1   **Effect of gypsum content in sprayed cementitious matrices: early age**

2   **hydration and mechanical properties**

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5   **C. Herrera-Mesen [a, 1], R.P. Salvador [a, b], S.H.P. Cavalaro [c, 2], A. Aguado [a]**

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8   [a] Department of Civil and Environmental Engineering, Barcelona Tech, Polytechnic

9   University of Catalonia, UPC, Jordi Girona 1-3, 08034, Barcelona, Spain.

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12   [b] Department of Civil Engineering, São Judas Tadeu University, 546 Taquari St.,

13   03166-000, São Paulo, Brazil.

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15

16   [c] School of Architecture, Building and Civil Engineering, Loughborough University,

17   Leicestershire, LE11 3TU, UK

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19

20   Corresponding authors.

21   E-mail addresses: [1]carlos.herrera.mesen@estudiant.upc.edu (C.Herrera-Mesen);

22   [2]S.Cavalaro@lboro.ac.uk (S Cavalaro).

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ABSTRACT

Sprayed materials must present short setting times and a fast early strength development for safety and productivity reasons. In order to improve these characteristics, the construction industry has focused on the development of new formulations of accelerators. Research and improvement of other components of the mix, such as cement or additions, have not advanced at the same rate despite being also crucial for the reaction kinetics. The objective of this work is to evaluate the influence of gypsum content on the hydration and mechanical strength development in sprayed mixes. Sprayed pastes and mortars were prepared with one type of cement, two types of accelerators and different gypsum contents. Kinetics, mechanisms of hydration and mechanical properties were evaluated. Results showed a better performance in sprayed mixes that contain ideal doses of gypsum. Such approach provides valuable information for the improvement of the formulation of cement used in sprayed concrete applications.

Keywords: Sprayed materials, sulfate balance, accelerators, hydration, mechanical strength.

1. Introduction

51   Sprayed cementitious materials are widely used in the construction industry, from

52   buildings to infrastructure. In some of these applications, accelerators are added to

53   achieve faster setting, to reduce rebound and to improve initial strength, adhesiveness

54   and cohesiveness of the sprayed cementitious materials [1,2]. Accelerators incorporate

55   dissolved aluminate ions into the matrix, thus modifying the kinetics and mechanisms

56   of hydration of cement [3–5]. These ions react with the sulfates from cement to form

57   calcium sulfoaluminate hydrates, which promote an early development of mechanical

58   properties [6].

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61   The molar aluminate-to-sulfate ratio (C_3A/SO_3) is a key parameter that regulates the

62   accelerator reaction. Ettringite is the main hydrate formed if the C_3A/SO_3 ratio is

63   between 0.67 and 0.90 [6]. This is hardly ever the case in accelerated matrices since

64   the additional amount of aluminate ions provided by accelerators generally leads to an

65   undersulfated condition, characterized by C_3A/SO_3 ratios higher than 0.90. In this

66   context, sulfates deplete rapidly, ettringite starts to be consumed by C_3A hydration

67   and converts into monosulfoaluminate [7,8]. The early formed monosulfoaluminate

68   covers cement particles and fills up the space available in the matrix. This decreases

69   the rate and extent of alite hydration, producing lower compressive strengths at later

70   ages [6] [9].

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73   To mitigate such effect, the construction industry developed new formulations of

74   alkali-free accelerators, which contain sulfate ions in their composition to balance the

75   C_3A/SO_3 ratio. However, mixes with these accelerators may still behave as

76   undersulfated [3,6,10] so that extra doses of sulfate are required to control C_3A and

77   C_4AF hydration. A proper addition of gypsum to the cement or the composition of the

78   matrix may provide a valid and inexpensive extra source of sulfates to change the

79   C_3A/SO_3 ratio towards an optimum compatibility with the accelerators.

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82   Little attention has been paid to the improvement of the composition of the matrix,

83   whereas efforts have focused on the improvement of the accelerator formulation.

84   Consequently, there is still space left for improving the matrix-accelerator

85   compatibility by defining better matrices. This study explores such approach and

86   assesses its validity. The main objective here is to evaluate the influence of the

87   gypsum content on the hydration behaviour and on the mechanical strength

88   development in sprayed mixes containing accelerators.

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91   An experimental program was conducted with sprayed pastes and mortars produced

92   with one type of cement, two types of accelerator and three different sulfate contents.

93   Powder X-ray diffraction (XRD), isothermal calorimetry and scanning electron

94   microscopy (SEM) were performed to evaluate the kinetics and mechanisms of

95   hydration. Needle and pin penetration resistance and compressive strength were

96   measured to evaluate the evolution of mechanical properties. To complete the

97   analysis, water accessible porosity (WAP) was also determined in sprayed mortars.

98

99

100   All tests were performed with sprayed mixes because the mixing process of

101   accelerated matrices significantly influences the reactivity of accelerators and the

102   morphology of the hydrates formed [10]. Results obtained to provide a better

103   understanding of how the sulfate balance in sprayed matrices influences their

104   hydration and mechanical properties. Furthermore, they provide useful criteria for the

105   design of cement and matrices specific for spraying, aiming to improve the

106   compatibility with the accelerator.

