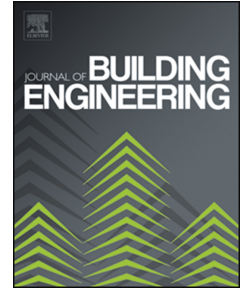


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An overview of a twofold effect of crystalline admixtures in cement-based materials:  
From permeability-reducers to self-healing stimulators

Aline de Souza Oliveira, Otávio da Fonseca Martins Gomes, Liberato Ferrara,  
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# AN OVERVIEW OF A TWOFOLD EFFECT OF CRYSTALLINE ADMIXTURES IN CEMENT-BASED MATERIALS: FROM PERMEABILITY-REDUCERS TO SELF-HEALING STIMULATORS

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## Abstract

This work presents an overview of the most relevant studies developed to understand the enhancement promoted by the double effect of the crystalline admixtures (CAs), both as permeability-reducers and as self-healing stimulators in cement-based materials. Thus, an in-depth investigation was carried out of the main mechanisms of CAs disclosed in the literature in order to associate the relationship between healing products and performance improvement in cementitious materials. Further, an examination of the impact of different factors in cementitious systems with CAs was reported, as well as the synergetic effects of CAs with other constituents. Finally, conclusions were drawn highlighting research needs and addressing future works in order to provide a substantial overview of the latest information in the literature for those who are working or intend to work with this type of admixture.

**Keywords:** crystalline admixture; self-healing stimulator; permeability-reducing admixture; mechanical recovery; durability.

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## 1. Introduction

59 The primary purpose of using chemical admixtures is to improve specific properties of cementitious systems in  
60 the fresh and hardened state related to an intended type of application. However, to perform certain functions,  
61 physical and chemical interactions occur in the cement-admixture system, as the presence of admixtures causes  
62 changes in the course of cement hydration reactions, in the nucleation kinetics and the growth of hydrates, as  
63 well as in the morphology of the hydration products [1,2].

64 Crystalline admixtures (CAs) are commercial products with a twofold effect: reducing the permeability of  
65 concrete and self-sealing the cracks. According to the different manufacturers, the crystalline technology  
66 provides the filling of cracks without intervention and is able to seal cracks up to 400  $\mu\text{m}$ , as a function of  
67 cracking age and exposure scenario. A broad group of materials belongs to the category generically called  
68 crystalline admixtures whose patented formulations are kept confidential. Some studies have also highlighted the  
69 difficulty of obtaining information regarding the chemical composition of these commercial products [3–5].

70 CAs are composed of particles of different size and chemical compositions, including cement, fillers, pozzolans,  
71 slag, sands, siliceous powders and “active chemicals” [4–12]. The physicochemical characteristics of CAs enable  
72 them to act both as inert materials and as active chemicals.

73 The European Standard 934-2 [13] classifies CAs as water resisting admixture and establishes three specific  
74 properties to be measured in CA-added concretes to test their effects and efficacy: capillary absorption,  
75 compressive strength and air content in the fresh state of concrete. However, the ACI 212.3R-16 [14] classifies  
76 CAs under the subcategory of permeability-reducing admixtures (PRA).

77 PRAs are subdivided according to their ability to reduce water penetration with or without hydrostatic pressure,  
78 in two subcategories: PRAN (permeability-reducing admixtures submitted to non-hydrostatic conditions) and  
79 PRAH (permeability-reducing admixtures exposed to hydrostatic conditions). Traditionally, PRANs are also  
80 known as damp-proofing admixtures and PRAH as waterproofing admixtures.

81 PRAN are recommended to delay, without blocking entirely, the entry and passage of water in liquid or vapor  
82 form, under less severe pressure conditions caused by capillary actions. Their effects make the concrete surface  
83 water-repellent or barely wettable; therefore, the significant contribution of PRAN is to maintain the aesthetic  
84 quality of the concrete in the long-term, preventing the entry of rainwater and groundwater [10,15]. Some studies  
85 have indicated that these water-repellent admixtures can reduce the water penetration capacity by 45%, due to  
86 the formation of a thin hydrophobic layer on the walls of the concrete matrix capillaries and also thanks to the  
87 precipitation of non-soluble materials in the capillary structure [16]. Al-Kheetan et al. [17] found that a  
88 crystalline hydrophobic admixture does not enhance the strength gain at the same level that it decreases the water  
89 absorption rate. More detailed information on the chemical composition of this type of admixture, the  
90 mechanism of layer formation, and its effects on concrete have been addressed by Rixom et al. [15]. This  
91 category is not part of the scope of this work.

92 CAs belong to the category of PRAHs, which in turn are indicated to prevent the passage of water under  
93 hydrostatic pressure; thus, reducing the permeability of concrete and self-healing the micro-cracks under  
94 hydrostatic conditions [9,10,14,15]. In addition, CAs can also improve concrete surface permeability and  
95 contribute to the aesthetics of the structures [18].

96 The evaluation of PRAH efficiency as a concrete permeability-reducing offers a wide field of studies to be  
97 explored. Esgandani et al. [16] pointed out that the significant growth of applications of this type of admixture  
98 did not imply an increase in suitable quantitative information to allow their use with greater reliability. These  
99 researchers reported some discordant results regarding its performance that resulted in a lack of confidence as it  
100 come to their application. Likewise, Cappellesso et al. [19] highlighted some points of concern, such as the  
101 scarcity of technical literature, the diversity of manufacturers and the different types of application.

102 Indeed, there are many reasons related to the choice of this product for its use as a self-healing stimulator. The  
103 technological appeal of CAs is related to the ease of acquisition and application in powder form on the  
104 cementitious materials. Besides, the construction industry aims to spread the use of CAs as a stimulator of  
105 autogenous healing of concrete, which represents an opportunity for the development of this kind of self-healing  
106 technology.

107 However, the wide variety of compositions represents a vast field of knowledge to be explored by the scientific  
108 community, as is also highlighted by De Belie et al. [20]. So far, most publications have focused on the effects of  
109 CAs rather than on the microstructural analysis. This trend confirms the demand for research focused on CAs  
110 mechanisms in order to understand reaction processes and associate them with the measured performance  
111 enhancement. Moreover, some findings reported in the literature are not entirely conclusive about the  
112 performance improvement, which may generate some insecurity in the use of CAs, especially from the  
113 perspective of different manufacturers. The influence of different, even aggressive, environmental conditions on  
114 the CAs performance as a healing stimulator also represents a field of investigation. Therefore, the use of  
115 crystalline technology requires confirmation of its potential to restore the original properties for the intended  
116 application.

117 This work lays out a critical overview of the most relevant works that used CAs as a permeability-reducing  
118 admixture or self-healing stimulator in order to discern their effects on the properties of cement-based materials.

119 First, a literature meta-analysis was carried out in order to identify the main works developed in this research  
 120 area, including countries and authors who accumulated the largest number of publications. Further, the main  
 121 mechanisms of CAs were discussed as reported in the literature in order to understand the processing of reactions  
 122 and the nature of the products formed. Analyses were based on the effects of CAs on the fresh- and hardened-  
 123 state properties of cementitious materials. Finally, some studies were carried out to investigate the CAs action in  
 124 the healing efficiency based on mechanical responses and durability-related aspects, as well on some own  
 125 unpublished results. This section also reported the main healing products provided by CAs in the cracks, along  
 126 with the interaction with some variables in CAs performance, such as the environmental conditions, the repeated  
 127 preloading application, and other components in the mixture.

128 It is worth highlighting that this review makes a distinction between the terms: self-healing, self-sealing, and  
 129 self-closing. The first one refers to gain with mechanical properties recovery, the second remits to the durability-  
 130 related aspects, and the last one considers the geometric characteristics of the cracks by image analysis.

131 This paper integrates a Ph.D. thesis of A. S. Oliveira [21], which one of the substantial contributions was to  
 132 correlate macro e microanalysis to understand the relationship between the nature of healing products and the  
 133 macrostructural properties recovered after autogenous healing stimulated by a commercial CA used as a self-  
 134 healing agent in oil well cement pastes [22,23].

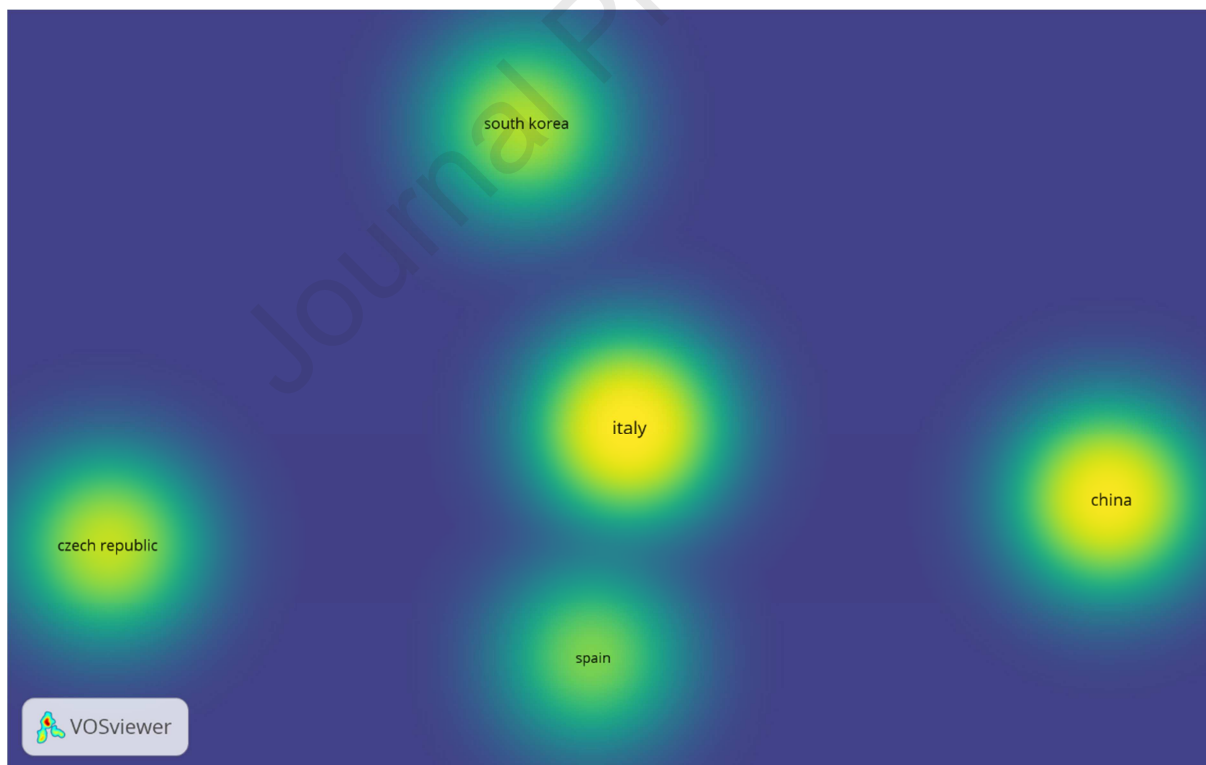
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## 136 2. Literature meta-analysis

137 The meta-analysis of the literature undertaken in 2020 identified works that have studied the effects of CAs as a  
 138 permeability-reducing and healing stimulator. The search criteria consisted of identifying countries and authors  
 139 that produced a minimum number of 5 and 4 documents, respectively. The keywords used in the search were:  
 140 “crystalline”, “admixture”, “concrete”, “self”, and “healing”.

141 According to the search out of 25 countries localized, 5 meet the thresholds. Italy, Spain, and China accumulate  
 142 the largest number of citations, followed by South Korea and the Czech Republic (**Fig. 1**). It is worth mentioning  
 143 that Italy and Spain developed studies with a focus on crystalline admixtures, while China covered crystalline  
 144 admixtures, expansive admixtures, and mineral admixtures (silica fume, fly ash and metakaolin) as well.

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146

147 **Fig. 1.** Density map with the identification of the countries with the largest number of publications provided by  
 148 the VOSviewer software.

149

150 **Fig. 2** mentions 7 authors who meet the threshold from the total results of 185 authors. Ferrara accumulates the  
 151 largest number of citations, followed by Roig-Flores and Serna. Several publications by Cuenca, Copuroglu,  
 152 Koenders, Sisomphon, and Krelani, each with more than 100 citations, also stand out for their relevant  
 153 contributions in this line of research. Notably, Žižková sticks out for the number of works that studied CA as a  
 154 permeability-reducing.

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**Fig. 2.** Density map with the identification of the authors with more publications and the interrelation of publications provided by the VOSviewer software.

**Table 1** summarizes an overview of the literature that has been published so far and a synopsis of experimental variables used to investigate the effects of CAs as a self-healing stimulator. **Table 2** has the same purpose, but in this case, the CAs were used as a permeability-reducing admixture.

165 **Table 1**  
 166 Synopsis of experimental variables used to investigate the effects of CAs as a self-healing stimulator from the literature.

