

1 USE OF TARTARIC ACID FOR THE PRODUCTION OF SUSTAINABLE 2 PORTLAND-FREE CSA-BASED MORTARS

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9 ABSTRACT

10 The purpose of the study is to evaluate the effect of a tartaric acid-based set retarding admixture on
11 rheological, elastic and physical performances of sustainable mortars manufactured with calcium
12 sulfoaluminate, anhydrite and Supplementary Cementitious Materials replacing totally OPC.
13 Experimental results indicated that the tartaric acid acts as superplasticizer and it is effective to
14 extend the pot-life of mortars up to about 2 hours. On the other hand, the set-retarding admixture
15 provides a strong retardation of binder hydration resulting in a reduction of initial expansion and
16 compressive strength at early ages. However, this retarding effect disappears at long ages.

17 KEYWORDS

18 Calcium sulphoaluminate cement; supplementary cementitious materials; tartaric acid; set-retarding
19 admixtures; sustainability

20 HIGHLIGHTS

- 21 • Sustainable OPC-free mortars with CSA and SCMs were investigated
- 22 • Tartaric acid acts as superplasticizer and set-retarding admixture
- 23 • Shrinkage and mechanical properties are influenced by tartaric acid addition
- 24 • About 60% reduction in Gross Energy Requirement and CO₂ emissions was achieved

INTRODUCTION

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The topics of sustainability and environmental protection in construction have become very important when Kyoto protocol was adopted in 1997 and, particularly, after the Paris Agreement (COP21, 2015) which was aimed to limit the temperature increase even further to 1.5°C above pre-industrial levels.

In this context, a sharp reduction of CO₂ emissions and in consumption of natural resources in production of construction materials is needed.

In 2016, about 4.2 billion tons of Portland-based hydraulic cement were used globally – about 2.4 billion tons in China – (1), and CO₂ emissions from the cement industry exceeded 7% of global anthropogenic greenhouse gases emission (2). Concrete industry is not eco-friendly since it consumes great amount of cement, aggregates and water.

In order to reduce the environmental impact of concrete industry, several authors (3,4) have identified different strategies: a) using alternative fuels and raw materials to reduce greenhouse gases emissions to produce Portland cement (5–7); b) replacing Portland cement clinker with low-carbon supplementary cementitious materials (SCM) (8–11); developing alternative low-carbon binders, such as alkali-activated materials, geopolymers and calcium sulphoaluminate cements (12,13); c) reducing natural resource consumption through to waste management and waste recovery (14–21); increasing durability of concrete structures by means of high-performance admixtures (22,23).

Between these strategies, calcium sulphoaluminate cements (CSA) are actually receiving increasing attention because they promise to provide a low-CO₂ and low-embodied energy alternative to Portland cement. In fact, compared to alite, which releases 0.578 CO₂ g/g, emissions of greenhouse gases, calcium sulphoaluminate clinker contributes only for 0.216 CO₂ g/g. In addition, the maximum kiln temperature to produce CSA clinker is typically 1250 °C, about 200°C lower than

50 that used for Portland cement clinker. Finally, the grinding process requires lower energy due to the
51 lower hardness of CSA clinker compared to Portland clinker (24–26).

52 In general, about 15-25 wt. % of calcium sulfate, in form of gypsum (G) or anhydrite (CS), is
53 blended with CSA-clinker to control setting time, strength development and volume stability.
54 Several authors (27–29) have shown a close correlation between the main properties of CSA-based
55 composites and calcium sulfate dosage. Nowadays, the use of calcium sulphoaluminate cement is
56 widespread for calcium sulphoaluminate – ordinary Portland cement – calcium sulfates ternary
57 binders in which OPC is present up to 60% with respect to binder mass (30,31).

58 One of the main issues related to the use of CSA for the production of concrete is the setting time;
59 indeed, it is well known that mixtures containing calcium sulphoaluminate cement are characterized
60 by a short pot-life and a pronounced workability loss over time (32–34). In order to face this
61 practical problem, several set-retarding admixtures were proposed by different authors. Sugama
62 proposed the use of citric acid as a set retarder (35). Velazco et al. (36) showed that the addition of
63 citric acid increased the setting time, modified the morphology of the ettringite needles, changed the
64 microstructural configuration and prevented the decreasing in compressive strength caused by
65 delayed ettringite formation. Moreover, Bishop et al. synthesized a novel retarding admixture based
66 on calcium nitrilotris(methylene)-triphosphonate (37) and investigated mechanisms responsible for
67 set and hardening retardation promoted by sucrose, tartaric acid and lignosulfonate in CSA-based
68 mortars (38). Results indicated that tartaric acid is the most effective in retarding C_3A hydration and
69 ettringite formation.

70 The purpose of the present study is to evaluate the effect of addition of a tartaric acid-based set
71 retarding admixture on rheological, elastic and physical performances of sustainable mortars
72 manufactured with CSA, anhydrite and supplementary cementitious materials (fly ash, metakaolin
73 and ground granulated blast furnace slag) replacing totally OPC.

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MATERIALS AND METHODS

Materials

A ternary binder based on ordinary Portland cement CEM I 52.5R (OPC: according to EN 197-1), commercial CSA clinker and technical grade anhydrite ($C\bar{S}$) was used to manufacture the reference mortar (CSA:OPC: $C\bar{S}$ = 40:40:20). Ground granulated blast furnace slag (S: according to EN 15167-1), metakaolin (MK: according to ASTM C618), V class fly ash (FA: according to EN 450-1 and EN 197-1) and hydrated lime CL90-S class (CH: according to EN 459-1) were employed to replace totally OPC in sustainable mortars (CSA:SCM:CH: $C\bar{S}$ = 40:35:5:20). CH was added to the mix in order to improve the pozzolanic reaction of SCM amount not consumed in the reaction with CSA; furthermore, sand/binder ratio was fixed equal to 3 (maximum diameter of natural siliceous aggregates equal to 2.5 mm). Tartaric acid-based set-retarding admixture was added up to 1.2% with respect to binder mass, while the mixing water was adjusted in order to attain, in absence of set retarding admixture, the same workability at the end of the mixing procedure, equal to 160 mm \pm 10 mm spreading.