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109   **2. Experimental Program**

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112   Figure 1 presents the diagram of the experimental program conducted in this study.

113   Tests were performed with sprayed pastes and mortars at the Laboratorio de

114   Estructuras Luis Agulló at the Polytechnic University of Catalonia (UPC) and at the

115   Scientific and Technological Center from the University of Barcelona (CCIT-UB).

116   The spraying procedure was based on recent publications by Galobardes *et al* [1,11]

117   in sprayed materials and by Salvador *et al* [6,10] in sprayed pastes and mortars.

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119

120   Figure 1. Diagram of the experimental program conducted in the study

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123   *<Insert Figure 1>*

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2.1. **Materials**

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129 An ordinary Portland cement type I (CEM I 52.5R) was used in this study. Table 1

130 presents its chemical composition and phase composition determined by XRF

131 spectrometry and XRD-Rietveld refinement, respectively. Its total sulfate ion (SO_4^{2-})

132 content was 4.23 % by weight and it was determined by dissolving 1.00 g of cement in

133 10.00 g of concentrated HNO_3 (65 %), according to [14]. The resulting solution was

134 diluted in a 250 mL volumetric flask using deionized water (Mili-Q, 18 ohm) and

135 analyzed by ion chromatography.

136

137

138 Table 1. Cement composition and specific surface

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140

Chemical composition		Mineralogical composition	
Oxide	Content (%)	Phase	Content (%)
CaO	62.6	C_3S	58.3
SiO_2	19.9	C_2S	11.2
Al_2O_3	4.7	C_4AF	13.4
SO_3	3.5	C_3A_c	4.1
Fe_2O_3	3.3	C_3A_o	0.6
MgO	1.9	CaO	1.1
K_2O	1.0	$Ca(OH)_2$	1.7
TiO_2	0.2	$CaCO_3$	1.9
Na_2O	0.1	$CaSO_4.2H_2O$	2.1
P_2O_5	0.1	$CaSO_4.0.5H_2O$	4.4
MnO	0.0	K_2SO_4	0.0
LOI	2.9	$K_2Ca(SO_4)_2 \cdot H_2O$	1.1
		MgO	0.0
		$MgCO_3$	0.0
		Total	99.9
Specific Surface BET (m^2/g)	2.96		

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142   In addition to table 1, the particle size distribution determined laser diffraction of the

143   cement employed is shown in figure 2.

144

145   Figure 2. Particle size distribution

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148   *<Insert Figure 2>*

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151   Distilled water and the Sikaplast® T1120 superplasticizer based on a polycarboxylate

152   solution (34% of solid content) were also employed. In field conditions, the

153   superplasticizer promotes the workability and pumpability of the mix. The same

154   superplasticizer was employed in [1,3,10] for laboratory tests with sprayed matrices.

155

156

157   A limestone aggregate with a density of 2.32 g/cm^3 and with an absorption of 5.46%

158   was used in the mortars. To avoid blockages of the spraying equipment, the particle

159   size distribution of the aggregate ranged from 0 mm to 1.25 mm.

160

161

162   Table 2 shows the chemical composition of the alkali-free accelerator (AF) and the

163   alkaline accelerator (AR) evaluated in this study. Both accelerators correspond to

164   formulations commonly found in underground constructions.

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166

167   Table 2. Chemical composition of accelerators

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Characteristics (mmol/g$_{cement}$)	AF	AR
Solid content (%)	47.6	43.0
Dosage (% bcw)	5.0	3.0
Al$_2$O$_3$ (%)	13.5	24.0
SO$_4^{2-}$ (%)	21.0	-
Na$_2$O (%)	-	19.0
pH at 20°C	3.0	12.0
Al$_2$O$_3$/SO$_4^{2-}$ molar ratio	0.6	-
Al$_2$O$_3$/Na$_2$O molar ratio	-	1.3

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173   2.2. **Mix Composition**

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176   The composition of the mixes selected was based in recent publications [1,3,10,11]. In

177   pastes, a water/cement (w/c) ratio of 0.32 was adopted. The superplasticizer dosage

178   was 1.0 % by cement weight (% bcw), according to the recommendation of the

179   supplier. The AF accelerator was added at 5.0 % bcw and the AR accelerator at 3.0 %

180   bcw. Both dosages were determined according to the procedure described in [1] to

181   assure equivalent mechanical performance in pastes.

182

183

184   Mortars contained the same accelerators dosages as cement pastes. They had a

185   sand/cement ratio of 1.7 by weight, w/c ratio equal to 0.51 and also contained

186   superplasticizer at the dosage of 1.0 % bcw. This composition presented an adequate

187   workability for pumping and spraying (spread diameter equal to 300 mm with no

188   bleeding, measured according to [12]). Although different w/c ratios were used for

189   pastes and mortars, the tendencies in the chemical and mechanical behaviour observed

190   are equivalent, because results are evaluated in a comparative manner depending on

191   the gypsum content.