Type of Cementitious Material	Manufactures and dosages of CAs (by weight of cement)	Type of cement	Cement content (kg/m <sup>3</sup> )	water/binder ratio	Other constituents	Crack induction method	Pre-cracking age	$W_{res}^f$ (μm)	Healing age	Healing conditions	Mechanical and durability tests	Microstructural techniques	References
NSC <sup>a</sup>	Penetron - 1.0% CA	CEM II 42.5	300	0.63	SP <sup>i</sup>	3-point bending	35 and 42 days	100 and 200	up to 1 year	water immersion at 20 °C, open-air and accelerated temperature cycles	3-point bending and ultrasonic pulse velocity	SEM <sup>u</sup> /EDS <sup>v</sup> and OM <sup>w</sup>	Ferrara et al. (2014) [24]
NSC <sup>a</sup>	BASF - 1% and 2% CA	CEM II/A-L 42.5 R	285 and 320	0.6 and 0.5	SP <sup>i</sup>	plastic shrinkage	up to 2 days	> 400	up to 28 days	water immersion and open-air at 20 °C and 60% RH	compressive strength and depth of penetration of water under pressure	SEM <sup>u</sup> /EDS <sup>v</sup> and OM <sup>w</sup>	Coppola et al. (2018) [25]
NSC <sup>b</sup>	Kryton – 2% CA	OPC <sup>g</sup> I and PLC <sup>h</sup>	358	0.532	-	standard crack-inducing jig	28-56 days	100-400	up to 210 days	water immersion and open-air	water permeability, compressive strength, electrical resistivity, RCM <sup>i</sup> ,	-	Azarsa et al. (2019) [26]
MSC <sup>b</sup>	Not mentioned - 2.0% CA	OPC 43	413	0.4	SP <sup>i</sup>	compressive strength	3 days	>400 (visual control)	42 days	water immersion	compressive strength and electrical resistivity	SEM <sup>u</sup>	Nasim et al. (2020) [27]
SHCC <sup>c</sup>	Xypex - 1.5% CA	CEM I 42.5 N	100	0.25	PVA <sup>m</sup> fibers, CSA <sup>1</sup> and SP <sup>j</sup>	4-point bending	28 days	10-50	28 days	water immersion, open-air and wet-dry cycle	4-point bending	SEM <sup>u</sup> /EDS <sup>v</sup> and OM <sup>w</sup>	Sisomphon et al. (2013) [28]
SFRC <sup>d</sup>	Not mentioned - 4% CA	CEM II/A-L 42.5 R	350	0.45	limestone and steel fibers	splitting tensile test	2 days	0-300	42 days	water immersion, water contact, humidity chamber and open-air	water permeability	OM <sup>w</sup>	Roig-Flores et al. (2015) [29]
SFRC <sup>d</sup>	Not mentioned - 4% CA	CEM II/A-L 42.5 R	350 and 275	0.45 and 0.60	limestone and steel fibers	splitting tensile test	2 days	100-400	42 days	water immersion at 15 °C, water immersion at 30 °C and wet/dry cycles	water permeability	OM <sup>w</sup>	Roig-Flores et al. (2016) [30]
SFRC <sup>d</sup>	Penetron – 0.8% CA	CEM II 42.5	360	0.5	steel fibers and SP <sup>i</sup>	double edge wedge splitting test	4 months	250 (after cracking-healing cycle)	first healing period: up to 6 months cracking-healing cycle: up to 1 year	water immersion, open-air and wet-dry cycle	compressive and flexural strengths	SEM <sup>u</sup> /EDS <sup>v</sup> and Digital Microscopy	Cuenca (2018) et al. [31]
SFRC <sup>d</sup>	Not mentioned - 1.1% CA	-	425.5	0.45	steel fibers	compressive strength and splitting	2 and 28 days	200-400	42 days	water immersion, water contact, wet-dry cycle and open-air	compressive, splitting tensile and flexural	SEM <sup>u</sup> /EDS <sup>v</sup> and FTIR <sup>y</sup>	Reddy et al. (2019) [32]

						tensile test						strengths.	
SFRC <sup>d</sup>	Penetron - 0.8% CA	CEM II 42.5	360	0.5	steel fibers and SP <sup>i</sup>	double edge wedge splitting test	4 months	250	first healing period: up to 6 months cracking-healing cycle: up to 1 year	water immersion, open-air and wet-dry cycle	compressive and flexural strengths	Digital Microscopy	Cuenca et al. (2020) [33]
FRC <sup>e</sup>	Home-made	P.O 42.5R OPC <sup>g</sup>	685	0.6	PP <sup>h</sup> fibers and SP <sup>i</sup>	compressive strength	28 days	-	28 days	water immersion	compressive strength and water permeability	SEM <sup>u</sup> , XRD <sup>s</sup> and OM <sup>w</sup>	Li et al. (2019) [34]
HPFRCC <sup>f</sup>	Penetron - 0.5% CA	CEM I 52.5	600	0.33	steel fibers, slag and SP <sup>i</sup>	4-point bending	2 months	*COD=500, 1000, 2000 and COD <sub>peak</sub> +500	up to 6 months	water immersion	4-point bending	SEM <sup>u</sup> /EDS <sup>v</sup> and OM <sup>w</sup>	Ferrara et al. (2016) [7]
HPFRCC <sup>f</sup>	Sika - 2% CA	-	550	0.43	SP <sup>i</sup> , VA <sup>o</sup> , steel fibers, and steel rebar	3-point bending	28 days	200	50 and 56 days	water immersion and open-air	3-point bending, tensile strength and water permeability	SEM <sup>u</sup>	Escoffres et al. (2018) [35]
HPFRCC <sup>f</sup>	Not mentioned - 1.1% CA	OPC <sup>g</sup> 53	494	0.3	SP <sup>i</sup>	splitting method adapted	28 days	100-400	42 days	water immersion, water contact, wet-dry cycle and open-air	compressive strength, RCM <sup>l</sup> , drying shrinkage and water absorption	SEM <sup>u</sup> /EDS <sup>v</sup> and FTIR <sup>y</sup>	Reddy et al. (2020) [36]
Steel Rebar Reinforced Concrete	Home-made	JPC <sup>i</sup> I	748	0.25 and 0.72	SP <sup>i</sup>	3-point bending adapted	3 and 28 days	100-300	25 days and 1 month	water immersion	-	SEM <sup>u</sup> /EDS <sup>v</sup> and OM <sup>w</sup>	Kishi et al. (2007) [37]
Wire-mesh Reinforced Concrete	Xypex - 1.5%, 3% and 4.5% CA	-	100	0.25	LWA <sup>k</sup> , CSA <sup>l</sup> , Na <sub>2</sub> CO <sub>3</sub> and CaHPO <sub>4</sub> .2H <sub>2</sub> O	3-point bending and splitting tensile test	7 days	200	up to 28 days	water immersion	gas permeability	SEM <sup>u</sup> and OM <sup>w</sup>	Wang et al. (2018) [38]
Lightweight Concrete	Xypex - 4.5% CA	OPC <sup>g</sup>	100	0.25	LWA <sup>k</sup> , CSA <sup>l</sup> , Na <sub>2</sub> CO <sub>3</sub> and CaHPO <sub>4</sub> .2H <sub>2</sub> O	3-point bending	7 days	150	up to 28 days	water immersion	RCM <sup>l</sup> , flexural and compressive strength	SEM <sup>u</sup> /EDS <sup>v</sup> , XRD <sup>s</sup> and OM <sup>w</sup>	Wang et a. (2020) [39]
Mortars	Not mentioned - 16% CA	P □ 52.5	-	0.45	-	compressive strength	7 days	-	28 and 58 days	water immersion	compressive strength, elastic modulus and water permeability	SEM <sup>u</sup> /EDS <sup>v</sup> , XRD <sup>s</sup> and FTIR <sup>y</sup>	Jiang et al. (2014) [40]

Mortars	Not mentioned - 1% CA	OPC <sup>g</sup> I	-	0.40	-	splitting tensile test	3 and 28 days	0-1000	up to 44 days	water immersion	-	digital microscopy and FTIR <sup>y</sup>	Jaroenratanapirom et al. (2010) [41]
Mortars	Not mentioned - 1% CA	OPC <sup>g</sup> I	-	0.40	-	splitting tensile test	3 and 28 days	0-50	up to 44 days	water immersion	-	digital microscopy and FTIR <sup>y</sup>	Jaroenratanapirom et al. (2011) [42]
Mortars	Xypex - 1.5% and 4% CA	CEM I 42.5 N	96 and 98,5	0.25	CSA <sup>l</sup>	splitting tensile test	28 days	100-400	up to 28 days	water immersion	water permeability	OM <sup>w</sup>	Sisomphon et al. (2012) [43]
Mortars	Penetron - 1% CA	CEM II 42.5 R	-	0.55	-	splitting tensile test	21 days	100-300	up to 84 days	water immersion at 20 °C, open-air, wet-dry cycle, immersion in a chloride solution, and wet and dry cycle in a chloride solution	compressive strength	Digital Microscopy	Borg et al. (2018) [44]
Mortars	“Home-made” - 3% CA	OPC <sup>g</sup> I	683	0.4	CSA <sup>l</sup> , bentonite	splitting method adapted	28 days	100-500	up to 56 days	water immersion at 20 °C	RCM <sup>l</sup>	-	Abro et al. (2019) [45]
Mortars	Penetron - 1.2% CA	OPC <sup>g</sup>	-	0.5	GGBS <sup>p</sup>	compressive strength and splitting method adapted	1 and 28 days	100-400 (visual observation)	up to 56 days	water immersion	compressive strength and sorptivity	SEM <sup>u</sup> /EDS <sup>v</sup> and XRD <sup>x</sup>	Li et al. (2020) [46]
Mortars	Harbin and “Home-made” - 0.2% and 2% CA	OPC <sup>g</sup>	450	0.5	SAP <sup>q</sup>	splitting method adapted	14 days	200	14 days	water immersion	water permeability	SEM <sup>u</sup> and OM <sup>w</sup>	Li et al. (2020) [47]
Lime Mortars	Penetron - 3.0% CA	-	-	-	Lime	compressive strength	28 days	-	14 days	water immersion	compressive strength	OM <sup>w</sup>	De Nardi et al. (2017) [6]
Fiber-Reinforced Mortar	“Home-made” - 3% and 6% CA	OPC <sup>g</sup> I	-	0.4	PVA <sup>m</sup> fibers	3-point bending	28 days	70-150	28 and 56 days	water immersion at 20 °C	3-point bending and water permeability	SEM <sup>u</sup> /EDS <sup>v</sup> and OM <sup>w</sup>	Buller et al. (2019) [48]
Fiber-Reinforced Mortar	Not mentioned - 5% CA	GGBS with NaOH	100	-	PVA <sup>m</sup> fibers and SP	splitting tensile test	7 days	50-300	up to 2 months	water immersion	compressive and splitting tensile strengths, sorptivity	SEM <sup>u</sup> /EDS <sup>v</sup> , X-ray tomography, ICP-OES <sup>z</sup> and OM.	Zhang et al. (2020) [49]
Steel Rebar Reinforced Mortar	Penetron - 1% CA	-	686	0.4	SP <sup>l</sup>	3-point bending	7 days	*90 and 400	60 hours	steam curing at 80 °C	3-point bending and compressive strength	SEM <sup>u</sup> , TGA <sup>aa</sup> and OM <sup>w</sup>	Xue et al. (2020) [50]
Cement pastes	Xypex - 1.5% CA	OPC <sup>g</sup>	86 and 88.5	0.3	CSA <sup>l</sup> , MgCO <sub>3</sub> and SAP <sup>q</sup>	splitting tensile test	7 and 28 days	200	up to 56 days	water immersion	water permeability	SEM <sup>u</sup> , XRD <sup>x</sup> and OM <sup>w</sup>	Park et al. (2018) [51]



<sup>a</sup>NSC: Normal Strength Concrete (water/cement between 0.5 and 0.6)  
<sup>b</sup>MSC: Moderate Strength Concrete (water/cement between 0.3 and 0.4)  
<sup>c</sup>SHCC: Strain-Hardening Cementitious Composites  
<sup>d</sup>SFRC: Steel Fiber Reinforced Concrete  
<sup>e</sup>FRC: Fiber Reinforced Concrete  
<sup>f</sup>HPFRCC: Fiber-Reinforced Cementitious Composites  
<sup>g</sup>OPC: Ordinary Portland Cement

<sup>h</sup>PLC: Portland Limestone Cement  
<sup>i</sup>JPC: Japan Portland Cement  
<sup>j</sup>SP: Superplasticizer  
<sup>k</sup>LWA: Lightweight Clay Aggregate  
<sup>l</sup>CSA: Calcium Sulfoaluminate Admixture  
<sup>m</sup>PVA: Polyvinyl Alcohol  
<sup>n</sup>PP: Polypropylene

<sup>o</sup>VA: Viscosity Agent  
<sup>p</sup>GGBS: Ground Granulated Blast Furnace Slag  
<sup>q</sup>SAP: Superabsorbent Polymer  
<sup>r</sup>W<sub>res</sub>: Residual Crack Width  
<sup>s</sup>COD: Crack Opening Displacement  
<sup>t</sup>RCM: Rapid Chloride Migration  
<sup>u</sup>SEM: Scanning Electron Microscopy

<sup>v</sup>EDS: Energy-Dispersive X-ray Spectroscopy  
<sup>w</sup>OM: Optical Microscopy  
<sup>x</sup>XRD: X-ray Diffraction  
<sup>y</sup>FTIR: Fourier Transformed Infrared Spectroscopy  
<sup>z</sup>ICP-OES: Inductively Coupled Plasma Optical Emission Spectroscopy  
<sup>aa</sup>TGA: Thermogravimetric Analysis

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**Table 2**

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Synopsis of experimental variables used to investigate the effects of CAs as a permeability-reducer from the literature.

