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Mineralization Reaction of Calcium Nitrate and Sodium Silicate in Cement-Based Materials

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Abstract: The research consists in the design of the new cementitious materials capable of mitigating microfisurative damage through autonomous healing. This lies in the characterization of the materials to employees, study of the expanding agents (sodium silicate and calcium nitrate) and analysis of its mechanical properties and durability. The results revealed that under laboratory conditions, the applied repair agents proved to be powerful in producing an increase in the content of ettringite, favoring the sealing of the fissure. When they heal themselves, they lead to an improvement in durability and mechanical performance.

Keywords: self-healing concrete; calcium nitrate; mineralization reaction; cracks

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1. Introduction

The deterioration of concrete can happen due to various environmental causes, which can chemically or physically attack the material. Regardless of the nature of the attack, cracks are inevitable in concrete structures, because it is a heterogeneous material. When cracks occur, they allow harmful substances to penetrate the material, without proper maintenance, the propagation of cracks can damage the concrete, putting their safety at risk. In recent years, self-healing techniques have been applied in concrete, these techniques can be identified through various methods, chemical encapsulation; bacterial; mineral mixtures; glass tubes with chemical substances, or by the same cement that was left without hydration.

Design, as well as the production of self-healing concrete, is a topic of great interest today. The great ownership of this type of concrete lies in the ability to mitigate problems related to cracking without external intervention, which leads to prolonging the life of structures and reducing maintenance costs. Healings can be of two types: autogenous and autonomous or autocurative. When the fissures are filled post-secondary hydration of anhydrous particles it is called autogenous healing, while autonomous healing is obtained by adding bacteria, polymer expansive agents, etc. [1–16]. Directly, the use of this type of material contributes to improving the environment, reducing cement consumption by increasing the lifespan of concrete structures.

The expansion agent is another self-healing system, calcium sulfoaluminate-based agents and crystalline additive can provide Ca^{2+} to efficiently improve the self-healing capacity of concrete. Based on this conception, $CaHPO_4{\cdot}2H_2O$ can not only act as a supplier of Ca^{2+} but also as a stabilizer for the healing product. Therefore, the approach of including mineral additives has been developed due to its excellent compatibility with concrete. Mineral additives can react with carbonates that are water-soluble carbon dioxide to form calcium carbonate crystals for crack healing; however, due to the unequal distribution of the concentration of water and carbonate from the surface of the concrete to the interior of the matrix, it is possible that there are fewer ions available within the concrete than on the surface, so the efficiency of self-healing is limited even with the addition of minerals.

This research will analyze the use of expansive agent calcium nitrate and sodium silicate as a repairing agent in cement mixtures. Study involves the implementation of a comprehensive testing program, starting with the individual identification of the main components. Then, in a second stage, self-separating mortar characterization tests are performed to know their mechanical properties, microstructure and durability.