192

193

194   In pastes and mortars, additional gypsum was included to evaluate the influence of

195   different sulfate contents on the chemical and mechanical performance of the matrix.

196   Three different mixes were produced for each accelerator. Reference mixes (REF)

197   contained only the sulfate of the cement (no additional gypsum was added). The ideal

198   dose of gypsum (ID) corresponds to the amount of sulfate necessary to react with all

199   the aluminate ions from the accelerators to form ettringite (Al/SO_4^{2-} equal to 0.66),

200   without consuming gypsum from the cement. This ratio in the mixture is calculated

201   according to equation 1.

202

203

$$\frac{Al_{(accelerator)}}{SO_4^{2-}\,_{(accelerator)} + SO_4^{2-}\,_{(additional\ gypsum)}} = 0.66 \qquad \text{Equation 1}$$

204

205

206   The excess of gypsum (GE) corresponds to the additional amount of sulfate necessary

207   to obtain ettringite as the final product from the reaction of the aluminate ions from the

208   accelerator and from C_3A hydration. The amount of gypsum necessary to fulfil that

209   requirement was calculated using equation 2.

210

211

$$\frac{Al_{(accelerator)} + Al_{(C_3A)}}{SO_4^{2-}{}_{(cement)} + SO_4^{2-}{}_{(accelerator)} + SO_4^{2-}{}_{(additional\ gypsum)}} = 0.66 \qquad \text{Equation 2}$$

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214

215   In pastes, gypsum was incorporated as an addition to the other components,

216   in order to maintain the same water/clinker and accelerator/clinker ratios. In mortars,

217   gypsum replaced the corresponding amount of the aggregate, to maintain the same

218   solid/liquid ratio of the matrix, according to equation 3.

219

220

$$\frac{Aggregate + Additional\ Gypsum}{Cement} = 1.7 \qquad \text{Equation 3}$$

221

222

223   Table 3 presents the composition and nomenclature of each mix used in this study. The

224   total gypsum content in the matrix corresponds to the sum of gypsum from cement and

225   the additional gypsum used.

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227

228   Table 3. Composition and nomenclature of mixes

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Accelerator	Additional gypsum (% by cement weight)	Total gypsum (% by clinker weight)	Nomenclature pastes	Nomenclature mortars
	-	7.58	PAF_REF	MAF_REF
Alkali-free	1.54	9.12	PAFG(ID)	MAFG(ID)
	7.42	15.00	-	MAFG(GE)

	-	7.58	PAR_REF	MAR_REF
Alkaline	3.64	11.22	PARG(ID)	MARG(ID)
	11.96	19.54	-	MARG(GE)

2.3. **Mixing Procedure**

Pastes and mortars were prepared in a planetary mixer type 65/2 K-3 in single batches of approximately 40 litres per case studied (see Table 3). This amount of material was needed to comply with the requirements of the spraying equipment, to assure a homogeneous flow of matrix through the pumping system and to fill up the panels for the tests [10,13].

In pastes, the cement and 90% of the total amount of water were mixed for approximately 2 min. The remaining 10 % and the superplasticizer were pre-homogenized and the solution obtained was added and mixed for 2 minutes more. Then, the additional gypsum was added if applicable and all mixes were mixed for an additional 4 min. After that, pastes were kept at 20 ºC until the spraying with the accelerators, which took place 1 h after the beginning of the mixing process.

The delayed incorporation of accelerators was already adopted by [10,13] to reproduce the conditions found in applications of sprayed matrices. Notice that, in practice, matrices commonly have to be transported to the worksite prior to being sprayed with accelerators. This procedure also contributes to a clearer assessment of

255 the heat flow attributed to the accelerator reaction, which otherwise would overlap

256 with the heat released during the initial mixing of cement and water.

257

258

259 The production of mortars followed the same steps as for the pastes. The only difference

260 was the incorporation of the aggregates that took place at the moment of gypsum

261 addition for ID and GE mixes. After that, mortars were kept at 20 ℃ until accelerator

262 addition in order to follow the same procedure as in cement pastes. Finally, mortars

263 were sprayed with accelerators 1 h after the beginning of mixing.

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266 2.4. **Spraying Process**

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269 The wet-mix spraying process was used here since it is the most commonly employed

270 to spray concrete around the world [11]. Figure 3 presents the equipment, which

271 corresponds to a small-scale version of a concrete spraying system used in previous

272 research [10]. The whole spraying process was performed inside a climatic chamber at

273 the temperature of 20 °C and relative humidity of 90%.

274

275

276 Figure 3. (a) Spraying equipment in laboratory conditions and (b) diagram of

277 the process

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280   *<Insert Figure 3>*

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283   The mix was pumped by the helical pump UP-Pictor (item #1, Fig 3.a), connected to

284   the 3 HP-air compressor (item #2, Fig 3.a) and transported through the hose up to a

285   spray gun. This type of pump is adequate for fluids like cement pastes and mortars in

286   contrast with piston pumps that are indicated to handle fluids with coarser particles

287   [14]. It also assures a more constant flow of material, eliminating the pulsation effect.

