques for recording self-healing efficiency and characterizing the healing products in cementitious materials, Mater. Design Processing Commun. 3 (3) (2021), https://doi.org/10.1002/mdp2.v3.310.1002/mdp2.166.
[12] L. Yuan, S. Chen, S. Wang, Y. Huang, Q. Yang, S. Liu, J. Wang, P. Du, X. Cheng, Z. Zhou, Research on the improvement of concrete autogenous self-healing based on the regulation of cement particle size distribution (PSD), Materials 12 (17) (2019) 2818, https://doi.org/10.3390/ma12172818.
[13] RILEM CPC 11.3, Absorption of water by immesion under vacuum, RILEM Committee, 1986.
[14] E. Tsampali, E.C. Tsardaka, E. Pavlidou, K.M. Paraskevopoulos, M. Stefanidou, Comparative study of the properties of cement pastes modified with nano-silica and Nano-Alumina, Solid State Phenom. 286 (2019) 133–144.
[15] M. Stefanidou, E.C. Tsardaka, A. Karozou, The influence of curing regimes in self-healing of nano-modified cement pastes, Materials 13 (2020) 1–15.
[16] E.C. Tsardaka, M. Stefanidou, The effects of single and combined nanoparticles in the properties of air lime pastes, Int. J. Archit. Heritage 00 (2019) 1–13.
[17] E.C. Tsardaka, E. Pavlidou, M. Stefanidou, The role of nanoparticles on the durability of lime-pozzolan binding system, Solid State Phenom. 286 (2019) 119–132.
[18] P. Hou, J. Shi, S. Prabakar, X. Cheng, K. Wang, X. Zhou, S.P. Shah, Effects of mixing sequences of nanosilica on the hydration and hardening properties of cement-based materials, Constr. Build. Mater. 263 (2020) 120226.
[19] T. Meng, Y. Hong, H. Wei, Q. Xu, Effect of nano-SiO 2 with different particle size on the hydration kinetics of cement, Thermochim Acta 675 (2019) 127–133.
[20] F. Sanchez, K. Sobolev, Nanotechnology in concrete - a review, Constr. Build. Mater. 24 (2010) 2060–2071.
[21] Z. Lv, H. Chen, Modeling of self-healing efficiency for cracks due to unhydrated cement nuclei in hardened cement paste, Procedia Eng. 27 (2012) 281–290.
[22] K. Van Tittelboom, N. De Belie, Self-healing in cementitious materials-a review, 2013.