Type of Cementitious Material	Manufactures and dosages of CAs (by weight of cement)	Type of cement	Cement content (kg/m <sup>3</sup> )	water/binder ratio	Other constituents	Curing	Fresh properties	Hardened properties	Microstructural techniques	Age	References
NSC <sup>a</sup>	Penetron and Xypex - 2% CA	-	-	-	-	-	-	depth of penetration of water under pressure and compressive strength,	-	up to 28 days	Pazderka et al. (2016) [3]
NSC <sup>a</sup>	Penetron - 1.5% CA	-	-	-	-	-	-	depth of penetration of water under pressure	-	28 days	Pazderka et al. (2016) [5]
NSC <sup>a</sup>	Xypex - 0.8% and 1.2 % CA	PC types: GP, GB-FA <sup>k</sup> and GB-slag	330 and 360	0.5 and 0.55	SP <sup>i</sup>	lime-saturated water or open-air	-	compressive strength, water permeability, drying shrinkage, sulphate resistance, RMC <sup>t</sup> , water absorption and AVPV <sup>u</sup> .	-	up to 180 days	Munn et al. (2005) [52]
NSC <sup>a</sup>	Xypex - 0.8 and 1.2% CA	PC types: SL, GB-FA <sup>k</sup> and GB-slag	330 and 360	0.5 and 0.55	SP <sup>i</sup>	humidity chamber	setting time	compressive strength, drying shrinkage, sulphate resistance and RMC <sup>t</sup>	-	up to 56 days	Munn et al. (2003) [53]
NSC <sup>a</sup>	Xypex - 0.8%, 1% and 2% CA	-	-	-	-	-	slump test	compressive strength	-	-	Nataadmadja et al. (2020) [54]
NSC <sup>a</sup> and MSC <sup>b</sup>	Not mentioned - 2% CA	CEMI 42.5N	350	0.4, 0.5 and 0.6	SP <sup>i</sup>	water immersion	-	capillary water absorption	SEM <sup>u</sup> /EDS <sup>v</sup> and TGA	up to 1 year	Elsalamawy et al. (2020) [55]
NSC <sup>a</sup> and MSC <sup>b</sup>	"Home-made" - 1%, 2%, 3%, 4% and 5% CA	-	370, 476 and 606	0.54, 0.42 and 0.33	-	water immersion at 20 °C	-	compressive strength and depth of penetration of water under pressure	SEM <sup>u</sup>	28 days	Kushartomo et al. (2019) [56]
NSC <sup>a</sup> and MSC <sup>b</sup>	Not mentioned - 1% CA	OPC <sup>g</sup>	450	0.4 and 0.6	FA <sup>k</sup> , GGBS <sup>p</sup> , and SP <sup>i</sup>	lime-saturated water	-	compressive strength, VPV <sup>f</sup> , depth of penetration of water under pressure	-	28 days	Esgandani et al. (2017) [16]
MSC <sup>b</sup>	Xypex - 2% CA	CEM II/A-S 42.5R	248	0.44	PP <sup>n</sup> fibers	aggressive or non-aggressive environments	-	water absorption, depth of penetration of water under pressure and pH values	SEM <sup>u</sup>	up to 18 months	Drochytka et al. (2019) [57]
MSC <sup>b</sup>	Penetron - 0.8% CA	BCP <sup>i</sup> (CP III-40 RS)	380	0.45	PP <sup>n</sup> fibers, SP <sup>i</sup> and polyfunctional admixture	moist curing	-	compressive strength and depth of penetration of water under pressure	-	28 days	Silva et al. (2017) [58]
MSC <sup>b</sup>	No mentioned - 0.8% CA	BCP <sup>i</sup> (Portland pozzolanic)	-	-	SP <sup>i</sup> and polyfunctional admixture	humidity chamber at 23 °C and HR > 95%	slump test	compressive strength, total absorption, depth of penetration of water under	-	28 days	Cappellesso et al. (2016) [19]

		cement)						pressure				
MSC <sup>b</sup>	Xypex - 0.8% and 1.2 % CA	PC types: GB-FA and GB-slag	435	0.4	SP <sup>i</sup>	lime-saturated water or open-air	-	compressive strength, water permeability, drying shrinkage, sulphate resistance and RMC <sup>t</sup>	-	up to 112 days	Munn et al. (2005) [59]	
Mortars	Kryton - 2% CA	OPC <sup>g</sup> and PLC <sup>h</sup>		0.5	-	water immersion at 23 °C	-	-	SEM <sup>u</sup>	up to 56 days	Azarsa et al. (2020) [12]	
Mortars	Xypex – 0.8%, 1.6% and 2.4% CA	CEM I 42.5 R	≈700	0.31 and 0.34	PP <sup>o</sup> fibers, SP <sup>i</sup> and EVA copolymer	humidity chamber at 25 °C and HR > 95%	setting time	compressive and flexural strengths	SEM <sup>u</sup>	60 days	Hodul et al. (2019) [60]	
Mortars	Xypex - 1%, 1.5% and 2% CA	CEM I 52.5 R	-	-	-	First stage: 28 days in humidity chamber at 20 °C and HR > 95%. Second stage: 90 days in a sulphuric acid or water immersion.	-	compressive strength, mass loss, ultrasonic pulse velocity and capillary water absorption	SEM <sup>u</sup>	118 days	García-Vera et al. (2018) [61]	
Mortars	No mentioned - 0.5% and 1.5% CA	CEM I 42.5 R	510,511 and 512	0.5	PP <sup>o</sup> fibers	first stage: 28 days at 23 °C and 95 % of HR second stage: 90 days an aggressive or non-aggressive environments	-	compressive and flexural strengths	MIP <sup>v</sup> , SEM <sup>u</sup> and TGA <sup>y</sup>	up to 118 days	Žižková et al. (2018) [8]	
Mortars with and without lime	Not mentioned - 3% CA	OPC <sup>g</sup> I	-	0.5, 0.8, 1.0, 1.2 and 1.4	-	water immersion at 23 °C	flow table	porosity, absorption, density, modulus of elasticity, compressive and flexural strengths	-	up to 28 days	Joa et al. (2015) [62]	
Mortars with and without fibers	Xypex - 0.5% and 1.5 % CA	CEM I 42.5 R	450	0.5	PP <sup>o</sup> fibers	first stage: 28 days at 23 °C and 95 % of HR second stage: 180 days an aggressive or non-aggressive environments	-	porosity, absorption, and density	-	118 days	Nevřivová et al. (2019) [63]	
Mortars with and without fibers	Xypex - 0.5% and 1.5 % CA	CEM I 42.5 R	450	0.5	PP <sup>o</sup> fibers	first stage: 28 days at 23 °C and 95 % of HR second stage: 180 days an aggressive or non-aggressive environments	-	compressive and flexural strengths	TGA <sup>y</sup> and SEM <sup>u</sup>	208 days	Žižková et al. (2018) [64]	
Mortars with and without fibers	Xypex - 0.5% and 1.5 % CA	CEM I 42.5 R	450	0.5	PP <sup>o</sup> fibers	water immersion and humidity chamber	-	compressive and flexural strengths	TGA <sup>y</sup> and SEM <sup>u</sup>	28 days	Žižková et al. (2018) [65]	
Cement pastes	Sika - 1% and 2% CA	CPP-G	≈1500	0.33	DE <sup>l</sup>	water immersion at 60°C	-	-	TGA <sup>y</sup> and XRD <sup>s</sup>	185 days	Oliveira et al. (2019) [22]	
Cement	“Home-made” - 1%, 2%,	OPC <sup>g</sup>	-	0.4	CSA <sup>1</sup> and	water immersion at 20 °C	-	-	isothermal	up to 91 days	Park et al. (2019)	

pastes	3% and 5% CA				GGBS <sup>p</sup>				calorimetry and SEM <sup>u</sup> /EDS <sup>v</sup>		[66]
Cement pastes	Xypex and "Home-made" - 1.5%, 2.5% and 5% CA	OPC <sup>g</sup>	-	0.35	CSA <sup>l</sup> , GGBS <sup>p</sup> , and MgCO <sub>3</sub>	water immersion at 20 °C	-	water permeability	isothermal calorimetry and SEM <sup>u</sup> /EDS <sup>v</sup>	up to 91 days	Park et al. (2019) [67]
Cement pastes	No mentioned - 1% CA	-	-	0.4	-	water immersion	-	-	SEM <sup>u</sup> and nanoindentation	up to 28 days	Hrbek et al. (2016) [11]
Grout	Penetron - 0.6%, 0.8%, 1.0%, 1.2%, 1.4%, and 1.6% CA	OPC <sup>g</sup> (P.O 32.5)	-	1.0	-	humidity chamber at 20 °C and HR > 95%	setting time, viscosity test, concretion rate test	compressive strength, water permeability and CT scanning	SEM <sup>u</sup>	up to 28 days	Zheng et al. (2019) [68]
	<sup>a</sup> NSC: Normal Strength Concrete (water/cement between 0.5 and 0.6)				<sup>l</sup> SP: Superplasticizer			<sup>l</sup> CSA: Calcium Sulfoaluminate Admixture			<sup>v</sup> EDS: Energy-Dispersive X-ray Spectroscopy
	<sup>b</sup> MSC: Moderate Strength Concrete (water/cement between 0.3 and 0.4)				<sup>k</sup> FA: Fly Ash			<sup>r</sup> RCM: Rapid Chloride Migration			<sup>w</sup> MIP: Mercury Intrusion Porosimetry
	<sup>g</sup> OPC: Ordinary Portland Cement				<sup>m</sup> PP: Polypropylene			<sup>u</sup> AVPV: Apparent Volume of Permeable Voids			<sup>x</sup> XRD: X-ray Diffraction
	<sup>h</sup> PLC: Portland Limestone Cement				<sup>p</sup> GGBS: Ground Granulated Blast Furnace Slag			<sup>v</sup> VPV: Volume of Permeable Voids			<sup>y</sup> TGA: Thermogravimetric Analysis
	<sup>i</sup> BCP: Brazilian Cement Portland				<sup>d</sup> DE: Defoamer Admixture			<sup>z</sup> SEM: Scanning Electron Microscopy			

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### 174 3. Chemical nature of crystalline admixtures

175 Even though CAs have been increasingly used as permeability-reducers or healing stimulators, the information  
 176 available on their chemical composition and characteristics is not progressing with the same proportion as their  
 177 use. The vast majority of CAs are commercial products whose chemical composition is mostly kept confidential;  
 178 there has been a general agreement based on the manufacturer's information that CAs are a mixture of different  
 179 compounds, including silicates, pozzolans, slags and fillers [4–12]. However, some homemade formulations are  
 180 based on carbonates, silicates, aluminates, tetrasodium EDTA, glycine and sodium acetate [34,37,45,47,48,66].  
 181 Generally, the regular use of this type of admixture is based on the information provided by the producers [16].  
 182 The diversity of manufactures increases the challenge to disclose eventual mechanisms or predict the behavior  
 183 promoted by CAs. The leading companies that have used CAs to study their effect are Xypex, Penetron, Sika  
 184 and, Kyrion. A recent research stated that the inclusion of a fumaric acid-based admixture enhanced concrete  
 185 self-sealing [25].

186 Beyond the range of industrial options, the substantial variation is remarkable in the chemical composition even  
 187 for the same manufacturer [28,39,43,51,61]. According to X-ray fluorescence results of CAs from Xypex, the  
 188 C/S (calcium/silica) ratio varies from 3.3 up to 7.4, which represents a considerable difference when it comes to  
 189 the main compounds. Thus, the low threshold of the C/S ratio is close to cement values, while the upper  
 190 threshold revealed the increase of CaO content as related to the SiO<sub>2</sub> content. Some results [69] attested a meager  
 191 C/S ratio of 0.01, confirming the prevalence of SiO<sub>2</sub> content instead of CaO.

192 Indeed, the change of supplier implies chemical and mineralogical variations. Some recent studies by X-ray  
 193 Diffraction (XRD) analysis found that CAs are mainly composed of limestone and cement [22], while others  
 194 described the presence of cement, silica and carbonated materials as the main components [55]. Some relevant  
 195 works [7,24,26,31,50] are allowed to disclose only the suppliers, while others do not mention any [29,30,35,49],  
 196 reserving the right to keep the chemical composition confidential.