288

289

290   Accelerators were added at the spray gun by an air-operated diaphragm pump type

291   P.025 (item #3, Fig 3.a) connected to a 2 HP-air compressor (item #4, Fig 3.a). This

292   type of pump presented a homogeneous suction for all accelerators, although their

293   viscosity varied according to their chemical composition.

294

295

296   Figure 4.a shows in detail the spray gun of the equipment. The mix enters by the main

297   pipe (item #1, Fig.4.a). Compressed air and accelerator entered by the inlets indicated

298   by items #2 and #3 in Figure 4.a, respectively. After that, they reached a chamber

299   (item #5, Figure 4.a) where both components were mixed. Finally, accelerators and

300   compressed air were homogenized with the cementitious matrix inside the nozzle

301   (item #6, Figure 4.a) and the resulting mix was sprayed into the square, metallic

302   panels. Figure 4.b shows the panels, whose dimensions and distribution inside the

303   climatic chamber were defined according to [15].

304

305

306   Figure 4. (a) Spray gun and (b) dimensions of the metal panels

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309   *<Insert Figure 4>*

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312   2.5. **Test methods**

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315   Table 4 presents the tests performed with sprayed pastes and mortars. Their

316   descriptions are presented subsequently. The moment of accelerator addition was

317   considered as the initial time (0 s) for all tests and results.

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319

320   Table 4. Tests performed on sprayed pastes and mortars

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Objective	Test	Age	Matrix	Specimen	Reference
Chemical characterization	Powder XRD	15 min and 1, 3, 12 h	Sprayed paste	Frozen and ground paste	[6,10]
	Isothermal calorimetry	0-24 h	Sprayed mortar	Fresh mortar	[6]
	SEM	15 min and 12 h	Sprayed paste	Freeze-dried paste	[6,10]
Mechanical properties	Needle penetration test	From 15 to 120 min every 15 min	Sprayed mortar	Mortar panels	[16]
	Pin penetration test	4, 6, 12 h	Sprayed mortar	Mortar panels	[17]
	Compression test	1, 3, 7, 28, 98 days	Sprayed mortar	Extracted cores	[18]
	Water accessible porosity	7, 28, 98 days	Sprayed mortar	Extracted cores	[19]

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326   Powder XRD was performed with the ID and REF mixes. The objective of this test

327   was to quantify the phases formed during hydration at early ages. Sprayed pastes were

328   frozen in liquid nitrogen to stop hydration at 15 min, 1 h, 3 h and 12 h after

329   accelerator addition. Then, they were crushed and ground to a maximum size of 63

330   μm. Pastes were not lyophilized because the stability and crystallinity of ettringite and

331   monosulfoaluminate could be compromised, as indicated by [20] .

332

333

334   A PANalytical X'Pert PRO MPD Alpha1 powder diffractometer in reflection Bragg-

335   Brentano θ/2θ geometry using Ni-filtered CuKα$_1$ radiation (λ = 1.5406 Å) with an

336   X'Celerator detector (active length of 2.122º) operating at 45 kV and 40 mA was

337   used. X-ray diagrams were obtained from 4 to 80 º2θ, using a step width of 0.017 º2θ

338   and 50 s per step, with a fixed divergence slit of 0.5º. Sample holders were spun at 2

339   rps. The diagrams obtained in the pastes were analyzed semi-quantitatively by

340   Rietveld analysis using the software X'Pert High Score Plus from PANalytical. All

341   structure models used for Rietveld refinement are shown in Table 5.

342

343

344   Table 5. Phase structures used for Rietveld refinement

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Phase	Formula	Crystal System	PDF Codes	ICSD	Ref
Alite	Ca_3SiO_5	Monoclinic	01-070-8632	94742	[21]
Belite	Ca_2SiO_4	Monoclinic (β)	01-083-0460	79550	[22]
Calcium Aluminate	$Ca_3Al_2O_6$	Cubic	00-038-1429	1841	[23]

Ferrite	Ca_2AlFeO_5	Orthorhombic	01-071-0667	9197	[24]
Gypsum	$CaSO_4^{2-}\cdot H_2O$	Monoclinic	00-033-0311	151692	[25]
Calcite	$CaCO_3$	Rhombohedral	01-083-0577	79673	[26]
Portlandite	$Ca(OH)_2$	Rhombohedral	01-072-0156	15741	[27]
Ettringite	$Ca_6Al_2(SO_4)_3\cdot(OH)_{12}\cdot26H_2O$	Hexagonal	00-041-1451	155395	[28]
Monosulfoaluminate	$Ca_4Al_2(SO_4)\cdot(OH)_{12}\cdot6H_2O$	Rhombohedral	--	24461	[29]

Isothermal calorimetry was conducted to analyze the kinetics of hydration of sprayed mortars. Tests were performed with approximately 15 g of mortar for 24 h at 20 °C using an I-cal 4000 isothermal calorimeter. The mortar was sprayed directly into the calorimeter cups and introduced in the equipment immediately after spraying.