Table 1 – Physical properties of binders

	OPC	CSA	$C\bar{S}$	CH	S	FA	MK
D_{50} [μm]	5.19	8.18	2.93	3.00	5.48	11.1	2.70
Specific surface [cm^2/g]	3`175	2`722	4`837	4`678	3`049	2`283	3`990
Specific mass [kg/m^3]	3`150	2`650	2`670	2`120	2`730	2`010	2`240

Table 2 – Composition of mortars

Composition [kg/m ³]	CSA	CEM I 52.5 R	CS	CH	GGBFS	FA	MK	Aggregates	Water	Tartaric acid
REF 40/40	183	183	91					1`370	279	
REF 40/40 0.4	183	183	91					1`370	279	1.82
REF 40/40 0.8	183	183	91					1`370	279	3.65
REF 40/40 1.2	183	183	91					1`370	279	5.48
S 40/35/5	183		90	25	156			1`355	275	
S 40/35/5 0.4	183		90	25	156			1`355	275	1.81
S 40/35/5 0.8	183		90	25	156			1`355	275	3.61
S 40/35/5 1.2	183		90	25	156			1`355	275	5.43
FA 40/35/5	170		85	24		147		1`277	298	
FA 40/35/5 0.4	170		85	24		147		1`277	298	1.70
FA 40/35/5 0.8	170		85	24		147		1`277	298	3.41
FA 40/35/5 1.2	170		85	24		147		1`277	298	5.11
MK 40/35/5	165		82	23			142	1`234	329	
MK 40/35/5 0.4	165		82	23			142	1`234	329	1.65
MK 40/35/5 0.8	165		82	23			142	1`234	329	3.29
MK 40/35/5 1.2	165		82	23			142	1`234	329	4.95

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Tests on mortars

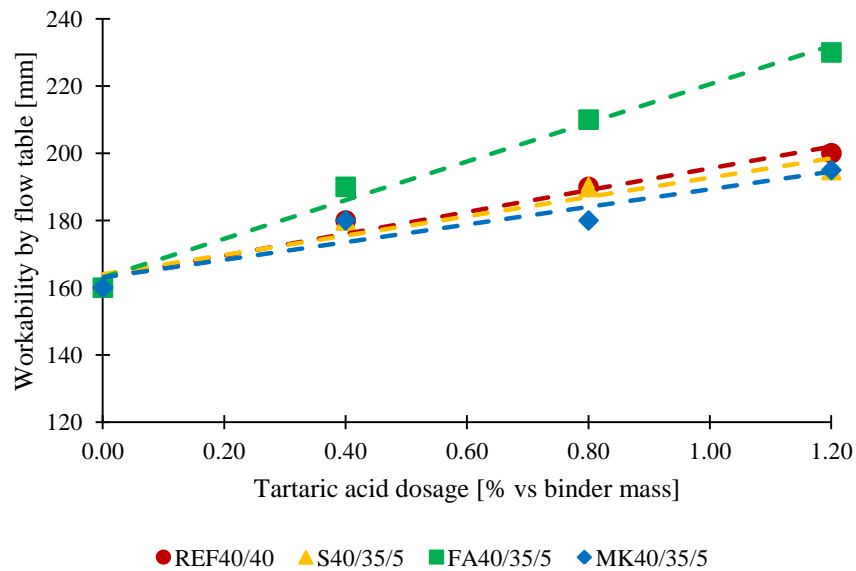
94 At the end of the mixing procedure, workability was measured by means of flow table according to
95 EN 1015-3. In addition, specific mass was evaluated on fresh mortars according to EN 1015-6
96 standard. Moreover, the pot-life of the mixture, which corresponds to time during which
97 workability by flow table is higher than 140 mm, was also detected. Specimens 40x40x160 mm³
98 were produced and cured under water at 20°C; in addition, only for mixture containing 0.8% of
99 tartaric acid, specimens were cured both under water at 20°C and in a climatic chamber at 20°C and
100 R.H. 60%. Specific mass, compressive and flexural strength at 1, 7 and 28 days were also
101 determined (EN 1015-11). Moreover, drying shrinkage was measured over time on specimens
102 stored in dry environment (20°C, R.H. 60%) both in plastic and hardened (according to EN 12617-
103 4) phase. Finally, SEM observation were performed on 28-day specimens cured under water.

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RESULTS AND DISCUSSIONS

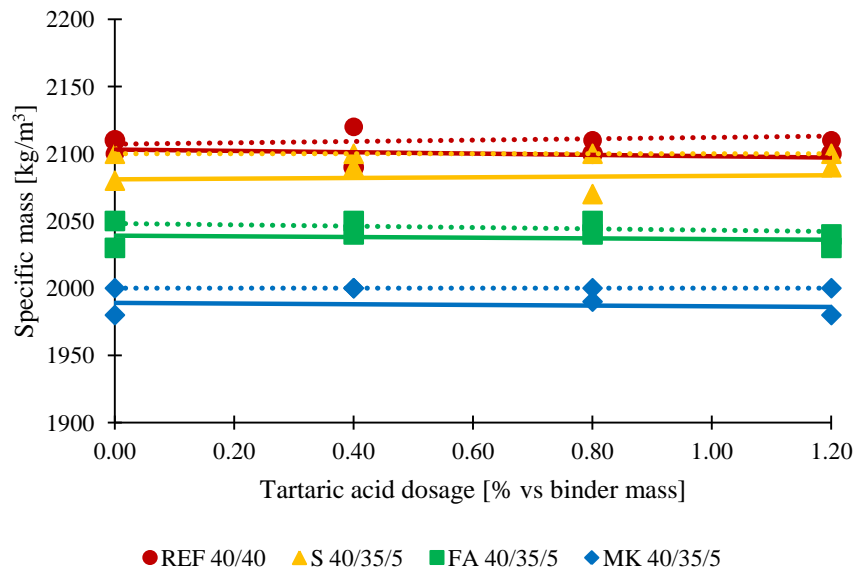
105 The amount of water to achieve the target workability (160 mm spreading) is, in the absence of set
106 retarding admixture, variable due to the different specific surface, texture and shape of binders