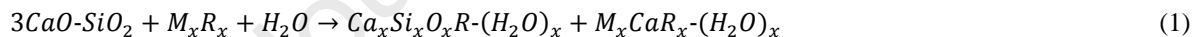
197 Further information in terms of physical properties, mineralogical and morphological characteristics of CAs was  
 198 recently compiled in a literature review [70]. Likewise, their chemical bases (carbonate, silicates, reactive silica  
 199 and crystalline catalysts) were grouped along with some crucial reports [71].

200

### 201 4. Mechanisms of action of crystalline admixtures

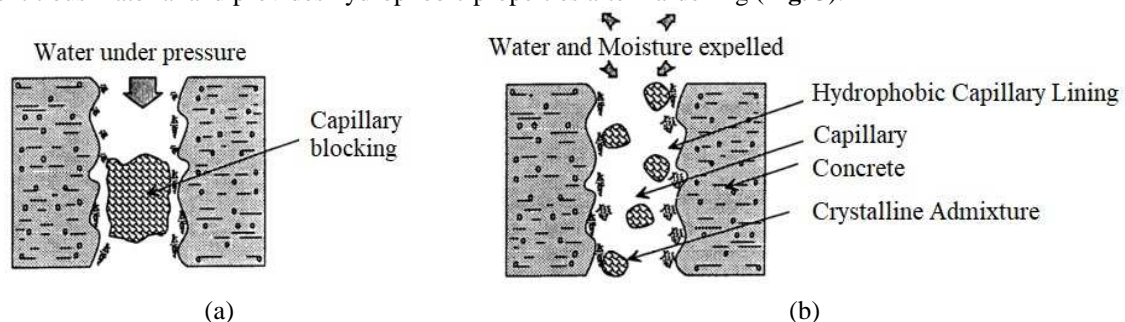
202 The water supply is essential to stimulate the precipitation of crystals in the crack, due to the hydrophilic and  
 203 reactive nature of CAs. The report ACI 212.3R-16 [14] proposes that the reaction between the active compound  
 204 of the CA, generically denoted as (M<sub>x</sub>R<sub>x</sub>), and C<sub>3</sub>S of cement in the presence of moisture causes the formation  
 205 of a denser calcium-silicate-hydrated (C–S–H) bounded with crystalline deposits and a precipitated pore blocker  
 206 (M<sub>x</sub>CaR<sub>x</sub>-(H<sub>2</sub>O)<sub>x</sub>) in the micro-cracks and capillaries, resulting in an increasing resistance to the penetration of  
 207 water under pressure. This mechanism is described by Eq. (1), and it also referenced in many works  
 208 [6,7,11,16,20,24,29,30,62,71–74]:

209



210

211 The effect of CAs may cause the blockage of the pores, the formation of a hydrophobic layer in the capillaries,  
 212 or both [9]. The presence of a non-soluble crystalline formation in the microstructure protects the concrete  
 213 permanently against the penetration of water and other liquids, which reduces the permeability of the  
 214 cementitious material and provides hydrophobic properties after hardening (Fig. 3).



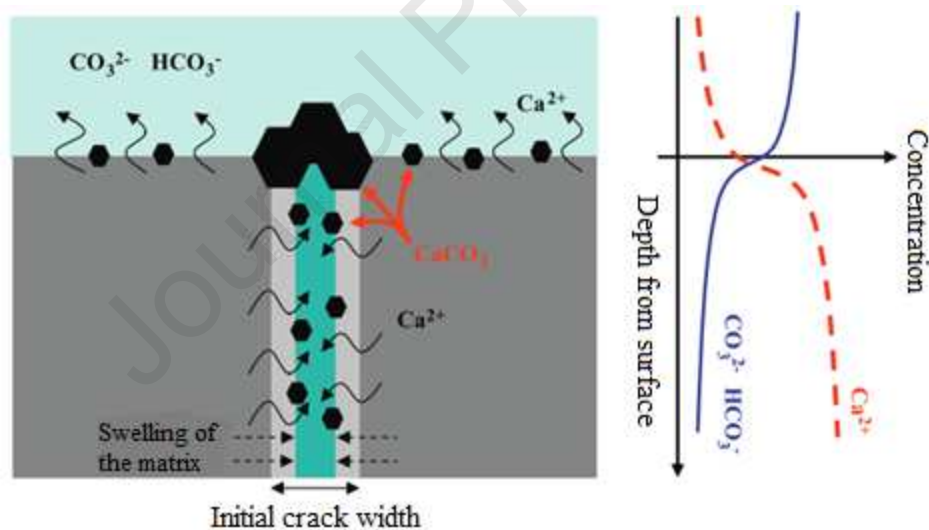
215

216 **Fig. 3.** Crystalline admixture action on blocking and hydrophobic coating in the cracks or capillaries. (a) under  
 217 pressure and (b) water and moisture expelled (adapted from Mailvaganam [9]).

218

219 Hydrophilic chemicals use water to catalyze and react with cement particles and produce the crystalline  
 220 structure. Physically, CAs block the pore system and precipitate hydrates in the cracks and in the transition zone  
 221 sufficiently to resist the penetration of water under pressure [75,76].

222 The hydrophilic nature of CAs, combined with their chemical constitution, composed of silicates, pozzolans,  
 223 slags and fillers, results in the mechanism of further or long-term hydration. The latent hydraulicity<sup>1</sup>  
 224 characteristic of these active chemicals is particularly attractive from the perspective of self-healing due to the  
 225 evolution of cracks during the service life of the structure. Therefore, CAs must hold hydration capacity even  
 226 after the initial curing period. The recrystallization occurs in the capillary porosity of the concrete and in the  
 227 cracks, as long as there are anhydrous binder, calcium hydroxide or portlandite (CH), and space available for  
 228 precipitation [7,9,10,77–80]. Termkhajornkit et al. [78] claimed that as long as there is CA, the healing capacity  
 229 can be activated by supplying CH in the solution, even whether CH is carbonated over long hydration periods or  
 230 not.  
 231 Jiang et al. [76] stated that the self-healing of cracks is a process that depends on time and environmental  
 232 conditions based on the release of ions responsible for crystallization due to the flow of water around the crack.  
 233 Therefore, environmental conditions can prolong the self-healing time.  
 234 Sisomphon et al. [28] proposed that the predominant mechanisms of internal healing of cracks are further  
 235 hydration and the expansion of unreacted particles, which are associated with the gain of mechanical properties;  
 236 thus, the main hydrates identified were C–S–H and ettringite (AFt). Otherwise, many studies highlighted the  
 237 pseudo pozzolanic reactions, which occur between the silicates from CAs with CH in the presence of moisture  
 238 and form an insoluble crystalline structure responsible for filling pores and cracks [6,19,28,43,81]. Ferrara et al.  
 239 [7] also suggested the processing of pozzolanic reactions promoted by CAs, based on the identification of C–S–  
 240 H by SEM/EDS. Likewise, Esgandani et al. [16] attributed the refinement of the concrete pore to the  
 241 replacement of CH by C–S–H based on the presence of active silica in CAs by the FTIR spectrum.  
 242 However, according to Sisomphon et al. [43], the primary mechanisms for an external closure of the crack is the  
 243 formation of calcium carbonate (CaCO<sub>3</sub>) stimulated by the presence of CA, which in turn promotes the  
 244 dissolution of Ca<sup>2+</sup> ions from the matrix. Thus, the external crack surface has optimal concentrations of Ca<sup>2+</sup>,  
 245 carbonate (CO<sub>3</sub><sup>2-</sup>), and bicarbonate (HCO<sub>3</sub><sup>-</sup>) ions dissolved in water. Consequently, this interaction leads to the  
 246 CaCO<sub>3</sub> precipitation that is hugely related to the increase of the material's durability (Fig. 4). Roig-Flores et al.  
 247 [30] identified qualitatively CaCO<sub>3</sub> in concrete cracks with and without CA.  
 248

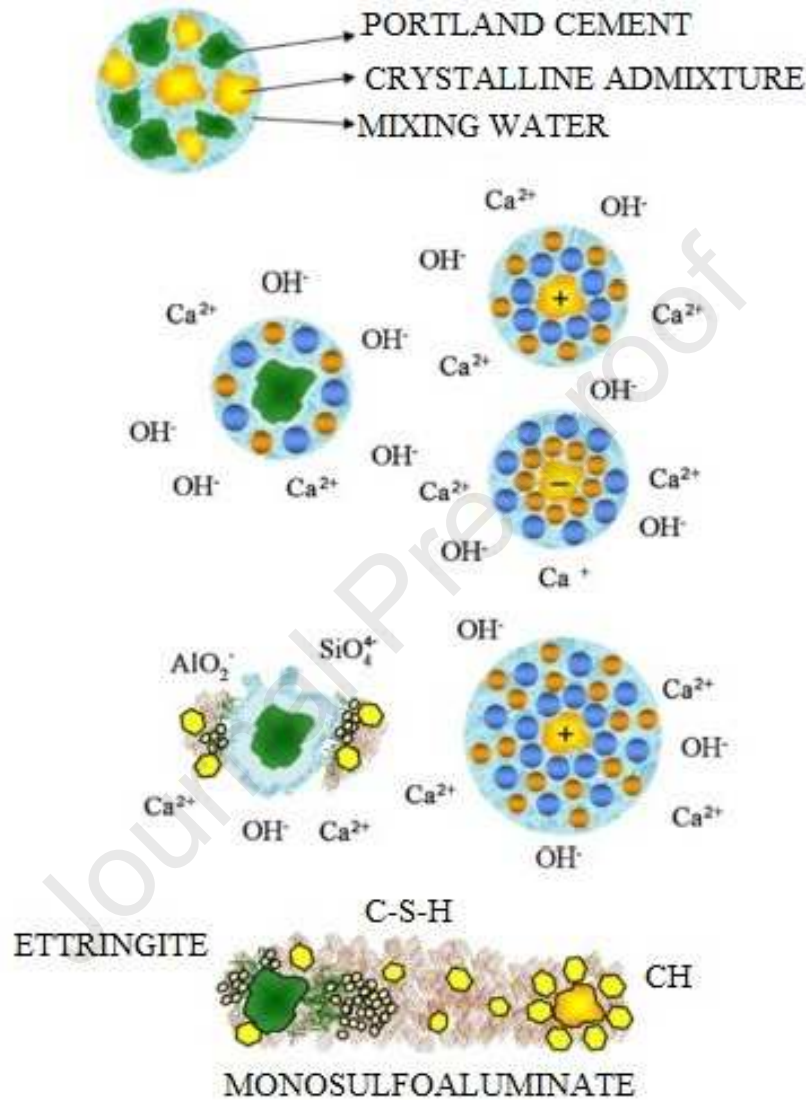


249  
 250 **Fig. 4.** Illustration of calcium carbonate precipitation stimulated by the crystalline admixture (adapted from  
 251 Sisomphon [43]).

252  
 253 Some authors have claimed that the process of recrystallization of CH leached from the bulk paste is one of the  
 254 most relevant mechanisms for autogenous healing [73,82]. The presence of CAs in the paste stimulates the  
 255 process of recrystallization through the increased dissolution of Ca<sup>2+</sup> ions. Žižková et al. [8] identified that CH  
 256 was the main hydrate identified in mortars with 1.5% CA. Likewise, other researchers have argued that the CAs  
 257 can stimulate the temporary formation of CH, based on the mechanism described below [3–5,8].  
 258 According to Rahhal et al. [83], mineral admixtures trigger hydration reactions, physically and chemically.  
 259 While the siliceous filler interacts with CH and produces C–S–H very slowly, the limestone filler reacts with the  
 260 C<sub>3</sub>A phase of the cement and forms monocarboaluminate (Mc). The different physicochemical interactions with  
 261 cement are due to the particular properties of each type and the geochemical origin of the admixture. The

<sup>1</sup> Latent hydraulicity characteristic means that the material only shows its hydration potential after the chemical reactions promoted by other compounds, or for the coexistence with products of the cement hydration in the mixture.