SEM was performed in pastes at the ages of 15 min and 12 h after accelerator addition. This analysis was conducted in a JEOL JSM 7100F microscope at the voltage of 20 kV. Pastes were frozen in liquid nitrogen to stop hydration, dried in vacuum during 24 h and coated with carbon. Morphology of the phases was analyzed in fracture surfaces and their chemical composition was assessed by energy dispersive X-ray analysis.

Needle penetration test was used to determine the penetration resistance of sprayed mortars until 2 h after accelerator addition. The test consisted of five penetrations of a needle into the mortar with a constant velocity of 60 mm/min until the penetration of 25 mm was reached. The result of force is divided by the sectional area of the needle to obtain the penetration resistance. Initial and final setting times were determined when the penetration resistance reached 3.5 MPa and 27.6 MPa, respectively.

369

370   Pin penetration test was employed to assess the indirect compressive strength of

371   sprayed mortars from 4 to 12 h after accelerator addition. The device used was a

372   Windsor® WP-2000 gun with a pin of 3 mm of diameter and 30 mm of length. Each

373   measurement corresponded to the average of 3 penetrations at each age. The indirect

374   compressive strength was calculated by a correlation table provided in [30].

375

376

377   Compressive strength was assessed in mortar cores measuring 25 mm in diameter and

378   50 mm in length. Cores were extracted from the sprayed panels 24 h after finishing

379   spraying and cured in water until the day of the test. Six cores were tested at each age,

380   using a universal test machine with a pressure application rate of 0.45 MPa/min.

381

382

383   Water accessible porosity was determined with spray mortars according to [19]. Cores

384   were extracted and cured following the same procedure of compressive test until the

385   age of the test (7, 28 and 98 days). Three specimens by age and mixture were

386   immersed in water for three days and their saturated weight (W_s) was measured after

387   that. Then specimens were dried at 60º C during five days and their dry weight (W_d)

388   was determined. Water accessible porosity was calculated with equation 4.

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$$\text{Water accessible porosity} = \frac{W_s - W_d}{W_d} \qquad \text{Equation 4}$$

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3. Results and discussion

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3.1. Chemical characterization

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Powder X-Ray Diffraction

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Figure 5 shows the evolution of the phase composition in sprayed pastes during the

first 12 h of hydration. To simplify the analysis, only gypsum (Fig 5.a), ettringite (Fig

5.b), alite (Fig 5.c) and portlandite (Fig 5.d) are presented. Slow reacting phases

(belite and ferrite) were not included.

407

408

Figure 5. Evolution of the content of the main phases found in sprayed paste: (a)

Gypsum, (b) Ettringite, (c) Alite and (d) Portlandite

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412

<Insert Figure 5>

414

415

Figure 5.a reveals that gypsum depletion in the reference paste occurs before the first

measurement was done (15 min after accelerator addition). In mixes PARG (ID) and

418   PAFG (ID), the same occurs between 3 and 12 h after accelerator addition. The

419   earlier depletion of gypsum observed in REF mixes may limit the formation of

420   ettringite by the reduction of sulfate concentration in the matrix.

421

422

423   Fig 5.b confirms this hypothesis. The additional gypsum regulates the fast sulfate

424   consumption caused by accelerators and promotes additional ettringite formation,

425   similarly to the observed by [6]. At 1 h of hydration, ettringite amounts in pastes PARG

426   (ID) and PAFG (ID) are 1.6 and 1.2 times larger than in the respective references. This

427   initial effect is stronger in paste PARG (ID) due to the absence of sulfate in the

428   formulation of the alkaline accelerator. Since ettringite is the main hydrate responsible

429   for the early mechanical properties of sprayed matrices [31], a better performance is

430   expected in ID mixes in comparison with the references.

431

432

433   Figure 5.c reveals that alite hydration is also affected by the gypsum amount added to

434   the system. In pastes PARG (ID) and PAFG (ID), with the additional gypsum, a

435   proper sulfate balance is achieved. Therefore, accelerated undersulfated C_3A reactions

436   and the consequent formation of AFm phases before the onset of alite hydration are

437   mitigated. Thus, the precipitation of AFm phases on the surface of cement particles is

438   limited [3]. As a result, alite hydration proceeds normally and higher degrees of

439   hydration are reached at 12 h in comparison with the reference pastes.

440

441

442   Figure 5.d shows that portlandite formation at 12 h of hydration in the ID mixes is

443   from 1.26 to 1.21 higher than the REF mixes. Portlandite formation is enhanced due

444   to the higher alite hydration in the ID mixes. In mixes PARG (ID) and PAR_REF, the

445   formation is higher than in PAFG (ID) and PAF_REF. This difference occurs because

446   the AR accelerator contains NaOH, which increases the concentration of OH^- ions in

447   the liquid phase and promotes portlandite precipitation [32].

448

449

450   *Isothermal Calorimetry*

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452

453   Figure 6 presents the heat of hydration curves of the 6 mixes. Figure 6.a and 6.b show

454   the heat of hydration from the accelerator peak that takes place in the period

455   comprehended between 0 and 0.5 h. Figures 6.c and 6.d show the heat flow until 24 h,

456   highlighting the main hydration peak that takes place between 4 h and 10 h. Table 6

457   shows the characteristic points of the heat flow curves, calculated according to [6].