107 (Tables 1 and 2). In particular, replacing OPC with GGBFS, no change in terms of mixing water
 108 was noticed. On the contrary, the use of FA determines an increase in water demand equal to 7%
 109 due to the high unburnt carbon content (L.O.I. = 4.9% according to EN 196-2 and ISO 10694),
 110 while employing MK in place of OPC water amount rise up about 18% respect to reference mortars
 111 due to the higher fineness of metakaolin compared to Portland cement. Furthermore, tartaric acid-
 112 based set-retarding admixture acts as a superplasticizer (Figure 1). The super-plasticizing effect is
 113 more pronounced in fly-ash based mortars (+45% spreading with respect to mixture without set-
 114 retarding admixture), while is almost the same for mortars manufactured with the other binders
 115 employed (+20%).



116
 117 **Fig. 1** – Workability by flow table of mortars vs set-retarding admixture dosage

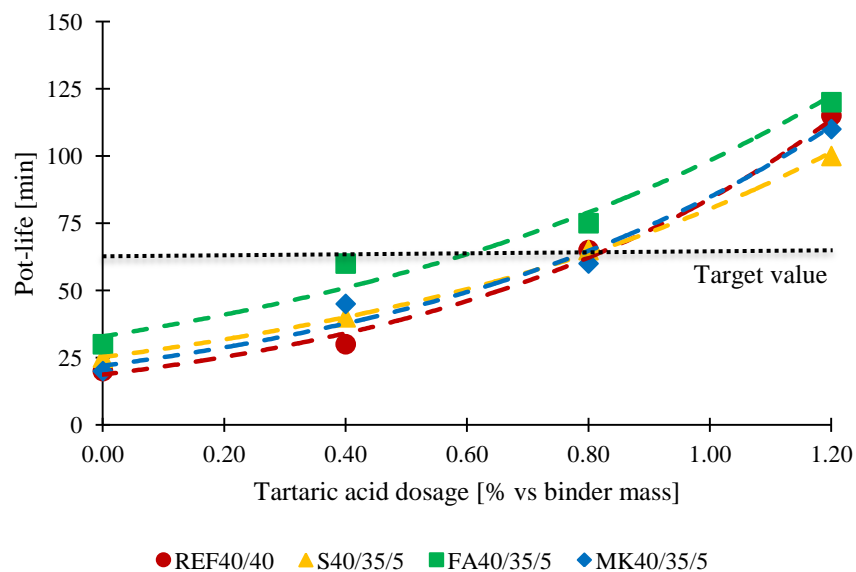
118 Tartaric acid addition does not produce any abnormal air entrapment; in fact, regardless of set-
 119 retarding admixture dosage, specific mass of mortars is substantially the same both in fresh and
 120 hardened state (Figure 2). On the contrary, the total substitution of OPC with SCMs modifies
 121 density of mortars; in fact, FA and MK-based mixtures showed specific mass (both in fresh and
 122 hardened state) lower than that detected on reference (containing OPC) and S-based mortars as a
 123 consequence of the increase of mixing water to achieve the target workability.



124

125 **Fig. 2** – Specific mass at fresh (continuous line) and hardened (dashed line) state of mortars vs set-retarding admixture
126 dosage

127 Figure 3 shows that the effectiveness of admixture with different binders is almost the same.
128 Regardless to the binder used, pot-life of mortars without tartaric acid is about 20 minutes, which is
129 not suitable for placing in the job-site; the addition of tartaric acid-based admixture extends the pot
130 life of mortars up to 110 minutes from mixing. The average time between mixing and placing a
131 mortar in the job-site is generally close to 60 minutes. Based on this target, it is possible to conclude
132 that the ideal set-retarding admixture dosage is equal to 0.8% vs. binder mass (Figure 3).



133

134 **Fig. 3** – Pot-life of mortars vs set-retarding admixture dosage

135 Results (Table 3) indicate that addition of tartaric acid-based admixture determines a strong
 136 retardation of binder hydration and, consequently, a general reduction of 24-hour compressive
 137 strength of both reference and SCMs mortars, except for MK-mixtures. The higher the tartaric acid
 138 dosage, the stronger the decrease of compressive strength (Figure 4).