2. Materials and Methods

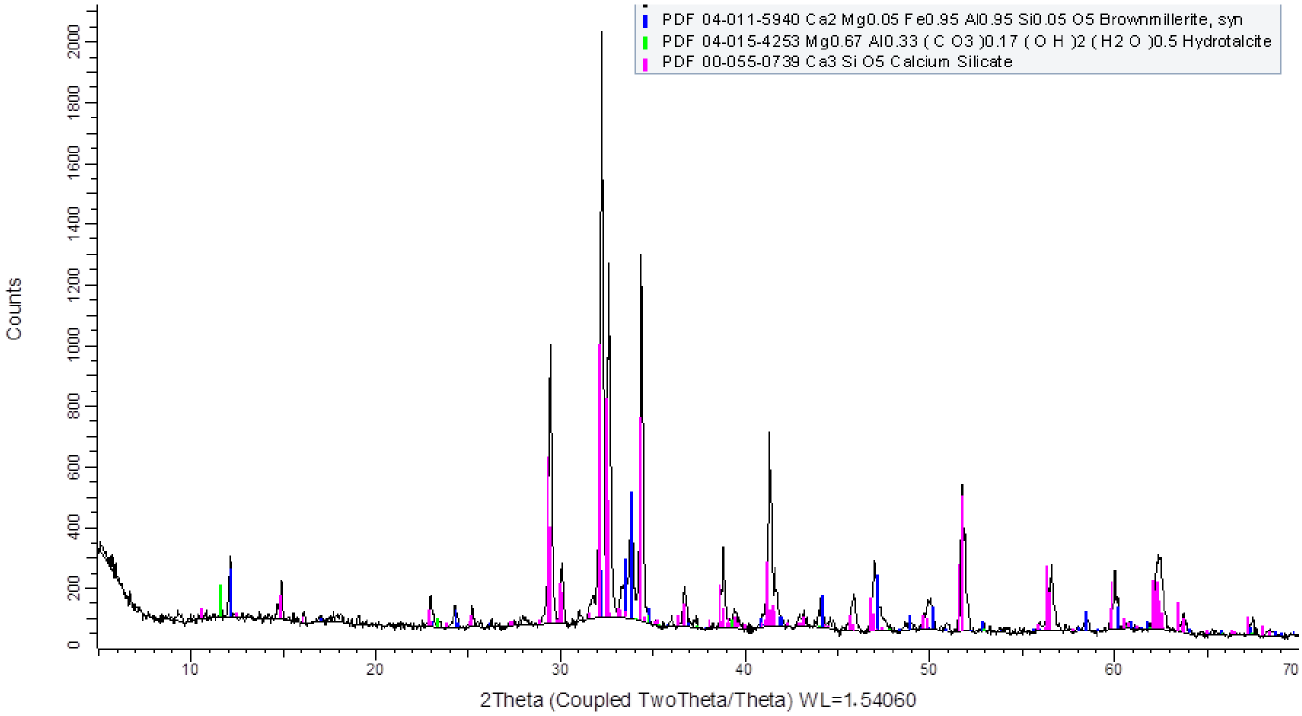
2.1. Characterization of Materials

Portland cement type I 52.5R, sodium silicate (MSS) and calcium nitrate (NC), whose chemical composition of the main components, expressed as oxides, was obtained by X-ray fluorescence, the results of which are listed in Table 1.

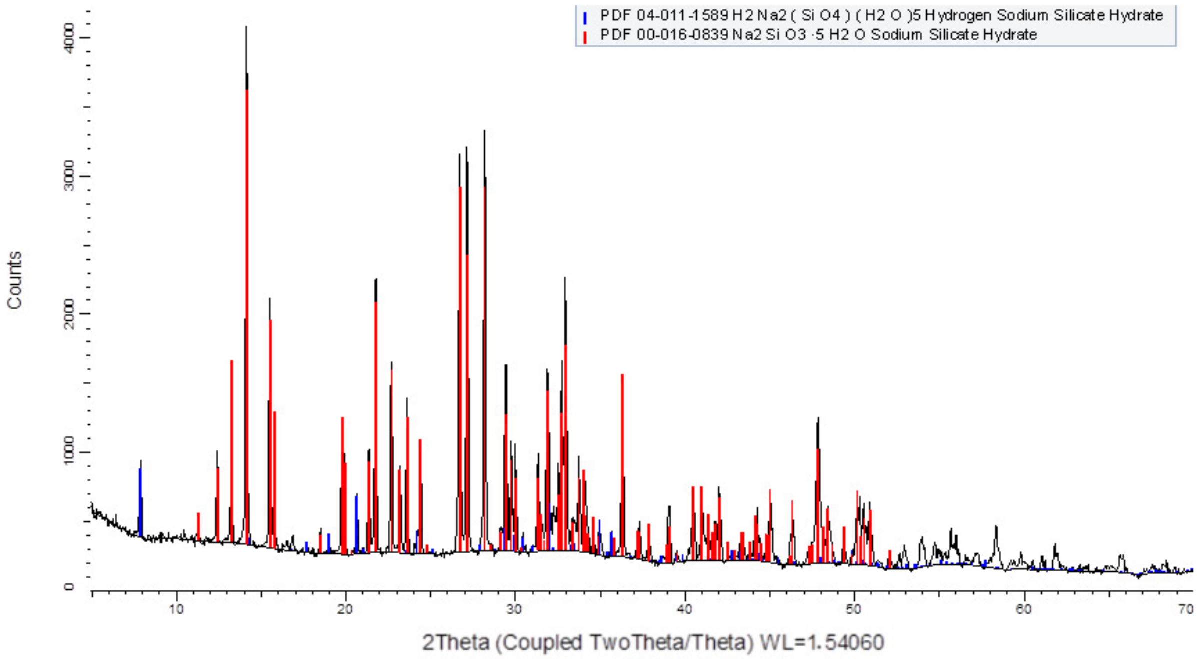
Table 1. Chemical composition of majority components.

	Cement	MSS	NC
ÓXIDE		**COMPOSITION (%)**	
CO_2	1.21	4.36	
Na_2O	0.372	32.13	
MgO	2.52		0.06
Al_2O_3	4.09	0.12	0.017
SiO_2	16.89	27.84	0.035
SO_3	4.061	0.022	0.0053
Cl	0.142	0.011	
K_2O	1.33	0.147	
CaO	64.74	0.014	
TiO_2	0.259		
Fe_2O_3	3.507	0.0209	0.0064
SrO	0.104		0.1577
$Ca(NO_3)_2$			75.85

The analysis of CEM I 52.5R cement to identify the main mineralogical phases is set out in Figure 1, where it is seen that at 11o-2o it has a gypsum peak ($CaSO_4{\cdot}2H_2O$), at peak 12 and 34o-2o it has a peak of calcium manganese aluminum iron oxide (Ca_2 $MnO{\cdot}2FeO{\cdot}8AlO_5$), and at 23 and 26o-2o you have the peaks of Anhidrita ($CaSO_4$), at 29, 30 and 33o-2o you have the peaks of calcium carbonate ($CaCO_3$). Sodium silicates were produced by melting sodium carbonate (Na_2CO_3) at high temperatures with specially selected silica sand. In the diffractogram it can be observed how the majority component appears with various peaks marked red "Sodium Silicate Hydrate" accompanied by hydrogen sodium silicate hydrate ($H_2Na_2[SiO_4][H_2O]_5$) (marked in blue). The peaks were very slender and high intensity, indicating that the sample is made up of particles with an ordered crystalline structure. Finally, in the analysis of the NC by X-ray diffraction we can see that it is a fundamentally amorphous material, by the deviation observed in the baseline. The majority component arises at the peak of nitrocalcite (marked in red) accompanied by calcium nitrate (marked in green) and calcium nitrate hydrate (marked in blue).