458

459

460   Figure 6. Heat flow curves in cement mortars from 0 to 0.5 h with (a) alkaline

461   and (b) alkali-free accelerator and from 0 to 24 h in cement mortars with (c) alkaline

462   and (d) alkali-free accelerators

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464

465   *<Insert Figure 6>*

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Table 6. Characteristic points of the heat flow curves

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	Maximum heat-flow - accelerator peak (mW/g)	Slope - accelerator peak (mW/g*h)	Energy released - accelerator peak (J/g) [1]	Energy released - main peak (J/g) [2]	Maximum heat flow - main peak (mW/g)	Slope - main peak (mW/g*h)	Energy released until 24 h (J/g) [3]
MAR_REF	28.80	576.06	28.05	174.41	5.24	0.51	202.73
MARG (ID)	96.99	4974.66	39.91	197.30	4.02	0.51	204.11
MARG (GE)	97.34	3796.31	49.96	168.59	3.45	0.42	177.35
MAF_REF	33.71	693.60	27.33	160.77	3.83	0.47	186.87
MAFG (ID)	92.16	2632.03	54.96	171.07	3.63	0.42	192.40
MAFG (GE)	112.55	2206.56	67.36	138.73	3.27	0.39	171.88

471

472

[1] The energy released corresponds to the area under the heat flow curve from 0 to

0.5 h.

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476

[2] The energy released corresponds to the area under the heat flow curve from the end

of the induction period until the time when the heat flow reaches 1.1 mW/g of cement

in the deceleration period.

480

481

[3] The energy released corresponds to the area under the heat flow curve until the 24 h

minus the energy released in the accelerator peak.

484

485

486   The maximum heat flow, the energy released and the reaction rate during the

487   accelerator peak depend on the amount of gypsum in the mortar, as observed in Figure

488   6 and in table 6. The values of these parameters are around three times higher in

489   mortars ID and GE, when compared to the reference mixes. Likewise, mortars GE

490   present a higher maximum heat flow and reaction rate than mortars ID.

491

492

493   The reason for this behaviour lies on the exothermic reaction of accelerators. Since

494   ettringite precipitation is the main process that occurs due to accelerator reaction,

495   gypsum additions favour the formation of this hydrate by increasing the sulfate

496   concentration and, therefore, higher values of heat flow, reaction rate and energy

497   released are observed. These results are in agreement with the XRD analysis (Figure

498   5).

499

500

501   As shown in Figures 6.c and 6.d, the main hydration peak occurs several hours after

502   the accelerator peak and is the result of alite and C_3A hydration. The first process

503   forms portlandite and C-S-H, while the second generates ettringite. The shoulder

504   caused by the reaction of the C_3A is indicated by the arrows in the curves from

505   Figures 6.c and 6.d.

506

507

508   In reference mortars, the shoulder related with C_3A hydration overlaps with that

509   generated by alite hydration, indicating that both processes occur simultaneously.

510   Since reactions are exothermic, the maximum heat flow and the reaction rate in the

511   main hydration peak are higher in reference samples.

512

513

514   A retardation on the reaction of the C_3A is observed when additional gypsum is used

515   (mortars ID and GE). As the overlapping of the C_3A and alite hydration does not

516   occur, the main hydration peak is wider in ID mortars. Moreover, the use of the ideal

517   amount of gypsum increases the sulfate concentration and in consequence reduces the

518   formation of AFm and favouring additional alite hydration. Therefore, mixes with the

519   ideal gypsum content display the highest total energy released in the main peak. This

520   increase in the degree of hydration may lead to higher mechanical strengths at this age

521   in ID mixes.

522

523

524   The energy released during the main hydration peak in mortars GE is the lowest

525   because the large gypsum amount used in this mortar inhibits alite dissolution by the

526   common ion (Ca^{2+}) effect. Furthermore, as the aluminate and the silicate hydration

527   compete to fill the spaces available in the matrix, the large amount of ettringite

528   formed by accelerator reaction may reduce the space for the precipitation of the

529   hydration products formed by alite hydration. Therefore, the more reactive accelerator

530   reaction , limits the extent of alite dissolution and further hydration [33].

531

532

533   In the mixes with additional gypsum, the energy released in the accelerator peak of

534   mortars produced with the alkali-free accelerators is always higher than the equivalent

535   mortar produced with the alkaline accelerator. This occurs because the alkali-free

536   accelerator contains dissolved sulfate ions in its composition. Therefore, accelerator

537   reactivity is enhanced because it does not depend exclusively on the sulfates

538   generated by gypsum dissolution, which occurs when the alkaline accelerator is used.

539

540

541   The accelerator type also influences the main hydration process. When the alkali-free

542   accelerator is used, C_3A hydration is retarded when compared with the mixes

543   produced with the alkaline accelerator. That is observed by the shoulder in the main

544   hydration peak, which occurs at 8 and 9.5 h in mortars MARG (ID) and MAFG (ID),

545   respectively. As a result, the maximum heat flow, the reaction rate and the energy

546   released in the main hydration peak are reduced when the alkali-free accelerator is

547   used.