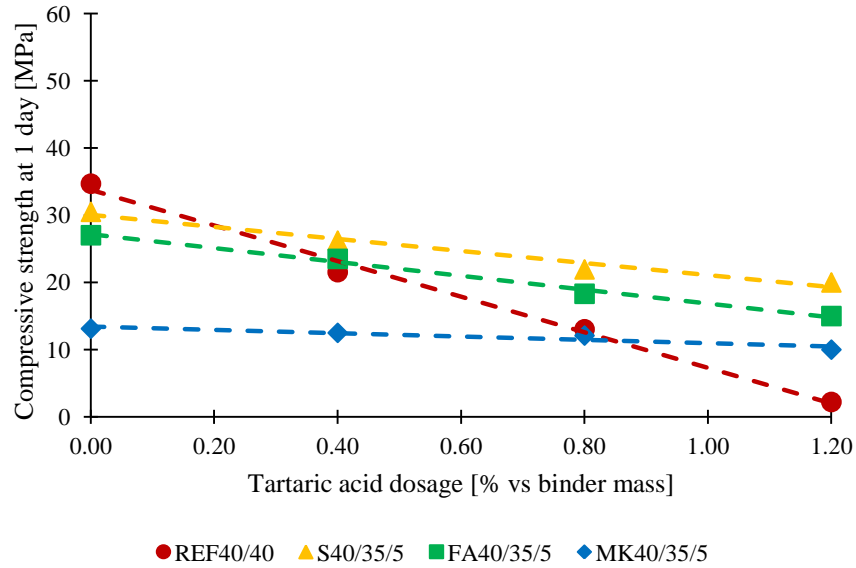
139 **Table 3** – Mechanical properties of hardened mortars wet cured

Composition	w/b ratio	R _f at 24 h [MPa]	R _f at 7 days [MPa]	R _f at 28 days [MPa]	R _c at 24 h [MPa]	R _c at 7 days [MPa]	R _c at 28 days [MPa]
REF 40/40	0.61	7.27	7.47	7.52	34.69	41.08	47.41
REF 40/40 0.4	0.61	4.69	5.02	6.86	21.53	39.13	44.06
REF 40/40 0.8	0.61	3.28	3.48	7.03	13.03	42.16	52.91
REF 40/40 1.2	0.61	0.82	2.11	7.03	2.22	27.84	47.81
S 40/35/5	0.61	5.09	5.29	5.39	30.50	32.59	35.56
S 40/35/5 0.4	0.61	5.16	5.19	5.25	26.22	31.44	36.69
S 40/35/5 0.8	0.61	4.69	4.69	5.16	21.94	30.22	34.13
S 40/35/5 1.2	0.61	0.96	2.29	4.99	19.98	24.12	34.98
FA 40/35/5	0.70	5.03	5.21	5.32	27.02	33.18	36.02
FA 40/35/5 0.4	0.70	4.92	4.92	5.25	23.50	31.52	35.86
FA 40/35/5 0.8	0.70	4.92	5.01	5.12	18.31	33.00	36.68
FA 40/35/5 1.2	0.70	1.12	2.53	5.33	14.69	22.13	35.82
MK 40/35/5	0.80	2.81	3.05	3.28	13.13	15.59	17.58
MK 40/35/5 0.4	0.80	3.52	3.75	3.75	12.50	17.94	20.06
MK 40/35/5 0.8	0.80	3.05	3.52	3.75	12.09	18.50	19.03
MK 40/35/5 1.2	0.80	0.56	1.88	3.19	10.06	13.09	18.42

140 Since the retarding effect of tartaric acid is more pronounced on OPC (39), the decrease of
 141 compressive strength in reference mortars, when the dosage of the set-retarding admixture
 142 increases, was significantly higher compared to slag and fly ash based mortars. Another effect
 143 responsible for the lower reduction of compressive strength of SCMs-based mortars should be
 144 attributed to a partial adsorption of tartaric acid by S, FA and MK particles. The lower amount of
 145 tartaric acid in the aqueous phase could justifies the lower retardation of these mortars.

146 This retarding effect totally disappears at 28 days for all mixtures (Figure 5). In general, the total
 147 replacement of OPC with SCMs causes a reduction in compressive strength ranging from 30% (for
 148 slag and fly ash) to 60% (for MK-based mortars). The effect of curing conditions was also
 149 investigated; specimens cured at 20°C under water evidenced compressive strength values about

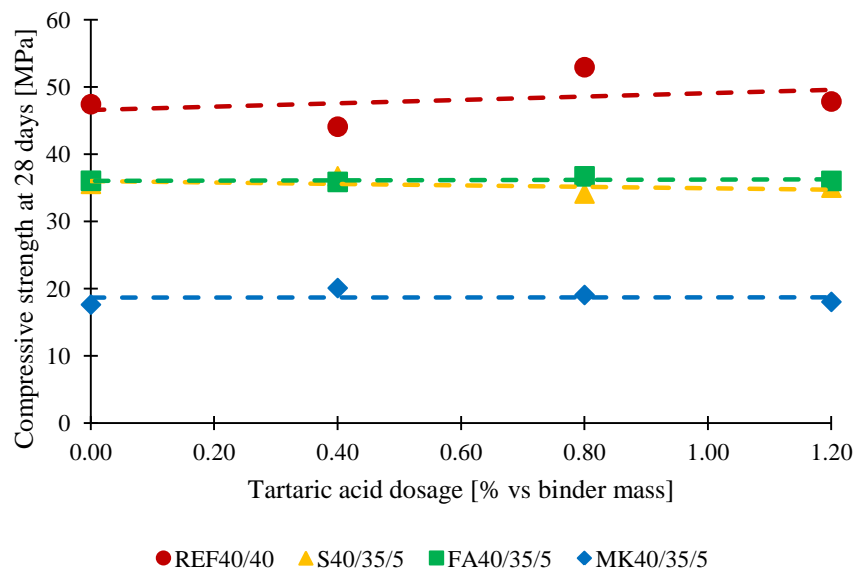
150 25% lower than that measured on mortars stored in dry environment (20°C, R.H. 60%),
 151 independently of the age and the SCMs used (Figure 6).