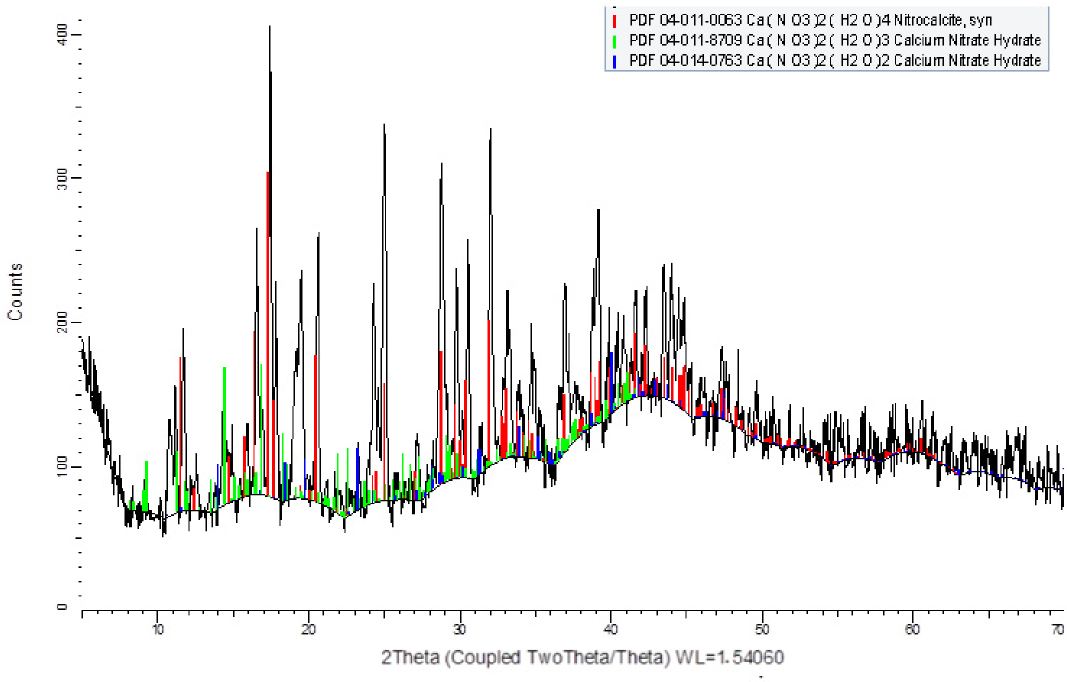


(**a**)



(**b**)

Figure 1. *Cont.*



(**c**)

Figure 1. Cement, MSS and NC X-ray diffractogram. (**a**) Cement, (**b**) sodium silicate (MSS) and (**c**) calcium nitrate (NC).

To analyze the behavior of self-healing mortar, the following mixtures were prepared: 450 g of cement, 1350 g of standard sand and 225 g of water. The NC and MSS content relative to cement weight was 3% and 6%. The test to determine compression resistance was conducted as established by UNE-EN196-1, at ages 7, 28 and 90 days. The carbonation depth has been executed in a carbonation chamber consisting of an airtight vessel to which a CO_2 bullet with continuous flow has been connected. To speed up the carbonation process, the atmosphere generated in the chamber has been 100% CO_2. The temperature has remained between 20 and 25 °C, HR between 60 and 70% and 40 × 40 × 80 mm prismatic specimens were used. After 90 days of curing, the specimens were conditioned at room temperature and humidity for 28 days. Of the six sides of the prism, 4 were protected with aluminum adhesive tape to direct the diffusion only on two sides. Carbonation is measured by contrast of phenolphthalein solution (UNE-112011) by measuring 3 and 7 days. Prior to the spraying of phenolphthalein, the specimens were in two halves. The result will be the average value of at least two distinct sections.

The colorimetric method is used for chloride analysis. The specimens for this test were 40 mm cubic. Five of the faces were painted to be waterproof and watertight to force the spread of chlorides on a single side. These remain submerged in dissolution with 3% sodium chloride until the age of 14 and 28 days.