548

549

550   The results of isothermal calorimetry indicate that the inclusion of additional gypsum

551   may improve the reactivity of the mix. More energy was released during the

552   accelerator peak, indicating the formation of larger amounts of ettringite, which may

553   contribute to increasing the mechanical strength of the matrix after the accelerator

554   reaction. Furthermore, alite reactivity is enhanced when the ideal dose of gypsum is

555   used, which may improve the mechanical strength at late ages.

556

557

558   *Scanning Electron Microscopy*

559

560

561   Figure 7 presents the SEM images of pastes PAR_REF and PARG (ID) at 15 min and

562   12 h. The regions analyzed by EDS are indicated by a circle in the corresponding

563   image. EDS results are represented as relative intensities of each element, placed

564   above each image. The peaks considered to measure the intensity of Ca, Si, Al, S and

565   Na correspond to the energies of 3.7, 1.8, 1.5, 2.3 and 1.1 keV, respectively.

566

567

568   Figure 7. Microstructure of (a) PAR_REF at 15 min, (b) PARG (ID) at 15 min,

569   (c) PAR_REF at 12 h and (d) PARG (ID) at 12 h

570

571

572   *<Insert Figure 7>*

573

574

575   The microstructure observed in paste PAR_REF (Figure 7.a and 7.c) is

576   heterogeneous. Hydrates formed by accelerator reaction at 15 min (Figure 7.a) are

577   small plate-like precipitates. These hydrates are characterized by an Al/S ratio equal

578   to 1.2, which indicates an early formation of AFm phases. This was also observed by

579   [3,10] in cement pastes produced with alkaline accelerators.

580

581

582   However, when additional gypsum is employed, the microstructure of the matrix is

583   significantly altered, as observed in Figure 7.b. The hydrates formed are characterized

584   by an Al/S ratio equal to 0.58-0.67, which indicates that ettringite is the main product

585   formed by accelerator reaction and that gypsum remains in the matrix. The presence

586   of AFm phases in paste PARG (ID) was not observed at 15 min and is in line with the

587   results of XRD (Figure 5) and isothermal calorimetry (Figure 6), which indicate that

588   accelerated undersulfated C_3A reactions are mitigated by an increase of sulfate

589   concentration with the addition of gypsum.

590

591

592   At 12 h, the microstructure observed in paste PAR_REF (Figure 7.c) contained

593   hydrates formed as plate-like crystals, which are embedded in the matrix. The Al/S

594   ratio of the hydrates is equal to 0.98, which indicates they might be composed by

595   AFm phases. The presence of AFm phases in paste PARG (ID) was not found at 12 h

596   (Figure 7.d) and the microstructure of the aluminate hydrates continue to be needle-

597   like crystals, with an Al/S ratio equal to 0.62. This suggests that ettringite is stable

598   from 15 min to 12 h and that undersulfated C_3A reactions do not occur during this

599   period.

600

601

602   Figure 8 shows the microstructure of pastes PAF_REF and PAFG (ID) at 15 min and

603   12 h after the accelerator addition. In Figure 8.a, the PAR_REF reveals a mix of AFt

604   and AFm phases (Al/S=0.98) at 15 minutes of hydration. On the other hand, the

605   hydrates found in the mix PAFG (ID) at 15 min (Fig 8.b) were ettringite and gypsum

606   (Al/S=0.60-0.64). This tendency was maintained at 12 h, with Al/S ratios of 0.67 and

607   0.51 in the mixes PAF_REF and PAFG (ID), respectively. Except for the presence of

608   sodium introduced by the alkaline-accelerator, these results are similar to those found

609   for pastes with the alkaline accelerator.

Figure 8. Microstructure of (a) PAF_REF at 15 min, (b) PAFG (ID) at 15 min,

(c) PAF_REF at 12 h and (d) PAFG (ID) at 12 h

<Insert Figure 8>

3.2. Mechanical Properties

Needle Penetration Test

Figure 9 presents the average results of needle penetration resistance from 15 to 120

min after accelerator addition. It corresponds to the initial period of mechanical

strength development.

Figure 9. Average results of needle penetration resistance in sprayed mortars with the

(a) alkaline and (b) alkali-free accelerators

<Insert Figure 9>

635

636

637   The early development of mechanical strength depends on the additional gypsum

638   incorporated. As analyzed in isothermal calorimetry (Table 6), the ettringite amount

639   formed by accelerator reaction is directly proportional to the amount of gypsum

640   added. Since ettringite is the main hydrate responsible for the initial evolution of

641   mechanical strength [31], a higher penetration resistance is obtained by increasing the

642   sulfate concentration when gypsum is added to the matrix.

643

644

645   A different trend was observed in the slope (rate of increase of penetration resistance)

646   for both accelerator types. The slope of the estimated regression line is the highest in

647   ID mixes, followed by REF and GE mixes. This means that the rate of increase of

648   penetration resistance is higher when the ideal dose of gypsum is incorporated. This

649   happens because accelerator reaction is enhanced with the increase of the sulfate

650   concentration by the incorporation of gypsum.