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Fig. 4 – Compressive strength of mortars after 24 hours vs set-retarding admixture dosage

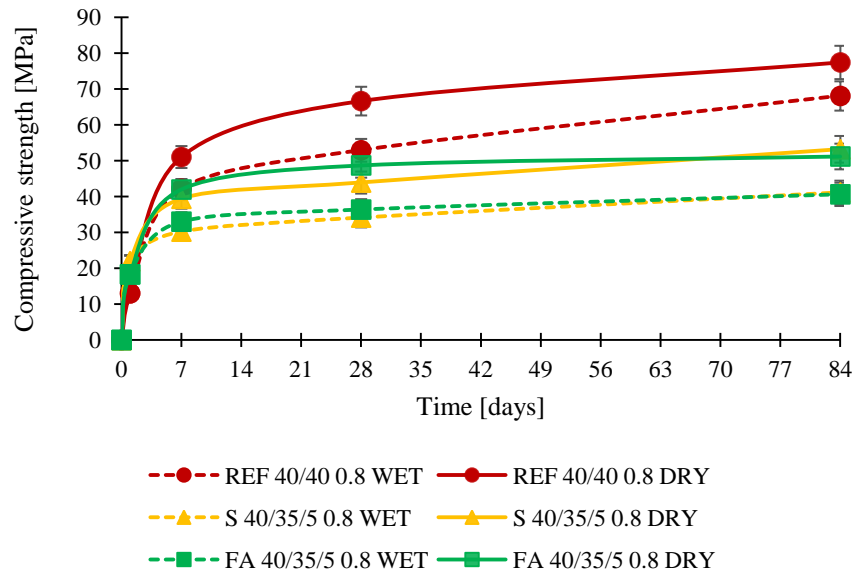


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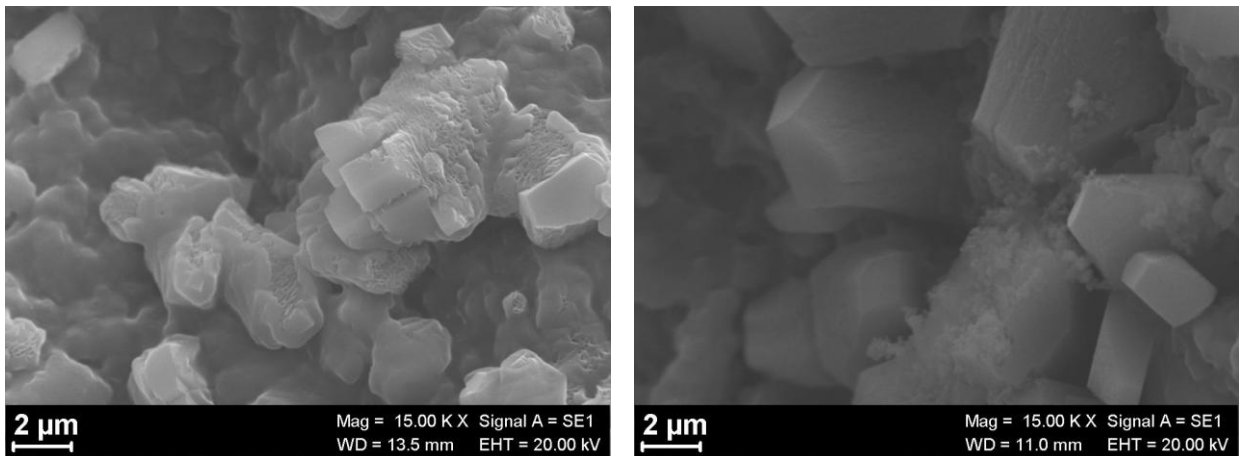
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Fig. 5 – Compressive strength of mortars after 28 days vs set-retarding admixture dosage (specimens under water at T = 20°C)

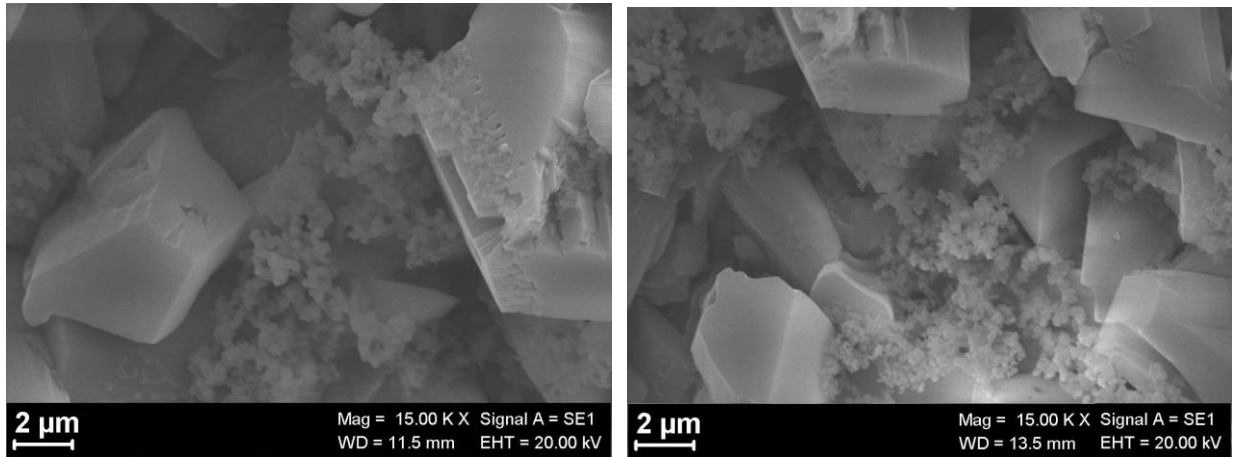


157
 158 **Fig. 6** – Development of compressive strength over time with different curing: under water (WET) and on dry
 159 environment at R.H. 60% (DRY)

160 The images collected by means of scanning electron microscope (SEM) on 28-day specimens
 161 showed a different microstructure between mortar containing Portland cement and those
 162 manufactured with SCMs (Figure 7 - 8). In particular, SCM-based mixtures are characterized by a
 163 homogeneous microstructure with rich amounts of needles covered by small Ca-rich particles of
 164 size 0.1-0.5 μm . The prismatic needles had a thickness of about 2-5 μm and a length approximately
 165 equal to 5-20 μm . On the contrary, the microstructure of CSA/OPC/C $\bar{\text{S}}$ mortar seems to be
 166 composed of denser crystals than those of SCM-based mixtures. In addition, the presence of Ca-rich
 167 particles highlighted in Portland-free mortars was not observed.