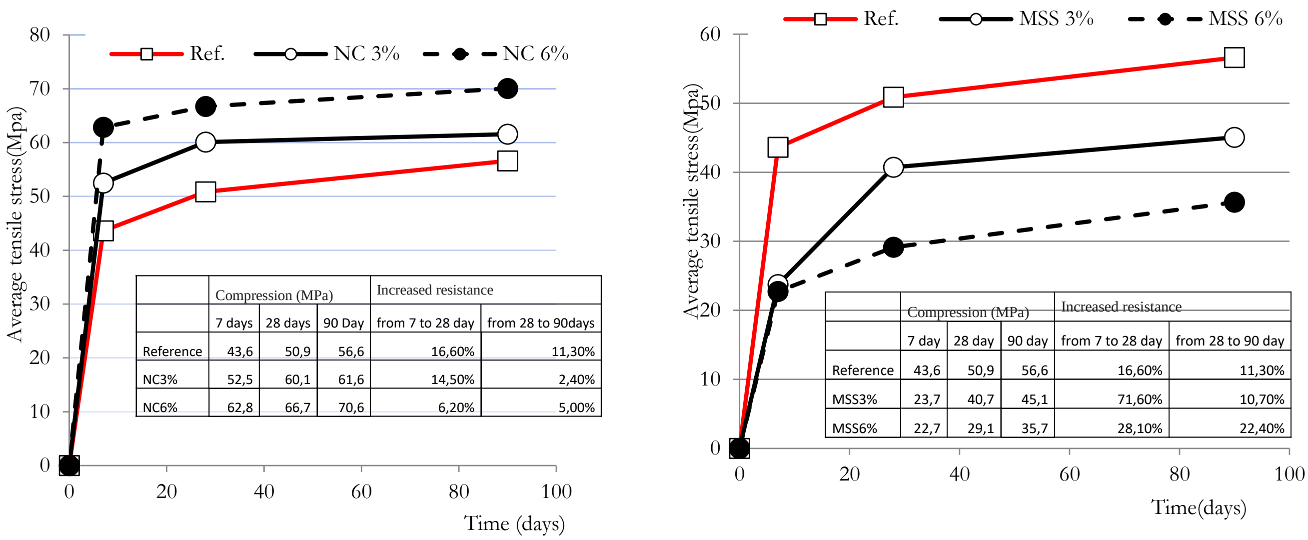
Microstructure analysis was performed by scanning electron microscope (SEM, FEI Quanta 650 FEG), optical microscope and porosity, using mercury intrusion porosimetry (MIP, AutoPore IV9500) following ASTM D4404-84 (2004).

3. Results and Discussion

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation as well as the experimental conclusions that can be drawn.

3.1. Effect of NC and MSS on Compression Resistance

The influence of different amounts of NC and MSS on the mechanical properties of cement paste, and the test results are presented in Figure 2. With the addition of 3% by weight and 6% by weight of NC, the compressive resistance of cement paste was improved in relation to the control sample. Compression resistances with 3% NC increased by 14.5% and 2.4% at 7, 28 and 90 days, respectively. Similarly, compression resistances of 6% increased by 6.2% and 5% at 7, 28 and 90 days, respectively.



(**a**) (**b**)

Figure 2. Compression resistance evolution (MPa). (**a**) Calcium nitrate and (**b**) silicate sodium. The comma between the numbers in the figure represents the decimal point.

The resistance of the mortar with sodium silicate is observed to be much lower than that of the reference mortar, the greater the greater the age of the specimens. The results found are consistent with what is reported by various researchers [14], who agree that the use of SS contributes to demean the mechanical behavior of the material but improves the autocurative properties.

3.2. Effect of NC and MSS on Carbonation and Chlorides

At 7 days the carbonation depth is greater than 3 days in all the mixtures studied (Figure 3a). According to Papadakis (2000) [13] and Mira et al. (2002) [17] the carbonation depth decreases as calcium components increase. The use of NC (6%) decreases the carbonated thickness, being smaller the higher its content, however it is observed that the differences between the other samples are small compared to that of reference to the age of 7 days. Porosity results presented in successive appliances show that the use of NC can have an impact on carbonation by reducing porosity and improving the capillary network, refining and creating greater tortuousness.

Calcium nitrate reduces the intake of Cl^- (Figure 3b), as we have seen above from CO_2, by presenting this a more refined porous structure. Chloride penetration decreases with the lowest porosity presented in samples with higher NC content and/or pore connectivity and decreased chloride binding capacity in the matrix.

3.3. Morphology and Microstructure

Figure 4 shows for each mortar the increase in mercury intrusion volume based on the equivalent pore diameter. Highlighting, the shift to the left of the curve black dots, belonging to the NC (6%), which implies a refinement of pores that transform into small capillary pores and that would explain the least detected amount of small pores. The largest critical diameter corresponds to the SS (6%), followed by mortars containing NC (3%) and, finally, by the SS (3%) NC (6%). As mentioned, this reduction in critical diameter entails a general refinement in the porous structure that can be seen by the shift to the left of the different curves.