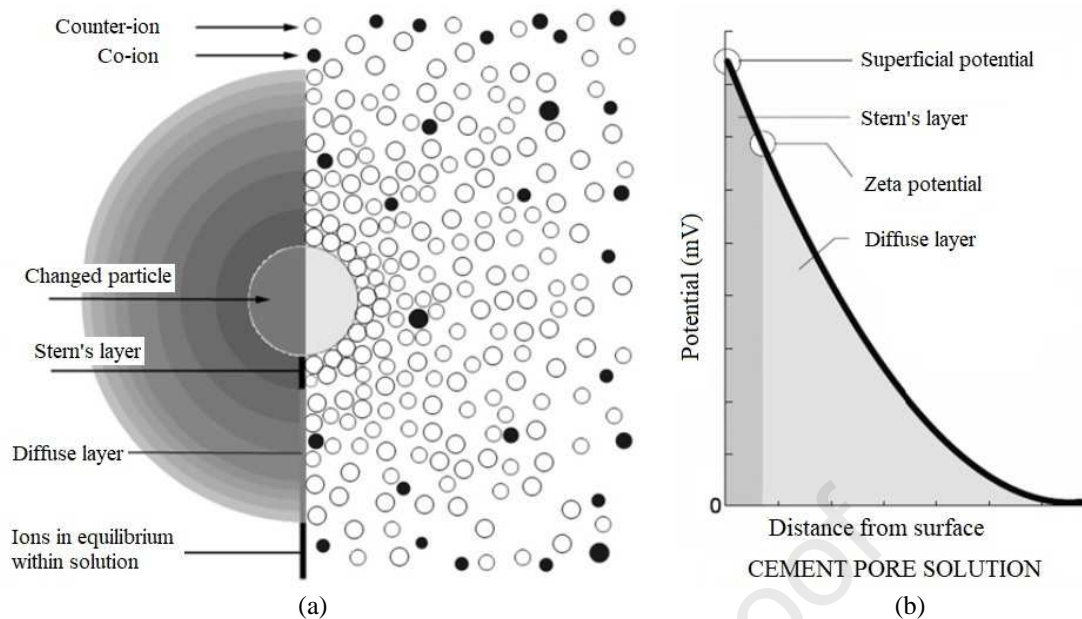
262 siliceous fillers act as nucleation centers and interact with CH; this type of fillers has an acidic chemical  
 263 character as well as a very compact texture. Otherwise, the limestone fillers act as precipitation centers for the  
 264 CH crystallization, and these fillers have a basic character with a granular texture (higher moisture absorption  
 265 capacity).  
 266 **Fig. 5** illustrates the filler particles that assume positive and negative charges when dispersed in water; as a  
 267 result, the particles act as a pole of attraction for  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions. As already mentioned, due to their chemical  
 268 nature, fillers can act as nucleation or precipitation centers to form CH, as detailed below [83].  
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**Fig. 5.** Schematic representation of cement hydration with fillers (adapted from Rahhal et al. [83]).

273 In terms of siliceous filler (ground quartz), when dispersed in water, its surface becomes negative, as the silanol  
 274 group ( $\text{Si-OH}$ ) loses a proton ( $\text{H}^+$ ) to the solution. The negatively charged particle surface mainly attracts  $\text{Ca}^{2+}$   
 275 ions (counter-ions) from the aqueous phase (**Fig. 6**). Due to the difference between ionic rays, the counter-ions  
 276 strongly adsorbed will not balance the surface charge. Consequently, a second layer of ions will be weakly  
 277 retained as it moves further away from the particle surface. The surface charge will be neutralized as the ionic  
 278 layer thickens and the electrostatic force of the particles decreases [83].  
 279



280 **Fig. 6.** (a) Electrostatic phenomenon in the solution for a charged particle and (b) Graphical description of the  
 281 Zeta potential (adapted from Rahhal et al. [83]).  
 282

283 The size of the double layer will mainly depend on the amount of charge on the particle surface. A higher charge  
 284 will result in a more extensive double layer that will prevent the particles from getting close to each other due to  
 285 electrostatic repulsion; this effect results in the deflocculation of the system. Otherwise, particles with a low  
 286 surface charge require fewer counter-ions and form thinner double layers, which lead to the flocculation.  
 287 Therefore, the zeta potential (mV) represents the energy needed to separate the particle from its inner layer of  
 288 counter-ions, moving it away from the outer layer [83].

289 The limestone filler reacts with the aluminate ( $C_3A$ ) phase of the cement and forms various types of calcium  
 290 carboaluminates (such as hemi, mono and tricarboaluminate). Moreover, carbonate ions can replace sulphate  
 291 ions without changing the reaction sequence during the formation of AFt [84–86].

292 According to Lothenbach et al. [87], the high affinity between ground limestone filler and calcium aluminate  
 293 phases favors the crystallization of Mc ( $C_4A\bar{C}H_{11}$ ) instead of monosulfate ( $C_4A\bar{S}H_{12}$ ); consequently, the amount  
 294 of AFt phases increases, which leads to a rise in the volume of hydrated phases and a decrease of porosity. These  
 295 authors still claimed that hemicarbonates ( $C_4A\bar{C}_{0.5}H_{12}$ ) transforms very slowly into Mc, probably due to the low  
 296 dissolution of the limestone filler. The transformation progresses as long as the amount of calcite dissolved in the  
 297 solution increases.

298 Oliveira et al. [22] appraised primarily Mc with high thermal stability and CH with a low crystalline degree by  
 299 thermogravimetric analysis. Therefore, the researchers suggested three main action mechanisms of CAs: the  
 300 further hydration by the formation mainly of C–S–H, the CH recrystallization, and the conversion of  $CaCO_3$  with  
 301 low thermal stability to Mc with a high thermal stability.

302 The limestone filler also leads to the formation of carbonated C–S–H or calcium-carbosilicate-hydrated [84].  
 303 This behavior is due to the incorporation of small amounts of the limestone filler in the structure of C–S–H  
 304 during the silicate phases hydration ( $C_3S$  and  $C_2S$ ); as a result, there is a slight increase in the Ca/Si ratio of C–  
 305 S–H [86,88]. As reported by Berodier et al. [89], the stimulation of C–S–H by the limestone filler is mainly  
 306 attributed to the decrease in the interparticle distance. Consequently, this condition produces more nucleation  
 307 centers due to the disturbance of the double layer, dispersing the ions through the mixture.

308 In brief, the chemical nature of CAs, characterized by a mixture of different compounds and active chemicals,  
 309 leads to the sum of several physicochemical mechanisms of action. In principle, CAs can react directly with  
 310 water, unhydrated grains, CH, and other components. These interactions lead to further hydration or pseudo  
 311 pozzolanic reactions; the first mechanism is strongly associated with cement in CA's composition, while the  
 312 second one with high  $SiO_2$  content in CA's nature.

313 Otherwise, CAs can promote the formation of different phases as well. A higher proportion of filler generates  
 314 more CH per gram of Portland cement. Thus, the greater amount of nucleation or precipitation centers causes an  
 315 increase in electrostatic force and, consequently, in the Zeta potential, resulting in the formation of more CH,  
 316 which leads to the formation of new products such as C–S–H in the long-term and different types of  
 317 carboaluminates.

318 The geochemical origin of CAs allows its action as a nucleation and precipitation center of CH for C–S–H or  
 319 carboaluminates and AFt phases. Notably, the limestone in CAs composition interacts with the  $C_3A$  phase and

320 forms Mc [22]. This process can also lead to the carbonated C–S–H formation due to the CAs incorporation in  
321 small amounts in the structure of C–S–H.  
322 Another possibility is CaCO<sub>3</sub> precipitation, from CH or C–S–H carbonation process, fostered by CAs through an  
323 increase of Ca<sup>2+</sup> dissolution [90]. The diversity of the mechanisms involved in the CA's crystallization process  
324 was highlighted by Bohus et al. [91] as well.

325  
326 4.1. Identification of products promoted by crystalline admixtures in the cracks and in the bulk-matrix  
327 Oliveira et al. [22] carried out a quantitative thermogravimetric analysis in bulk pastes in order to identify the  
328 healing products provided by CAs mainly composed of limestone and cement; thus, all crystalline phases were  
329 confirmed by XRD analyses. The major phases found in cement pastes with 2% CA dosage were 29% of CH,  
330 followed by 22% of Mc, and 17% of total combined water, representing the dehydration of gypsum, C–S–H,  
331 AFt, AFm and aluminate calcium hydrates. The amount of CaCO<sub>3</sub> below 3% endorses that CA did not  
332 effectively produce this phase. Li et al. [34] also reported CH and CaCO<sub>3</sub> in the XRD patterns from the cracks;  
333 in this case, the homemade CAs used were carbonate-, silicate- and aluminate-based, as well as glycine,  
334 tetrasodium EDTA.

335 Elsalamawy et al. [55] performed a quantitative and qualitative characterization of the phases formed by  
336 concretes with different types of CAs. According to SEM/XRD investigations, the primary phase identified in  
337 mixtures with CAs was C–S–H with high Ca/Si ratios; these values were generally greater than those exhibited  
338 by the control mixture. In contrast, Reddy et al. [36] did not find a vast difference in a Ca/Si ratio of C–S–H  
339 from high-strength concretes with and without CA, which means stability in the quality of the hydrate formed;  
340 another phase exclusively identified was CaCO<sub>3</sub> in concretes produced with CA. The chemical nature of CAs  
341 used in both works was not mentioned [36,55].

342 Some works [32,35,41,46] identified mainly CaCO<sub>3</sub> on the crack surface in cement-based material regardless of  
343 the CA presence after the healing process. The CA dosage ranged between 1 and 2%, and the techniques usually  
344 employed were XRD, SEM/EDS, and FTIR. Jiang et al. [40] confirmed the preferential presence of CaCO<sub>3</sub>  
345 crystals on the crack surface in cementitious mixtures with various mineral admixtures by XRD and SEM/EDS.  
346 The qualitative evaluation of the healing products formed on the crack surface suggests CaCO<sub>3</sub> precipitation for  
347 both concretes with 4% CA and the reference [30]. The chemical composition of CAs was not revealed in any of  
348 these studies.

349 As reported by Cuenca et al. [31], the healing products at the crack surface and identified by SEM/EDS, after  
350 three months of immersion in water, suggested mainly the presence of C–S–H in concrete with 0.8% CA. The  
351 morphology of the products also indicated the presence of AFt. Ferrara et al. [24] attested the same trend  
352 favorable for C–S–H and AFt formation revealed by SEM/EDS. The observations were made on the crack  
353 surface and in the bulk region in control samples and with 1% CA healed by three months of immersion in  
354 water. In general, Azarsa et al. [12] found typical hydration phases such as C–S–H and CH; AFt crystals were  
355 also distinguished depending on the type of CAs. Esgandani et al. [16] also suggested the intensified C-S-H  
356 production booted by the silica fume present in CAs composition. Finally, Hrbek et al. [11] proposed the  
357 formation of C-S-H with low density caused by the incorporation of CaCO<sub>3</sub> and modified C<sub>3</sub>S in cement pastes  
358 with CA, based on the correlation between SEM and nanoindentation analysis. In general, these works used CAs  
359 predominantly composed of cement and sand.

360 Works performed by Sisomphon et al. [28,43,92] propose that the nature of the healing products varied  
361 according to the crack location in mixtures with CA. Thus, in the internal crack region were found CaCO<sub>3</sub>, C–S–  
362 H and AFt, which in turn vary with the exposure condition [28], while in the external crack region, the primary  
363 phase identified was CaCO<sub>3</sub> involved possibly by AFt crystals [43,92]. The types of oxides found in CAs  
364 composition were CaO and SiO<sub>2</sub>, which proves the cement presence as the main compound.

365 Kishi et al. [37] identified the presence of C–S–H, C–A–S–H, AFt, AFm, and CH in samples with CA  
366 carbonate-based (Na<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub>). Park et al. [66] also studied the effect of CA carbonate-based, such as  
367 Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and Li<sub>2</sub>CO<sub>3</sub> in cement pastes. Semi qualitative analysis by SEM/EDS suggested the formation  
368 of AFt and CaCO<sub>3</sub> as the primary healing products. Among the different types of CA carbonated-based,  
369 isothermal calorimetric investigations revealed that Li<sub>2</sub>CO<sub>3</sub> exhibited the best further hydration potential for  
370 advanced age of hydration (28 and 91 days). Based on isothermal calorimetry studies [67], a blended  
371 cementitious system, including CA, Calcium Sulfoaluminate Admixture (CSA) and MgCO<sub>3</sub>, exhibited higher  
372 healing potential than the reference at 7 days, which was not observed at 91 days.

373 Few studies deployed the phases' identification in the bulk-matrix promoted by CAs. Oliveira et al. [22] found  
374 mainly CH, Mc, C–S–H and anhydrous grains in the bulk matrix by thermogravimetric analysis (TGA) and  
375 XRD. Likewise, Žižková et al. [8] proved by DTA analysis that the CA's presence increased the CH formation  
376 and a qualitative rise of AFt phases. In the first study [22], limestone and cement were the major components  
377 present in CAs' composition, while in the second one [8], cement was the primary compound.

378  
379 **5. Effects of crystalline admixtures on the properties of cement-based materials as permeability-reducers**



380 There are few reports in the literature regarding the effect of CAs as permeability-reducers on the physical and  
381 mechanical properties of cement-based materials. Even though there is increased use of waterproofing products,  
382 the number of publications does not increase in the same proportion. Moreover, the scarcity of technical  
383 literature is aggravated by the diversity of products and applications. This lack of adequate quantitative  
384 information may challenge the rational use of the CAs in practice [16,19,62]. Thus, this section aims to discuss  
385 the CAs' effects on the fresh and hardened state properties of cement-based materials to verify if there is a  
386 consensus about their performance and their behavior expected predictably. The dosages of CAs, usually found  
387 in the literature, ranged from 0.5% up to 3% by weight of cement (bwoc). In this paper, given dosages are  
388 always referred to in this term.