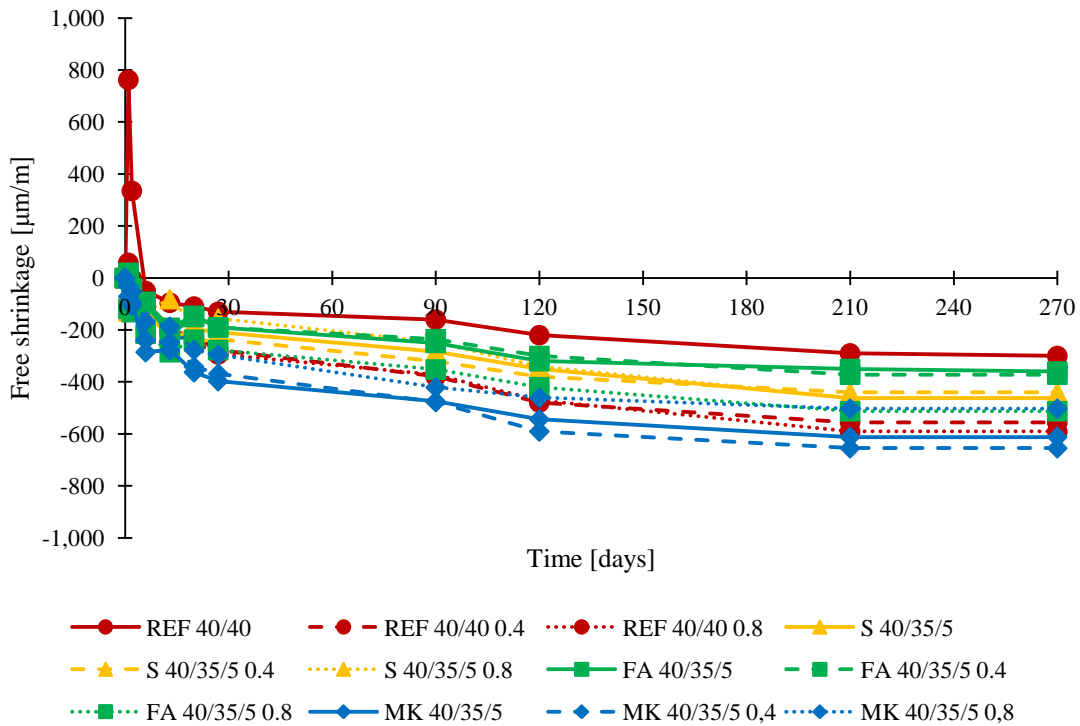


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 169 **Fig. 7** – SEM images of reference mortar (on the left) and S-based mortar (on the right)



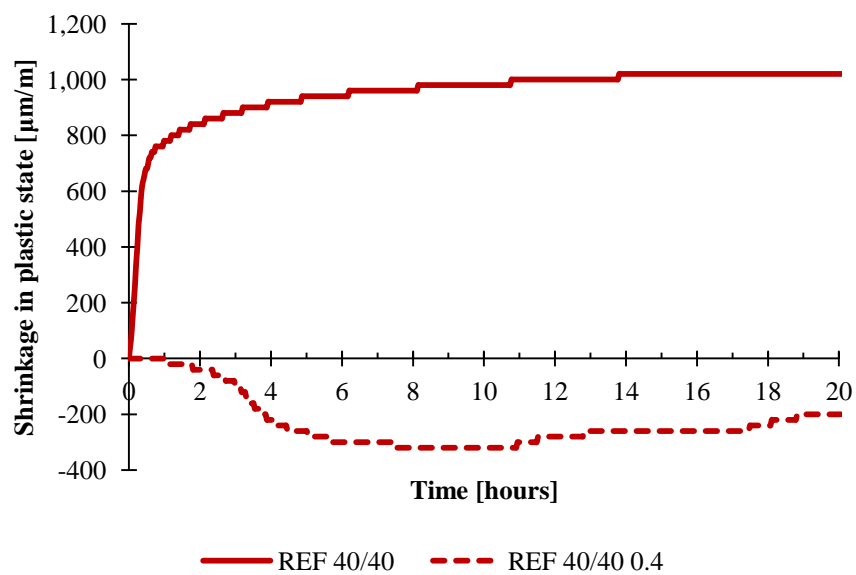
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171 **Fig. 8** – SEM images of FA- mortar (on the left) and MK-based mortar (on the right)

172 Shrinkage tests were performed up to 270 days on prismatic 40x40x160 mm specimens stored at
 173 20°C and R.H. 60% (Figure 9). Reference mortar manufactured without tartaric acid shows a
 174 marked expansive behavior (up to +800 μm/m at 24 hours from casting) followed by shrinkage (-
 175 400 μm/m at 270 days). Total replacement of OPC with SCMs and hydrated lime determines – in
 176 absence of set-retarding admixture – a sharp reduction of the initial expansion followed by
 177 shrinkage (about -500 μm/m after 270 days), independently of the nature of SCM replacing OPC.