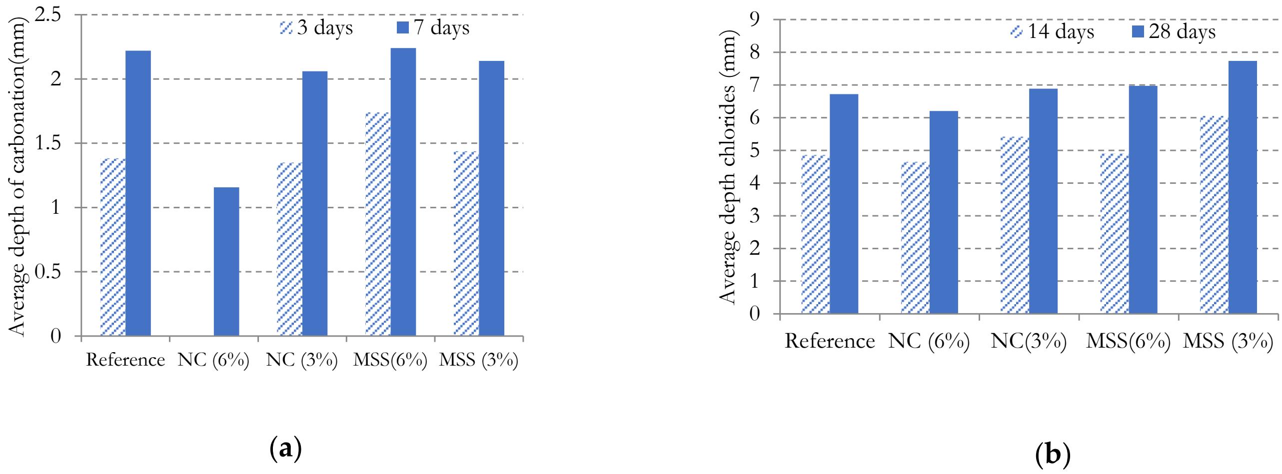


Figure 3. Carbonation depth and chlorides (mm) (**a**) Carbonation (**b**) Chlorides.

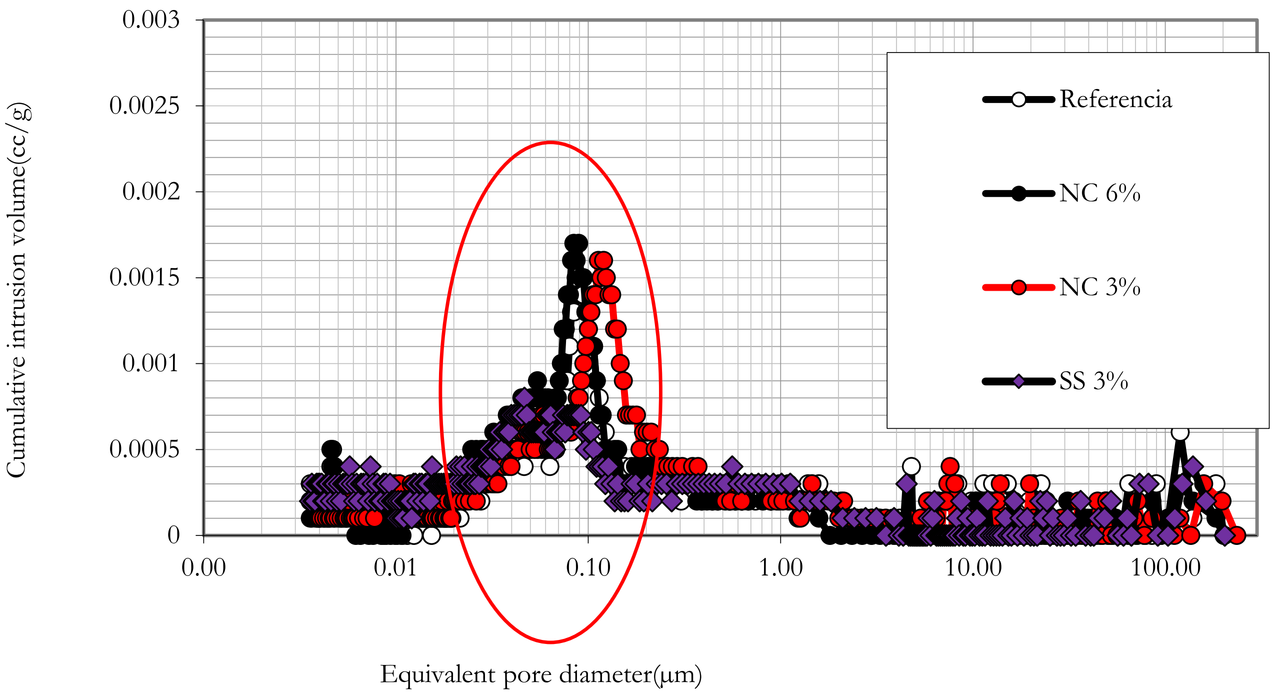


Figure 4. Mercury intrusion volume (cc/g).

Summary shows Table 2 reflecting critical diameter values, where the use of healing agents with 6% NC and 3% MSS results in a decrease in diameter size. The NC sample (6%) has lower values of mean pore diameter (am) than the reference sample, the average pore size is 0.086 om and 0.08 om, respectively. This fact is indicative that the NC has a more refined porous structure than the sample without it, which is expected to exhibit better behavior to prevent the penetration of aggressive agents, resulting in greater durability. Another important parameter that would be related to the finesse of the porous structure is the pore size corresponding to the maximum concentration of the pore. The sample of NC

6% and MSS 3% has a smaller threshold diameter (U) and critical diameter (C), which is consistent with a more refined porous microstructure.

Table 2. Porosimetric analysis.

	Ref	NC (6%)	NC (3%)	MSS (6%)	MSS (3%)
Total intrusion volume (cc/g)	0.0626	0.0591	0.0687	0.0750	0.0620
Total pore area (m^2/g)	9.1708	7.9084	8.7333	16.0074	11.5510
Average pore diameter (ˆm)	0.086	0.080	0.106	0.830	0.046
Total porosity (%)	13.6710	13.0107	14.8482	16.0074	13.3789
Apparent density (g/mL)	2.1826	2.2019	2.1622	2.1338	2.1587

The mercury intrusion porosimetry test also provides total porosity data. Total porosity, with 13.67% for the reference mortar and 13.01% for NC (6%), shows that it decreases with the use of NC. This is due to the densification of the cement matrix by the formation of non-oriented ettringite together with tobermorite, which make the internal structure of the cement denser, because in the spaces between ettringite needles is formed tobermorite, which makes the pores of the internal structure of the cement smaller and increases its durability, this will be best reflected in SEM trials.