#### 389 5.1. Fresh state

391 As reported by ACI 212.3R-16 [14], CAs affect some properties in the fresh state, such as the reduction in water  
392 demand, increase in entrapped air content, and extension in the setting time. Some works [10,53] also reported  
393 the delay in setting time, whereas others [68] showed no impacts on the setting time and viscosity in grouts with  
394 up to 1.6% CA. Wang et al. [69] did not verify any considerable impact in the slump test, but the air content  
395 increased in grouts with CA. The findings obtained by Azarsa et al. [26] indicated that 2% CA slightly increased  
396 the air content, and clearly reduced the slump in concretes regardless of the type of cement. In contrast, other  
397 result [54] noticed an increase in the slump values of concretes with CA. Innovative formulations promise to  
398 reduce the collateral effects of CAs in concretes when it comes to the negative impact on the workability,  
399 entrapped air and density [25].

400 There has been no clear consensus about the effect of CAs on workability. This behavior may be related to the  
401 different chemical compositions of CAs, and the presence of organic and inorganic carbon in some formulations  
402 [22]. It is worth mentioning that the majority of the works measured qualitatively the workability through slump  
403 test; thus, it would be worth investing in rheological tests in order to identify the rheological parameters of the  
404 fluid mixture, including yield stress and viscosity.

405 The effect of the air entrapped might be favored by a group of surfactants that process at the air-water interface  
406 in the cement-water system. The structure of the active chemicals consists of a nonpolar hydrocarbon chain and a  
407 hydrophilic polar group. Thus, the ionized polar group is aligned in the water phase lowering the surface tension  
408 while the hydrocarbon chain orients into the air within the bubble. Some authors [93,94] described in more detail  
409 the sequence of this mechanism composed of dissolution and dissociation, followed by orientation and  
410 adsorption.

#### 411 5.2. Hardened state

413 Silva et al. [58] reported a successful case of using 0.8% CA in anti-flotation slabs on the sealing ability  
414 evaluated through the water depth penetration under pressure. Otherwise, based on the same dosage, Cappellesso  
415 et al. [19] pointed out that silica fume was more efficient than CA to increase compressive strength and decrease  
416 water absorption capacity and water depth penetration under pressure. The results exhibited a slight  
417 improvement of 14% in the compressive strength and even an undesirable increase in water penetration and  
418 absorption at 28 days. Some works [52,53] attested that the inclusion of 0.8% and 1.2% CA did not significantly  
419 improve the compressive strength at 28 days of conventional concretes with ordinary cement Portland [52,53].  
420 Nevertheless, Borg et al. [44] still identified a drop in mortars with 1% CA at 84 days. Other studies [59] only  
421 realized a considerable rise in compressive strength of concretes higher than 24% when 1.2% CA was added  
422 along with blended cement with 25% fly ash at 3, 28 and 91 days.

423 Esgandani et al. [16] verified that CAs had less influence than the water/binder ratio and the type of binder on  
424 compressive strength, water absorption capacity, and water depth penetration under pressure. As a result, 1% CA  
425 has demonstrated a slight improvement of almost 10% on the compressive strength of conventional and high  
426 performance concretes at 28 days, as well as there was no considerable difference in the total water absorption.  
427 Likewise, Ferrara et al. [24] noticed that 1% CA did not affect the compressive strength up to 30 days for  
428 conventional concretes compared to concretes without CA.

429 Studies [63] revealed that 1.5% CA decreased the apparent porosity of fiber-reinforced mortars, particularly  
430 when cured in a controlled environment at 95% of relative humidity (RH), as well as in an aqueous solution with  
431  $\text{SO}_4$  and  $\text{NH}_4$ . However, Sisomphon et al. [28] realized that the inclusion of the same CA content did not  
432 considerably improve the recovery of the mechanical properties of Strain-Hardening Cementitious Composites  
433 (SHCC) exposed to different curing conditions for 28 days.

434 Žižková et al. [8,64,65] investigated mortars with up to 1.5% CA with different approaches. Firstly, the findings  
435 revealed that the humidity conditions did not drastically affect the compressive strength at 28 days. However,  
436 curing at 95% RH ensured the best porosity behavior rather than 50% RH or water immersion; this improvement  
437 was attributed to the higher content of hydrated phases identified by DTA analysis [65]. Further, the compressive  
438 strength was not significantly changed at 118 days, and the flexural strength did not show a clear trend with the  
439 increase in CA dosage; nevertheless, the increment in CA content reduced the porosity of mortars after exposure

440 in some aggressive environments such as chlorides, sulfates and CO<sub>2</sub> [8]. Finally, the increase in CA dosage did  
441 not produce an enhancement of the compressive strength in the environment exposed to gaseous CO<sub>2</sub>; however,  
442 the values were slightly raised in a freezing cycle [64]. The modest improvement in the compressive strength is  
443 consistent with the findings revealed by Oliveira et al. [22], which identified a considerable increase in the CH  
444 and Mc contents after controlled curing at 60 °C for 198 days. In contrast, Zheng et al. [68] noticed that CA  
445 dosage up to 1.6% improved the compressive strength, particularly for 28 days, and reduced the water  
446 permeability.

447 Some modest reduction in the compressive strength may be related to the early age of assessment, which was not  
448 sufficient to ensure a notable change in the short-term. In fact, CAs need to wait for some cement hydration  
449 products to have better effects in the long-term due to the further hydration mechanism.

450 Coppola et al. [25] also verified that the CA's inclusion up to 2% did not negatively impact the compressive  
451 strength up to 28 days. On the contrary, the water penetration under pressure was reduced in the range of dosage  
452 between 1% and 2% CA; this behavior may be related to the type of hydration products formed in the  
453 microstructure with a predominance of CH and the sealing capacity of CAs that may be able to recrystallize the  
454 matrix and densify the porosity without necessarily mechanical gain [22]. This work [25] also confirmed two  
455 crucial points: CA's effect depends on the water/cement ratio and the curing conditions, which are near related to  
456 the water supply. These findings were based on water absorption under low-pressure tests in concretes with two  
457 different water/cement ratios and three types of CAs. Elsalamawy et al. [55] stated that the performance of CAs  
458 improves with the increase of water/cement ratios due to the reduction of Si concentration. On the contrary, the  
459 inexpressive difference in Si concentration showed that the use of CAs is unnecessary in concretes with low  
460 water/cement ratio regardless of their presence.

461 Azarsa et al. [26] confirmed that 2% CA in concretes reduced the depth of water penetration dramatically by  
462 around 40%, while the compressive strength and electrical resistivity values at 28 days exhibit a negligible  
463 change. Some studies [3,5] also attested a considerable durability improvement in concrete produced up to 2%  
464 CA, through the depth water penetration test under pressure even in early ages between 12 and 28 days.  
465 However, others [91] only observed a better performance after six months in mixtures with 2.2% CA. Some  
466 works [3,60] did not report a considerable impact on mechanical properties in cementitious materials, with up to  
467 2.4% CA.

468 Drochytka et al. [57] investigated the influence of the associated use of fly ash with 2% CA on durability related-  
469 aspects in aggressive environments. The findings attested to the importance of the exposure condition on the  
470 water-resistance properties and the long-term effect on the performance improvement promoted by CA.  
471 Likewise, a report [61] attested that mortars with CA up to 2% contributed to increasing the compressive  
472 strength in a sulphuric acid attack rather than in a non-aggressive environment; however, the same trend was not  
473 followed for capillary water absorption, regardless of the type of exposure.

474 Some results [56] showed that the CA's inclusion reduced the water penetration depth in normal strength  
475 concretes. The performance of CA was considerably better in conventional concretes rather than in a high-  
476 strength concretes. This study also verified that the compressive strength was not affected by a CA addition from  
477 1% up to 5%. Another work [62] did not observe a considerable enhancement in compressive strength, water  
478 absorption capacity, and porosity in mortars, with 3% CA evaluated up to 28 days. The modulus of elasticity was  
479 the only property that improved; however, more research needs to be carried out to draw a substantial conclusion  
480 about this trend.

481 Wang et al. [69] evaluated the contribution of 6% CA to some mechanical properties in grout enriched two-  
482 graded roller compacted concrete (RCC). The researchers observed that CA's presence resulted in a modest  
483 increase of less than 10% in some mechanical performance up to 90 days, including compressive strength,  
484 modulus of elasticity, splitting tensile strength, direct tensile strength, and ultimate tensile strain. These tests  
485 were performed following DL/T 5433-2009.

486

## 487 **6. Performance of crystalline admixtures as a self-healing stimulator**

488

### 489 6.1. Effects of crystalline admixtures on the self-healing capacity and related performance recovery

490 This section gathers the most relevant studies on the performance of CAs used as a stimulator for autogenous  
491 self-healing of cracks in cement-based materials, with a focus on the ability to recover mechanical properties and  
492 durability related-aspects [95]. Initially, the approach is based on works that investigated crack healing with a  
493 mechanical recovery caused by CAs. Further, the crack sealing capacity provided by CAs in cementitious  
494 mixtures is discussed considering the durability improvement mostly through water permeability tests as there is  
495 only one report that employed gas permeability technique for this purpose [96].

496

#### 497 6.1.1. Mechanical recovery

498 The results of this section are divided according to the type of cementitious material. Firstly, the effect of CAs  
499 was discussed on the mechanical gain in plain concretes. Secondly, the action of CAs has been addressed on the

500 mechanical recovery, which has been evaluated by flexural tests in High-Performance Fiber-Reinforced  
 501 Cementitious Composites (HPFRCCs) and similar mixtures. In this case, the analysis has been based on two  
 502 main parameters: the stiffness recovery and the 'residual' post-cracking strength.  
 503 Ferrara et al. [24] found that 1% CA accelerated the healing process; as a result, the Normal Strength Concrete  
 504 (NSC), with a water/cement ratio of 0.63, recovered the stiffness and residual post-cracking flexural load  
 505 capacity, measured by three-point bending tests, in pre-cracked samples ( $\approx 200 \mu\text{m}$ ). In general, the findings also  
 506 showed that the presence of CA ensured better recovery with lower dispersion of results than the reference in  
 507 water immersion and open-air exposure conditions. Nasim et al. [27] found that the inclusion of CA increased  
 508 the compressive and electrical resistivity recoveries in Moderate Strength Concrete (MSC), with a water/cement  
 509 ratio of 0.4, at 42 days (see **Tables 1** and **2** for detailed explanation). In contrast, Jiang et al. [40] observed a  
 510 modest increase in the compressive recovery and a considerable stiffness gain in the mixtures with 16% CA  
 511 carbonate-based compared to the reference and other types of mineral admixtures, such as CSA and metakaolin.  
 512 Buller et al. [48] noted that CA performed better in samples with crack widths narrower than  $100 \mu\text{m}$ ; in this  
 513 case, the inclusion of CA provided an Index of Strength Recovery<sup>2</sup> higher than the reference concrete. Moreover,  
 514 the Index of Damage Recovery<sup>3</sup> and the Index of Dissipation Energy Gain<sup>4</sup> exhibited a more pronounced  
 515 increase for the same conditions. Likewise, Ferrara et al. [7] confirmed that 0.5% CA improved the autogenous  
 516 healing capacity in HPFRCCs, even for lower CA dosage. In contrast, Escoffres et al. [35] noticed that 2% CA  
 517 did not provoke a substantial improvement on the mechanical recovery of HPFRCCs by bending and tensile tests  
 518 in water immersion and open-air exposure; these researchers just attested that the presence of CA caused a  
 519 higher toughness gain during the reloading. Sisomphon et al. [28] realized the same trend, mainly a slight  
 520 improvement on the flexural properties in SHCC produced with 1.5% CA compared to the reference.  
 521 Nevertheless, a remarkable mechanical recovery was achieved with the associated use of 1.5% CA with 10%  
 522 CSA in SHCC evaluated in terms of flexural strength, stiffness, and deformation capacity. Xue et al. [50] also  
 523 did not observe a substantial contribution of CA in the flexural recovery of steel rebar reinforced mortar.

524

#### 525 6.1.2. Permeability measurement

526 Roig-Flores et al. [29] concluded that Steel Fiber Reinforced Concretes (SFRCs) with 4% CA under immersed  
 527 curing condition achieved the highest sealing capacity compared to the reference and other exposure conditions.  
 528 In contrast, Roig-Flores et al. [30] did not confirm the same trend in two different classes of SFRCs with 4%  
 529 CA. The findings revealed that the addition of CA did not have a pronounced influence on the sealing capacities  
 530 in comparison to the control mixtures for both water immersion and wet-dry cycle conditions. However, this  
 531 research pointed out that the inclusion of CA caused a slightly better performance with low dispersion in high-  
 532 strength concretes rather than in conventional ones.

533 According to Sisomphon et al. [43], even though the presence of CA significantly reduced permeability more  
 534 than in the reference mixture, the increase from 1.5% to 4% CA did not necessarily imply an increase in sealing.  
 535 However, the use of CA with the CSA revealed an excellent ability for sealing the cracks.

536 Likewise, Coppola et al. [25] realized that the increase in dosage from 1% to 2% CA did not result in any  
 537 substantial enhancement of the self-sealing of cracks induced by plastic shrinkage. According to the water  
 538 absorption under low pressure, concretes with 1% CA showed a negligible value from 7 days.