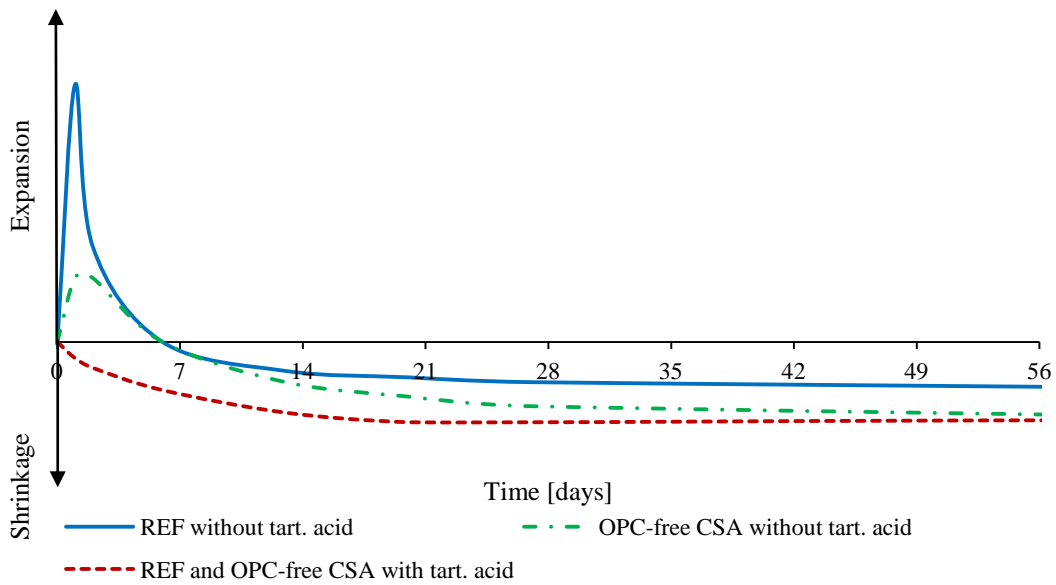
178
179 **Fig. 9** – Free shrinkage over time in dry environment ($T = 20^{\circ}\text{C}$, R.H. 60%)

180 By using tartaric acid, CSA-based mortars (both that containing OPC and those manufactured with
 181 SCMs) did not evidenced the initial expansion, but they began to shrink just after the final setting
 182 time has occurred. This could be ascribed to the delay in the development of ettringite when the
 183 tartaric acid is used. These mixtures, however, despite the absence of initial expansion, present a
 184 quite stable behavior over time, with a free shrinkage lower than $-500 \mu\text{m/m}$ after 270 days.
 185 The role of tartaric acid is also evident on the expansive behavior in the plastic phase (Figure 10);
 186 reference mortar (containing OPC) manufacturing without set-retarding admixture achieves an
 187 expansion equal to $1'000 \mu\text{m/m}$ already after 6 hours from casting while the reference mortar
 188 manufactured with 0.2% set-retarding admixture is essentially stable over time. In general, use of
 189 tartaric acid-based set-retarding admixture, independently of the presence of OPC and the nature of
 190 SCM, eliminates the initial expansion typical of reference CSA-OPC-CS $\bar{\text{S}}$ without admixture (Fig.
 191 11). In other words, the “expansive/shrinkage” behavior of the mortar in the absence of tartaric acid
 192 is transformed in an “exclusively shrinkage” behavior. However, the final contraction detected for
 193 mortars containing set-retarding admixture was substantially the same of that measured in reference
 194 mortar (containing OPC) without tartaric acid.



195

Fig. 10 – Shrinkage of reference mortars in plastic state over time in dry environment ($T = 20^{\circ}\text{C}$, $R.H. 60\%$)



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Fig. 11 – Expansive/shrinkage behavior of CSA-based mortars without tartaric acid compared to stable behavior of mortars manufactured with set-retarding admixture

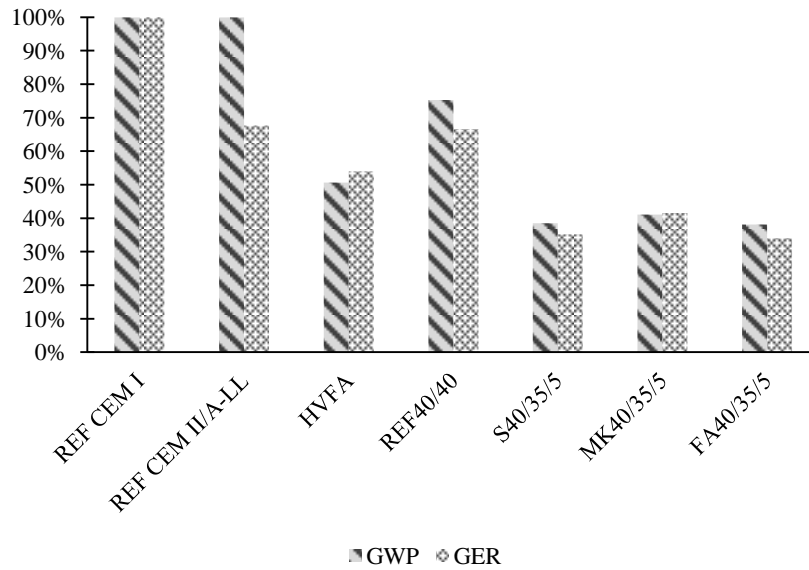
From a practical point of view, mixtures with “exclusively shrinkage” behavior - at the same value of 270-day shrinkage of expansive/shrinkage mortar - seems to be more promising in repair of existing concrete structures since the tensile stress induced by restrained contraction is lower. As a consequence of more stable behavior of SCM mortars manufactured with the tartaric acid, although the sharp decrease detected for 28-days compressive strength when OPC is replaced by SCMs, FA- and S-based mortars showed mechanical performances suitable for mixtures devoted to “cosmetic repair” of existing reinforced concrete structures, where shrinkage is the main design parameter. In particular, CSA-Portland free mortar can be classified as R3 strength class ($R_c \geq 25$ MPa at 28 days) according to EN 1504-3 and, hence, suitable for repair of existing concrete structures that present corrosion of rebars and spalling of concrete cover. Furthermore, the worsening in mechanical strength of SCMs mortars is fully offset by a marked improvement in environmental sustainability. Indeed, at equal strength class, gross energy requirement (GER) and global warming potential (GWP) parameters of Portland-free mortars are lower than those of both high volume fly ash (HVFA) mortars (40), traditional mixtures manufactured with OPC and ternary binders based on