The self-healing efficiency of the cracks was characterized by the repair ratio of the area, the permeability coefficient and the healing depth. Meanwhile, the morphologies and polymorphs of the precipitates were analyzed by SEM equipped with an EDS and XRD.

The Figure 5 shows the fissured area with sodium silicate (6%), and the comparative analysis of the elemental composition by dispersed energy. An area with a higher concentration of Ca, Si and Na atoms can be observed. The presence of Na in the cement zone is very significant, since this element is practically absent in the chemical composition of cement [18], as we have seen in Section 2.1.

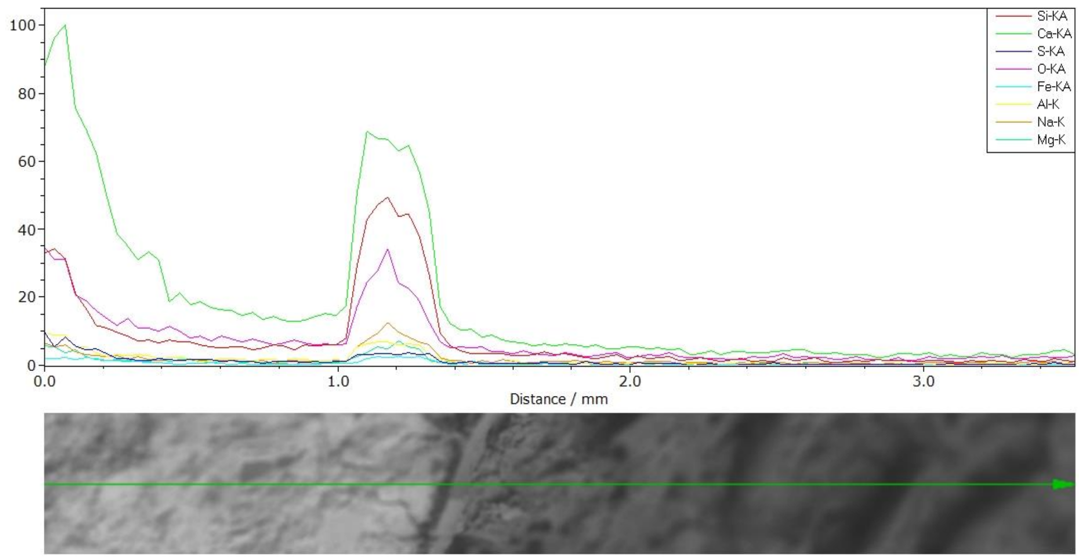


Figure 5. EDS sodium silicate (6%).

From the EDS analysis, the main chemical elements of the healing products are Si, O, Ca and Na. It is observed that there is no Ca in the original healing agent "sodium silicate", but there is a transfer of this compound to the cracked area. Since soluble silicates react almost instantaneously with multivalent metal cations to form the corresponding insoluble metal silicate [18], the chemical element Ca in healing products reveals that calcium cations from the cementing matrixes with the sodium silicate solution, and thus, CSH is formed in the cracks. However, there are not enough calcium cations to replace all of the sodium cations in solution. According to the previous discussion, the main resolution mechanism promoted by sodium silicate solution is the reaction of calcium cations with dissolved sodium silicate and the crystallization of available sodium silicate.

That is, in pastes containing sodium silicate repair material (Na_2SiO_3) in solid state, it has been observed through SEM images, which react with $Ca(OH)_2$(portlandite), naturally present in cementing material to form a calcium silicate hydrate (CSH), a compound that works by sealing cracks.

These results coincide with research conducted by Huang and Ye (2011) [19], which also state that the healing products formed in the fissures are the compounds formed by CSH and sodium silicate. Therefore, the main mechanism of self-management that is generated when using a sodium silicate solution is the reaction of calcium cations with dissolved sodium silicate, resulting in the crystallization of sodium silicate.

Figure 6 shows a micrograph of a cement sample with hydrated sodium silicate and on the right its respective EDS analysis at the age of 28 days.

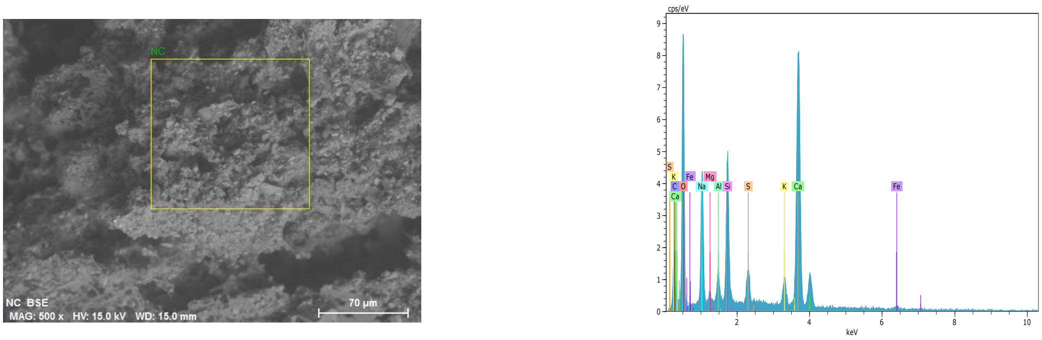


Figure 6. The chemical elements of EDS-tested healing products.