539 Jaroenratanapirom et al. [41,42] attested that mortars with 1% CA showed a better sealing performance than the  
 540 reference, especially for samples with the young age of pre-cracking. These researchers also found complete  
 541 closure in narrow cracks (less than  $50 \mu\text{m}$ ), while in larger ones ( $100\text{-}300 \mu\text{m}$ ) the samples with CA  
 542 demonstrated less efficiency compared to the reference.

543 Buller et al. [48] evaluated fiber-reinforced mortars with a CA and with blended mineral admixtures (CA, CSA  
 544 and bentonite) through water permeability tests. The results confirmed the contribution of CA in increasing the  
 545 self-sealing capacity, especially for the mixture produced with three types of admixtures.

546 Escoffres et al. [35] studied the water permeability under loading in HPFRCCs with and without CA. The  
 547 findings revealed that 2% CA did not dramatically reduce water permeability; thus, the total sealing capacity was  
 548 achieved in the long-term regardless of the presence of CA. Wang et al. [38] performed gas permeability tests in  
 549 concrete with mineral admixtures (CA, CSA, and  $\text{CaHPO}_4$ ) and sodium carbonate in order to improve healing  
 550 capacity. The overall findings showed that mixtures with mineral admixtures achieved better sealing  
 551 performance compared to the reference at 28 days, which resulted primarily from the surface crack closure.

552

#### 553 6.2 The influence of different factors on the self-healing capacity of crystalline admixtures

554

<sup>2</sup> The Index of Load Recovery can be defined as the ratio between the reload after the self-healing process and the load at the pre-cracking stage.

<sup>3</sup> The Index of Damage Recovery can be defined as the ratio between the flexural stiffness at the reloading stage and the flexural stiffness under half of the peak load at the pre-cracking stage.

<sup>4</sup> The Index of Dissipation Energy Gain can be defined as the ratio between the dissipation energy gain due to the healing effect and the total dissipation energy of the reference specimen.

### 555 6.2.1. Environmental conditions

556 The literature survey has confirmed that the availability of water is crucial to enhance the self-healing process.  
557 Thus, there is quite a general agreement that specimens immersed features the best performance. Cuenca et al.  
558 [31,33] confirmed that the exposure condition and the initial crack width are the most relevant factors for self-  
559 sealing capacity. SFRCs exposed to the air exhibited less crack closing, while samples immersed in water  
560 showed a better performance in terms of stability of the post-cracking residual strength [33] and even under  
561 cracking-healing cycles up to one year after the first cracking.

562 Sisomphon et al. [28] also pointed out the importance of the exposure condition for the self-healing process and  
563 its influence on the healing product's nature. According to these authors, specimens (with 1.5% CA and 10%  
564 CSA) underwater immersion without renewal exhibited scattered healing products mostly composed of AFt  
565 phases. In contrast, water immersion with periodic renewal showed a denser C-S-H typically with high silica  
566 content. The renewal of water is fundamental for increased precipitation due to the continuous supply of  $\text{Ca}^{2+}$   
567 ions concentrations from the matrix and  $\text{CO}_3^{2-}$  from water [97]. Moreover, the presence of CSA may have  
568 contributed to the precipitation of AFt.

569 Ferrara et al. [74] highlighted the outstanding importance of water for the healing process with CA, given its  
570 hydrophilic nature and the exceptional performance of samples in water immersion. Roig-Flores et al. [29] also  
571 confirmed the importance of a water supply for the development of self-sealing with or without CA; thus, the  
572 authors proposed the following decreasing order on the sealing capacity: water immersion>water contact>wet  
573 curing>open-air exposure.

574 Some studies [29,30] have demonstrated that the exposure conditions play a stronger influence on the crack  
575 sealing/closing than the CA addition. In contrast, others [24] have claimed that the presence of CAs ensured a  
576 suitable healing performance even in an environment with low healing potentials, such as in open-air exposure or  
577 humid chamber. The role of wet/dry cycles in healing enhancement has been quite controversial; some studies  
578 showed that wet/dry cycles could be even better than water immersion, while others disagree with this statement.  
579 Ferrara et al. [74] indicated that CA's inclusion did not significantly improve the crack sealing capacity of Fiber  
580 Reinforced Concretes (FRCs) under wet/dry cycles compared to the reference. Likewise, Roig-Flores et al. [30]  
581 stated that the wet/dry cycles were worse than water immersion in conventional and high-performance concretes  
582 with 4% CA. Some works [31–33] also attested that specimens under wet/dry cycles featured an intermediate  
583 healing recovery, which was worse than water immersion and better than open-air exposure.

584 In contrast, the results obtained by Sisomphon et al. [28] allowed to classify the influence of exposure conditions  
585 on the mechanical recovery in the following order: wet/dry cycles>water immersion with renewal>water  
586 immersion without renewal>open-air exposure. Reddy et al. [36] showed that samples cured under dry-wet  
587 cycles performed as well as underwater immersion, which in turn overcame the healing capacity of the samples  
588 in water contact and under open-air exposure in terms of compressive strength gain, sealing capacity and  $\text{CaCO}_3$   
589 precipitation. These uncertainties might be related to the admixture's type and the frequency of the wet/dry  
590 cycles, as the cycles varied from 12 hours up to 4 days according to a specific study.

591 A work [6] carried out in mortars with lime investigated the influence of 3% CA and the exposure conditions. In  
592 terms of open-air exposure, the findings attested that the CA's addition accelerated the compressive recovery of  
593 pre-cracked specimens compared to the uncracked ones; however, there was no significant difference in the final  
594 mechanical recovery at 196 days. When it comes to water immersion, the CA's specimens exhibited the best load  
595 recovery index compared to the reference and samples under open-air exposure. Therefore, it is clear the high  
596 impact of exposure conditions on the performance of CAs, which in turn may vary according to their type.

597 There are few studies about the influence of different exposure conditions in aggressive environments in  
598 cementitious materials with CA. Some results revealed that mortars with CA showed better performance  
599 underwater immersion and wet/dry cycles than open-air exposure in chloride environments; the water contact  
600 ensured the ability to seal crack widths up to 300  $\mu\text{m}$  [44,98]. This study also showed that the maximum  
601 effective dosage to achieve the chloride impermeability and the crack sealing was 1% bwoc according to the type  
602 of admixture used.

### 603 6.2.2. Impact of repeated loading applications

604 The pre-cracking induced in specimens employed in self-healing investigations aims to simulate the real service  
605 conditions experienced in the structures by the load action. Repeatability represents cracking-healing cycles over  
606 the structure lifespan, caused by variations in loading or temperature. The absence of imposed loading may  
607 overestimate the healing capacity causing erroneous predictions [99]. Ferrara et al. [74] verified that the  
608 application of compressive stress in pre-cracked beams improved the autogenous healing of the cracks with the  
609 mechanical recovery in FRCs with and without CA.

610 Cuenca et al. [31] produced the first publication based on the methodology to assess the enhancement of CA  
611 under repeated cracking-healing cycles. These authors [31] stated that 0.8% CA contributed to the long-term  
612 self-sealing ability under repeated cracking-healing cycles in FRCs; thus, the best performance was realized in  
613 narrow cracks width up to 150  $\mu\text{m}$  under water immersion, probably due to the osmotic migration by the CA. In  
614

615 contrast, Escoffres et al. [35] found that the presence of sustained tensile loading decreased the healing kinetics  
616 in HPFRCCs especially with CA; however a higher load was required to reach again the initial permeability in  
617 mixtures with CA.

618 Lo Monte et al. [100] have recently proposed a methodology for the assessment of the self-healing based on  
619 cracking-healing cycles in HPFRCCs beam specimens stimulated by CA underwater immersion. The mechanical  
620 recovery was measured in terms of stiffness and load-bearing capacity. The effects of different cement types  
621 were investigated (CEM I 52.5 and CEM III 52.5), both used combined with slag (50% by cement volume and  
622 water/binder ratio equal to 0.18). The results confirmed the critical crack width role on the healing capacity and  
623 the faster recovery of stiffness than the load-bearing capacity. The results also showed a better behaviour of the  
624 mixture with CEM III than with CEM I, especially in the earlier cycles. The differences tended to be levelled off  
625 for longer healing ages up to 6 months. This tendency was probably due to the development of the delayed  
626 hydraulic activity of the slag, as all pre-cracked specimens were older than two months. The methodology  
627 proved the importance of crack pattern characterization in terms of the opening distribution of the single cracks,  
628 which was strictly correlated to the mechanical recovery and the persistence under repeated cracking-healing  
629 cycles. It is worth mentioning that these findings correspond to the category of materials investigated and to a  
630 given damage level (expressed by the maximum residual flexural strain achieved during the cracking-healing  
631 cycles). In this study, the crack width distribution peak shifted from 15-30  $\mu\text{m}$  after pre-cracking to 20-50  $\mu\text{m}$   
632 and 40-60  $\mu\text{m}$  after one and three months of healing upon repeated re-cracking, respectively. The crack closing  
633 ratio was in the range of 65-93% for continuous immersion without re-cracking, 62-84% for cyclic  
634 immersion/re-cracking after the first month, 40-69% and 40-61% between 1 and 3 months, and 31-42% and 26-  
635 40% between 3 and 6 months. Similar trends were also measured for the stiffness recovery.

#### 636 6.2.3. Efficiency of CA performance in the crack width

637 Cracks previously induced and cured by autogenous healing tend to reopen when they are reloaded [96]. This  
638 behavior is of particular concern for autogenous healing due to the consumption of the materials needed for the  
639 healing process over time, especially in extreme cases such as large cracks ( $> 150\text{--}200 \mu\text{m}$ ) and underexposure  
640 conditions without a continuous supply of water.

641 The range of healed crack widths by stimulated autogenous healing is not yet fully established.  
642 Jaroenratanaiprom et al. [42] verified that mortars with CA presented an efficient sealing ability in narrow cracks  
643 smaller than 50  $\mu\text{m}$ . Otherwise, Ferrara et al. [96] stated that CA's use could promote crack closure even in the  
644 range up to 300 and 500  $\mu\text{m}$  in HPFRCCs (with high cement content and in the long term). In contrast, De Belie  
645 et al. [20] indicated that this type of mechanism is generally limited to a crack width between 100 and 150  $\mu\text{m}$  in  
646 the most frequent cases. A recent review [101] attested that CA's inclusion, along with water immersion  
647 condition favored self-sealing in cracks up to approximately 100  $\mu\text{m}$ . Buller et al. [48] undertook research that  
648 confirmed a better performance of CA in terms of mechanical recovery for crack widths up to 100  $\mu\text{m}$ .

649 Studies reported that CA promoted the healing even for large cracks up to 400  $\mu\text{m}$ , with the flexural strength  
650 recovery through a three-point bending test in FRCs [74]. Another work highlighted that CA ensured the  
651 recovery of flexural parameters in cracks of 200  $\mu\text{m}$  width by underwater immersion [24]. On the contrary,  
652 Sisomphon et al. [28] established that SHCC with CA had no significant improvement in the recovery of flexural  
653 properties in cracks up to 50  $\mu\text{m}$  from the four-point flexural test.

654 In order to improve the healing efficiency promoted by CAs, some works proposed the combination of CA and  
655 CSA in mortars, which was successful in healing crack widths up to 400  $\mu\text{m}$  [43]. Another positive report was  
656 proposed by incorporating CA and super absorbent polymers (SAPs) in mortars that boosted the total sealing  
657 capacity in cracks larger than 300  $\mu\text{m}$  [47]. Therefore, the performance of CAs is closely related to the mix  
658 composition. The high cement content and the inclusion of some strategies such as CSA, SAPs, and mineral  
659 additions may enhance the effect of CAs. Moreover, some authors [25,55] identified an improvement in CA's  
660 action in concretes with high water/cement ratios (0.5 and 0.6).

661

#### 662 6.2.4. Investigation of the synergetic effects of crystalline admixtures with other constituents

663 Li et al. [46] studied mortars with 1.2% CA and different granulated blast furnace slag (GGBS) contents by  
664 cement replacement. The optimum dosage achieved was 10% GGBS, which provided the best performance by  
665 compressive strength recovery at 28 and 56 days. This study still reported that mortars with CA exhibited a  
666 lower rate of water absorption (sorptivity) than the reference at 56 days, and the dosage of 20% GGBS enhanced  
667 the effect of CA in mortars.

668 Zhang et al. [49] assessed the action of 5% CA in the replacement of GGBS in fiber-reinforced composites. The  
669 findings revealed that the contribution of CA improved the overall properties in terms of a crack closing by  
670 digital microscopy, mechanical properties, and rate of water absorption (sorptivity). The primary phase identified  
671 ( $\text{CaCO}_3$ ) in all mixtures, with and without CA, seems to be a synergetic contribution of the exposure conditions  
672 and the PVA fibers. PVA fibers act as preferential nucleation sites for  $\text{CaCO}_3$  due to a strong polar group ( $\text{OH}^-$ )  
673 in their molecular structure. The polar force of the hydroxyl ions present in the PVA attracts calcium ions ( $\text{Ca}^{2+}$ )  
674

675 from cement and tend to form hydrogen bonds in aqueous solutions. Therefore, the availability of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$   
 676 provided by water increases the interaction with the hydroxyl group. Moreover, the CA's presence enhances the  
 677 supply of  $\text{Ca}^{2+}$ , hydroxyl ions, and total dissolved ions in the curing solution. This ionic offer results in a strong  
 678 affinity with hydroxyl ions in the PVA molecular structure.