214 CSA. In particular, starting from data on CO₂ emissions and energy production of binders (CEM I,
 215 CEM II/A-LL, CSA, C \bar{S} and CH), supplementary cementitious materials (S, FA and MK) and
 216 aggregates (Table 4), the reduction of GER and GWP deriving from the use of limestone Portland
 217 cement, HVFA, CSA-OPC- C \bar{S} ternary mixtures and CSA-SCMs-CH-C \bar{S} blends in place of
 218 Portland cement was determined. It is possible to conclude that, at the same strength class, the use
 219 of traditional CSA-based ternary mixture in place of Portland cement or limestone Portland cement
 220 determines a reduction in terms of GER and CO₂ emissions ranging from 25% to 35% while the
 221 total replacement of OPC with SCMs slumps GER and GWP of about 60% (Figure 12). Finally,
 222 GER and GWP of Portland-free CSA-based mixtures reach lower values than those shown by
 223 HVFA mortars.

224 **Table 4** – Environmental parameters of binders, SCMs and aggregates. Source: Ecoinvent 3.0 Database

	GER [MJ/kg]	GWP [Kg CO₂/ Kg]
CEM I 52.5 R	5.50	9.8 · 10 ⁻¹
CEM II/A-LL 42.5R	3.60	8.8 · 10 ⁻¹
CSA	2.70	7.4 · 10 ⁻¹
C\bar{S}	1.30	2.4 · 10 ⁻¹
CH	4.50	4.2 · 10 ⁻¹
S	0.31	1.7 · 10 ⁻²
FA	0.10	5.3 · 10 ⁻³
MK	1.50	9.2 · 10 ⁻²
Aggregates	0.13	2.4 · 10 ⁻³

225



226

227 **Fig. 12** – Global Warming Potential (GWP) and Gross Energy Requirement (GER) of mortars at the same strength
 228 class normalized by those of CEM I-based traditional mortar

229

FURTHER RESEARCH

230 Further experimentations are needed to measure Young modulus and the adhesion properties of
 231 these eco-friendly ternary binders. In addition, durability issues of mortars and concretes
 232 manufactured with CSA-based Portland-free binders have to be thoroughly investigated, especially
 233 in chloride and sulfate-rich environments or in presence of freeze and thaw cycles.

234

CONCLUSIONS

235 In this paper, the influence of tartaric acid-based set-retarding admixture was evaluated on the
 236 performances of sustainable Portland-free CSA-based ternary mortars manufactured with
 237 supplementary cementitious materials. Results indicated that the tartaric acid, independently of the
 238 nature of SCMs replacing OPC, acts as superplasticizer and it is effective to extend the pot-life of
 239 mortars up to about 2 hours. No side-effects were detected on specific mass in fresh and hardened
 240 state by increasing the set-retarding admixture dosage; on the other hand, total substitution of OPC
 241 with fly ash or metakaolin cause a decrease in specific mass due to the higher water demand to
 242 attain the target workability at the end of the mixing procedure. The use of tartaric acid determines

243 a strong retardation of binder hydration and, consequently, a reduction of compressive strength at
244 early ages, especially in reference mortars containing OPC. No retarding effect was detected at 28
245 days from casting. In general, the total replacement of OPC with supplementary cementitious
246 materials and hydrated lime determines a sharp reduction in terms of compressive strength ranging
247 from 30% (for mixture containing fly ash and slag) to 60% (for mortars manufactured with
248 metakaolin). In addition, as opposed to OPC-based mixtures, mortars containing CSA, SCM,
249 hydrated lime and anhydrite show higher compressive strength values when cured in dry
250 environment respect to that measured on specimens stored under water.

251 Mortars without tartaric acid showed an initial expansion during the first 5-7 days as a consequence
252 of the ettringite formation, than the mixtures shrink. When set-retarding admixture is used, the free-
253 expansion totally disappears and shrinkage begins immediately after final set has occurred.
254 However, after 270 days shrinkage is substantially the same for mortars with and without tartaric
255 acid. In other words, the “expansive/shrinkage” behavior of the mortar in the absence of tartaric acid
256 is transformed in an “exclusively shrinkage” behavior. However, the final contraction detected for
257 mortars containing set-retarding admixture was substantially the same of that measured in reference
258 mortar (containing OPC) without tartaric acid. Although the compressive strength of SCM-based
259 mortars is lower than the reference mixtures containing OPC, the more stable behavior evidenced
260 by these Portland-free materials makes them suitable for “cosmetic repair” of existing reinforced
261 concrete structures, where shrinkage is the main design parameter. In particular, CSA-Portland free
262 mortar can be classified as R3 strength class ($R_c \geq 25$ MPa at 28 days) according to EN 1504-3 and,
263 hence, suitable for repair of existing concrete structures that present corrosion of rebars and spalling
264 of concrete cover.

265 Finally, CSA-SCM-CH-C \bar{S} mortars are characterized by a reduction both in energy requirement
266 (GER) and greenhouse gases emissions (GWP) close to 60% respect to traditional OPC-based or
267 CSA-OPC-C \bar{S} mortars at equal strength class.

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