Visual inspection of the fissure is also performed through an optical microscope. This consists of sweeping the fissure taking photos so that there is overlap between the previous and subsequent ones for subsequent reconstruction of the fissure. Through Figure 7, the follow-up over time is observed for 79 days of a cracked cement paste with 6% MSS, where the sewn of it is observed due to the presence of new crystals, this coincides with the results obtained by SEM. The lack of cohesion or sewn that is shown in the fissure, reduces as hydration progresses, since much of these cracks are filled with new hydration products improving in this way, the compactness of the internal microstructure by densification of it. At the age of 28 days it was almost cured, the new rehydration and self-healing products between the fissures were clearly observed after 12 days, and after 79 days of rehydration, as shown in the figure the fissure is almost completely sealed (pictured right below). MSS reacts with calcium hydroxide, a product of cement hydration, and produces a hydrated calcium-silica (C-S-H) of gel-a natural bonding material with concrete. The C-S-H gel (x.($CaO{\cdot}SiO_2$)$\cdot H_2O$), partially fills the fissure, and allows some recovery of force.

Figure 7. Images of a mortar crack with MSS (6%) at the age of 79 days.

Figure 8 presents by SEM image a mortar with 6% NC, at the age of 28 days of curing micrographs is taken as convention E: ethringite, T: tobermorite and P: portlandita.

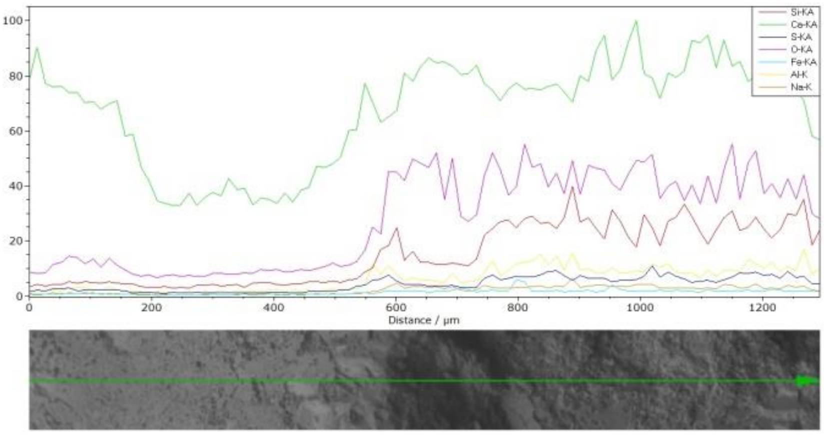


Figure 8. SEM images at 1200 magnifications and composition analysis.

The use of NC increases the amount of ettringite present in the structure of the cement, and, also, presents itself in the form of non-oriented needles, making a sewing effect among the other mineral phases. These results explain the improvement in compressive resistance (Section 3.1) where it is reflected that mortars replaced with NC had higher resistances than the Reference samples, especially at early ages, this is due to the shape of non-oriented needles as shown in Figure 9. In the image you can see: ettringite crystals filling a pore (marked in red). Ettringite crystals in air vacuums and fissures are typically two to four micrometers in cross section and twenty to thirty micrometers long. Under conditions of extreme deterioration or decades in a humid environment, white ettringite crystals can completely fill in voids and fissures [20].