679 Li et al. [47] evaluated the synergetic effect of CA and SAPs in the healing efficiency of macro-cracks in  
 680 mortars. Among the five types of CAs studied, the best performance was exhibited for the one that had citric acid  
 681 in its chemical composition. As a result, the spaces unreachable by SAPs were filled by proper orientation of  
 682 calcium ions to the cracks provided by citrate ions and optimized production of  $\text{CaCO}_3$ .

683 Park et al. [51] performed a water flow test in cementitious pastes with 1.5% CA and SAPs with three distinct  
 684 particle sizes. This work revealed that SAPs with smaller size presented a higher initial water flow due to the  
 685 particles, which can be washed out from the crack surface; however, the water flow reached zero within 25 days  
 686 for all the different mixtures.

687 Azarsa et al. [26] investigated the effect of 2% CA in concretes produced with two classes of cement (ordinary  
 688 and with limestone). In general, water permeability results did not reveal a considerable decrease after four days  
 689 regardless of the type of mixtures pre-cracked in a range between 100 and 400  $\mu\text{m}$ .

690 Sisomphon et al. [28,43] employed the combined use of 1.5% CA with 10% CSA to appraise the healing  
 691 efficiency. This association showed an outstanding flexural response and sealing capacity. Another work [45]  
 692 reported that mortars produced with a mixed inclusion of CA and other mineral additions (CSA and bentonite)  
 693 exhibited better performance than another produced only with CA in terms of the recovery of the chloride  
 694 diffusion coefficient.

695 Wang et al. [39] proposed a cementitious system with lightweight clay aggregate (LWA) for carrying self-  
 696 healing agents, along with a combination of four types of admixtures (CA, CSA,  $\text{Na}_2\text{CO}_3$ , and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ).  
 697 Based on an optical microscope observation, the presence of admixtures enhanced the self-closing ability.

698 Reddy et al. [36] investigated the healing performance in concretes produced with only 1.1% CA and others with  
 699 the associated use of CA with different silica fume (SF) contents. The finding indicated the mixture with CA and  
 700 10% SF showed the best overall healing performance in terms of strength recovery, chloride penetration  
 701 resistance, as well as total water absorption and voids in all exposure conditions evaluated.

702 Recently Cuenca et al. [102,103] have studied the effects of CA in HPFRCCs (at 0.8% bwoc) combined with  
 703 either alumina nanofibers (at 0.25% bwoc) or cellulose nanofibrils and nanocrystals (at 0.15% bwoc). The  
 704 nanoparticles provided more effective control in terms of crack pattern and self-curing efficiency, while the  
 705 nanocellulose also boosted CA's stimulating effect on the self-healing capacity. As a result, an overall gain was  
 706 achieved in terms of crack closure ratio, recovery of both mechanical properties (stiffness and load-bearing  
 707 capacity) and durability-related aspects (permeability and sorptivity).

708

## 709 7. Conclusions

710 CAs are commercial products offered by a broad range of suppliers. As a result, their performances must be  
 711 closely related to the specific composition of every single product and manufacturer; this condition makes it  
 712 difficult to predict the global behavior of these admixtures, although some general conclusions can be  
 713 highlighted and summarized in the following:

- 714 • CAs are a mixture of different binder types and active chemicals, which results in distinct  
 715 physicochemical mechanisms of action. In principle, CAs can react directly with water, unhydrated  
 716 cement grains, CH, and develop a synergetic action with other components. These interactions trigger  
 717 further hydration or pseudo pozzolanic reactions that mainly lead to a denser C–S–H.
- 718 • The geochemical origin of CAs allows their action as nucleation or precipitation centers of CH.  
 719 Siliceous fillers act as a nucleation center and produce C–S–H very slowly from the CH interaction. In  
 720 contrast, limestone fillers form Mc and AFt phases through the direct reaction with the  $\text{C}_3\text{A}$  phase. In  
 721 this case, they act as precipitation centers and lead to carbonated C–S–H formation and  $\text{CaCO}_3$   
 722 precipitation.
- 723 • The healing products promoted by CAs present the same chemistry nature as those produced by  
 724 ordinary cement-based materials. The vast majority of works mention the formation of  $\text{CaCO}_3$ , C–S–H  
 725 and AFt as major healing products by SEM/EDS; however, recent research also disclosed mainly CH  
 726 and Mc by TGA in advanced ages.
- 727 • In general, CAs dosage from 0.5% up to 3% bwoc did not negatively affect the compressive strength.  
 728 Some modest reduction may be related to the assessment age up to 28 day, which did not ensure a  
 729 notable change in the short-term due to the further hydration mechanism of CAs.
- 730 • CA contents up to 2% bwoc showed a dramatic reduction in water penetration under pressure even for  
 731 early ages from 12 days; however, their addition did not considerably affect the water absorption  
 732 capacity and even provoked an unsuitable increase of this property in some cases.
- 733 • The main effects on the fresh state were the increase in the air-entrapped content and the setting time  
 734 extension, while there has been no consensus in terms of workability.

- 735 • The CAs performance as healing stimulators depends on their type and the mix design. The optimal CA  
736 dosage is around 1% bwoc; thus, the inclusion above 2% may not bring significant improvements.
- 737 • In general, the stiffness recovery and toughness gain were higher than the load-bearing capacity in  
738 FRCs or HPFRCCs, which is more appreciable than in ordinary concretes.
- 739 • The water permeability showed some controversial results even for CA dosages up to 4% bwoc; thus,  
740 early pre-cracking ages and narrow crack width had stronger influences on the sealing ability.
- 741 • Most works recognize the crucial role of water to enhance CAs performance; therefore, water  
742 immersion with periodic renewal was the best exposure condition, while open-air exposure was the  
743 worst one. The effect of wet/dry cycles on the CAs performance is not a consensus in the literature.
- 744 • Few studies investigated the CAs influence on healing capacity in real service conditions. One study  
745 pointed out that CAs did not improve mechanical and permeability behavior under loading. Another one  
746 attested that CAs assured the sealing ability under repeated loadings in narrow cracks. A single report  
747 stated that the presence of through-crack compressive stresses seems to promote healing regardless of  
748 CAs presence.
- 749 • The further hydration promoted by CAs matches the demand needed to reduce autogenous healing due  
750 to the supply of healing products over time in the cracks, which may be reopened for different reasons.  
751 Some works reported that CAs stimulate the healing in crack widths from 50 up to 400  $\mu\text{m}$ ; however,  
752 not always with mechanical recovery. The associated use of CAs with SAPs or CSA has been  
753 successfully described to seal macro cracks between 300 and 400  $\mu\text{m}$ .
- 754 • The combined use between CA and GGBS has been proved a promising strategy. The GGBS leveraged  
755 the CA's effect in the sorptivity, compressive and splitting tensile strengths recoveries.
- 756 • The synergetic effect between CAs and PVA fibers boosted the  $\text{CaCO}_3$  precipitation on the fiber's  
757 surface, this specific mechanism is not exactly the same for PP or steel fibers, which have another  
758 molecular structure.
- 759 • The combined use of CAs with nano-constituents provided an overall benefit for HPFRCCs. The  
760 internal curing capacity of nano-additions improved the mechanical performance through the double-  
761 effect in the pore refinement and matrix densification. The nano-constituents' hydrophilic action also  
762 enhanced the repeatability effect of CAs after repeated cracking-healing cycles, and the durability-  
763 related aspects.
- 764 • The associated use between CAs and SAPs has been demonstrated to be a valid attempt. Studies have  
765 shown that CAs tend to contribute with an extra filling in the crack space left by SAPs.
- 766 • Some works successfully combined CAs with CSA in order to improve flexural recovery and sealing  
767 performance.  
768

## 769 8. Research gaps and the scope of future work

770 This literature survey allowed to highlight some topics that still need to be deeper investigated. The scientific  
771 community and the construction industry should gather efforts of moving together towards the beneficial  
772 incorporation of self-healing technologies in cement-based materials when it comes to the code-based design  
773 practice, including suitable Life Cycle Analysis tools [104]. According to the authors' opinion, the topics and  
774 aspects discussed below require the most urgent coordinated effort:

- 775 • CAs formulations demand constant enhancement in order to achieve the proper technical requirements  
776 with a minimum collateral effect on the fresh state and overall success on the hardened properties [25].  
777 At the same time, these products should ensure compatibility with the different binders and other  
778 concrete constituents.
- 779 • The further hydration is the primary CA's mechanism, which provides healing products over time  
780 [6,7,11,16,20,24,29,30,62,71–74]. Thus, the duration of the CA's effect should be investigated to satisfy  
781 the safety and maintenance requirements, as well as the durability and sustainability related aspects  
782 during the project's service life. This accomplishment requires either a combined experimental and  
783 modelling approach or a science/model-based and data-based [105,106] to extrapolate the results to a  
784 time scale compatible with the expected structural lifespan [107,108].
- 785 • The vast majority of works assume the C-S-H as a major hydrate formed; however, it is worth  
786 confirming the occurrence of Mc phases [22]. This comprehension has a substantial role for CA's  
787 rational use as a project requirement for practical applications.
- 788 • It is crucial to invest in quantitative analysis to predict the nature and amount of healing products over  
789 time for different CA's types and dosages [22,55]. TGA and XRD by the Rietveld method cover the  
790 identification and quantification of both crystalline and amorphous phases. They are alternatives to  
791 SEM/EDS's semi-quantitative investigations performed in most studies so far [109]. Besides that, X-ray  
792 micro-tomography ( $\mu\text{CT}$ ) allows the detection of the healing products in entire crack volume [110].

- 793 • The mechanical and durability-related aspects evaluations in the long-term are fundamental to draw  
 794 substantial conclusions about the CAs effect, particularly on the flexural strength and modulus of  
 795 elasticity [8,62]. It is also suggested to perform a rheological analysis of fluid behavior.  
 796 • Understanding of residual post-cracking flexural/tensile stresses have become more critical due to their  
 797 influences on design parameters in FRCs and HPFRCCs. Therefore, post-cracking stresses can play  
 798 some crucial roles as far as the serviceability limit state is concerned, such as the control of crack width  
 799 and the deflection through tension stiffening effects.  
 800 • The eventual chemical pre-stressing in fibers from CAs precipitation must be further investigated and  
 801 the different behavior of different types of fibers [7,35].  
 802 • Developing a comprehensive work that encompasses CAs action as a closing, sealing and healing  
 803 stimulator simultaneously, and taking into account the depth of healing products in the cracks [39,100].  
 804 • It is worth confirming the optimum CA dosages that enhance durability-related aspects, considering the  
 805 admixture type and the effects expected in cementitious material [30,35,43]. Besides that, air  
 806 permeability tests seem to be a counter test for water permeability tests.  
 807 • The literature lacks more in-depth investigations regarding the correlation between the healing products'  
 808 nature and material performance gain after the healing process. Thus, the interconnection between  
 809 micro- and macro-structural techniques is recommended to clarify the influence of experimental  
 810 variables that govern the complex phenomena of self-healing provided by CAs [74].  
 811 • The healing process evaluation in real structural service conditions is still scarce in the literature,  
 812 especially in terms of the healing performance under sustained mechanical stresses or cyclic actions.  
 813 • There is a demand for self-healing research in general and CAs as healing stimulators to recover  
 814 mechanical properties and durability under repeated cracking-healing cycles [31,35].  
 815 • Healing kinetics, nature and frequency are other critical approaches of the process according to the  
 816 exposure conditions.  
 817 • There has been no clear consensus about the range of crack widths effectively healed by CAs in the  
 818 literature. However, some crucial studies allow concluding that cracks up to a few hundred microns  
 819 may be healed or sealed, especially in favorable exposure conditions and with enough time.  
 820 • The associated use of CAs with SAPs demands further investigation in terms of exposure conditions  
 821 and mechanical gain [47,51].  
 822 • The combined use between CAs and nanoparticles so far scarcely addressed also deserve further  
 823 investigation [102].  
 824

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 831

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**Highlights**

- ✓ This paper presents a literature meta-analysis about the effect of Crystalline Admixtures (CAs) as permeability-reducing admixtures and as healing stimulators.
- ✓ The primary mechanisms along with the healing products provided by CAs are addressed.
- ✓ The effects of CAs on the properties of cement-based materials as permeability-reducing admixtures are discussed.
- ✓ The enhancement promoted by CAs on the self-healing capacity is analyzed focusing on the mechanical recovery and durability-related aspects.
- ✓ Moreover, the influence of different aspects, such as the environmental exposure, repeated preloading, crack width, and synergic effect with other components, on the self-healing ability of CAs are analyzed.

**Declaration of interests**

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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