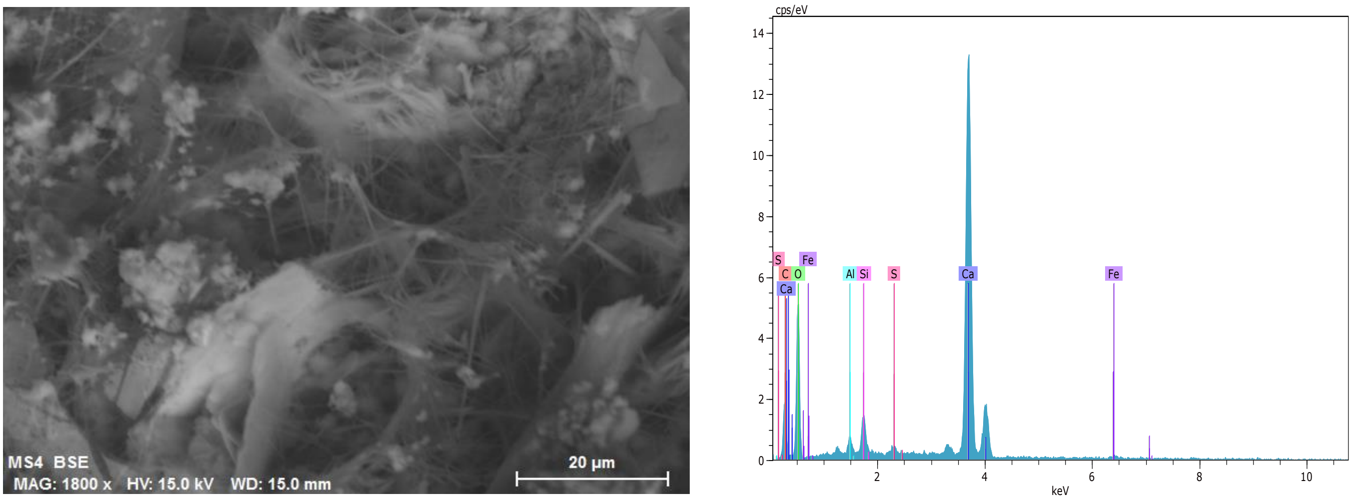


Figure 9. Microfissures filling with new ettringite-type hydration products.

In Figure 10 right, you can see bermorite products. Most bermorite has a distinctive morphology, which is described as crystals in the form of leaves or plates found in open spaces where they have enough space to grow. The most bermorite confers excellent mechanical properties. Photomicrography, also, shows a high concentration of ettringite (they look well crystallized and look perfectly in the form of fine elongated needles or "hedgehogs" characteristic of this).

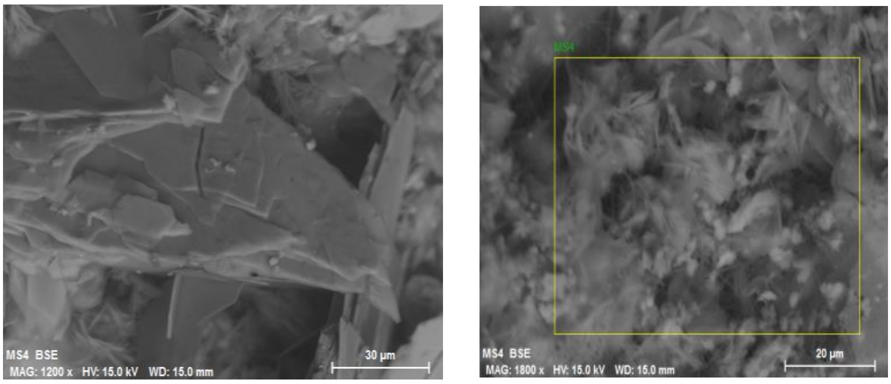


Figure 10. SEM image of cement paste with NC 6%.

The use of NC (6%) facilitates the formation of ettringite by penetrating water into the fissure as shown in the optical microscope images (Figure 11). Regarding crystallization, other researchers have tried to take advantage of the formation of crystals with great capacity of expansiveness to achieve the healing of the fissure thanks to its increase in volume or simply generate a large amount of crystals that are deposited and sealed the fissure, such as those obtained in this research with the use of 6% NC. XRD analysis showed that the precipitates in the crack mouth were calcite. When water comes into contact with the non-hydrated cement, greater hydration occurs. In addition, dissolved CO_2 reacts with Ca^{2+} to form $CaCO_3$ crystals.

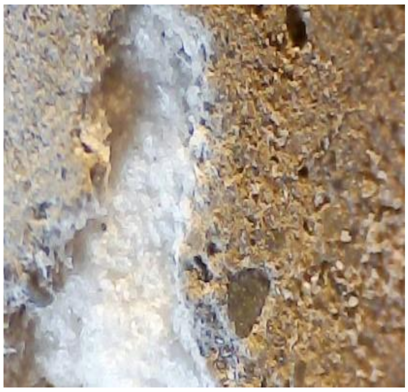


Figure 11. Sealed images of mortar cracks with 6% NC.

4. Conclusions

- The results showed that although self-adapting properties increase in the case of "sodium silicate", the greatest improvement corresponds to the use of "calcium nitrate" as a self-hoarding agent, as well as its durability properties.
- Micrographs taken at 28 days of SEM curing show that the use of NC increases the amount of ettringite present in the structure of the cement, it is presented in the form of non-oriented needles, making a sewing effect with the other mineral phases The formation of these crystals favors the healing of the fissure by sealing it.
- Use of NC curing agent (6%) in the manufacture of mortars allows obtaining improvements above 20% on the reference mortar, in compression resistance.
- The NC in the cement matrix favors the generation of ettringite and tobermorite, in addition leaves little C3A available for the generation of secondary ettringite, improving durability. The formation of ettringite and tobermorite densifies the cement matrix, resulting in a decrease in its total porosity which results in a reduction in the depth of carbonation and chlorides.
- The results indicated that the rate of calcification using calcium nitrate as a source of calcium had a good efficiency of self-healing in the cracks of the mortar.

Author Contributions: All the authors have contributed in the same way in carrying out the research. Conceptualization, I.M.B. and F.J.B.S.; methodology, M.C.S.; validation, P.H.T. and C.J.P.C.; formal analysis, J.d.P.M., V.M.P. and C.L.R.L.; investigation, F.J.B.S., I.M.B. and P.H.T.; resources, V.M.P. and P.H.T. writing—original draft preparation, I.M.B.; writing—review and editing F.J.B.S. All authors have read and agreed to the published version of the manuscript.

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