651

652

653   The initial setting is reached before 15 min, at 40 min and after 60 min in GE, ID and

654   REF mixes, respectively. An enhancement of accelerator reactivity reduces the time

655   of the initial setting, according to the results of isothermal calorimetry. In line with

656   that, the reference mixes require more time to set and harden.

657

658

659   The final setting follows the same pattern of the initial setting. It occurs at 1.5 h, 2.2 h

660   and after 3 h in GE, ID and REF mixes, respectively. According to the isothermal

661   calorimetry results (Figure 6), GE mixes present the highest energy released during

662   the accelerator peak, which is translated into a higher penetration resistance observed

663   in these matrices.

664

665

666   *Pin penetration test*

667

668

669   Figure 9 shows the average results of indirect compressive strength at 4, 6 and 12 h

670   after the accelerator addition. This period corresponds to the main hydration peak in the

671   curves of isothermal calorimetry (Figure 6).

672

673

674   Figure 10. Average results of indirect compressive strength obtained with (a)

675   alkaline and (b) alkali-free accelerator

676

677

678   *<Insert Figure 10>*

679

680

681   Results obtained in this test are significantly influenced by the amount of gypsum in

682   the matrix. With both accelerator types, ID mixes presented the highest values of

683   indirect compressive strength during the period analyzed. This happens because C_3A

684   hydration is better controlled when the ideal amount of gypsum is used, increasing the

685   sulfate concentration and in consequence avoiding a retardation in alite hydration by

686   the early formation of AFm phases.

687

688

689   At 4h, mortars GE present a higher indirect compressive strength than reference

690   mortars because the ettringite amount formed is larger due the enhanced accelerator

691   reactivity caused by the sulfates in the gypsum addition. As hydration progresses, the

692   opposite tendency is observed due to the possible excess of porosity caused by the fast

693   setting of the GE mixes.

694

695

696   The mechanical strength from 4 to 12 h is directly proportional to the reaction rate

697   observed in the main hydration peak obtained by isothermal calorimetry (Figure 6).

698   The ID mixes present the highest mechanical strength during the period analyzed due

699   to the higher degree of alite hydration. At 12 h, the GE mixes present the lowest

700   indirect compressive strength because alite dissolution and hydration are suppressed

701   by the common ion effect (Ca^{2+} generated by gypsum dissolution) and by the large

702   amount of ettringite formed by accelerator reaction, as discussed in the isothermal

703   calorimetry results (figure 6).

704

705

706   *Compressive Strength*

707

708

709 In order to provide additional information to analyze the results of compressive

710 strength, the water accessible porosity results are shown in figure 10. An important

711 difference is observed in the values of water accessible porosity when the

712 concentration of sulfate is increased by the gypsum incorporation to the mortar. In all

713 the cases, GE mixes present the highest porosity, while the REF mixes present the

714 lowest. This follows the inverse order observed in the penetration resistance test

715 (Figure 9).

716

717

718 Figure 11. Average results of water accessible porosity in sprayed mortars with

719 (a) alkaline and (b) alkali-free accelerators

720

721

722 *<Insert Figure 11>*

723

724

725 When large gypsum amounts are employed, ettringite formation is favoured by the

726 increase of the sulfate concentration, reducing the setting time of the mortar. Due to the

727 fast setting, mortars do not consolidate properly and do not eliminate entrapped air

728 during the spraying process, which leads to higher porosities [9].

729

730

731 The reduction in the values of WAP from 7 to 98 days is the highest in GE mixes and

732 the lowest in REF mixes. This happens because the additional gypsum increases the

733 sulfate concentration and retards the conversion of ettringite to monosulfoaluminate

[7], which occurs with increases in porosity because ettringite has lower density and higher molecular volume than monosulfoaluminate [9]. Since alite hydration is not inhibited by undersulfated C_3A reactions, pores are filled by portlandite and C-S-H, reducing the total porosity of the matrix.

Figure 12 presents the average results of compressive strength obtained with extracted cores at 1, 3, 7, 28 and 98 days (time in logarithmic scale). Similarly, to the evaluation of water accessible porosity, compressive strength varies significantly in mortars with gypsum addition.

ID mixes present the highest compressive strength at all ages. As observed in XRD and isothermal calorimetry (Figures 5 and 6), mixes with the ideal amount of gypsum present a higher degree of hydration because accelerated undersulfated C_3A reactions are avoided and alite hydration proceeds normally.

Figure 12. Average results of compressive strength in sprayed mortars with (a) alkaline and (b) alkali-free accelerators

<Insert Figure 12>

759   Despite being less porous, mortars REF present smaller compressive strength than

760   mortars ID. In REF samples, AFm phases generated by undersulfated C_3A reactions

761   precipitate on the surface of cement particles. This decreases their solubility and

762   degrees of hydration, also reducing the compressive strength. The lowest values of

763   compressive strength are found in GE mortars because they have the highest porosity

764   (Figure 11).

765

766

767   **4. Conclusions**

768

769

770   The following conclusions may be derived from the results obtained in this study.

771

772

773   • The increase of sulfate concentration by the addition of gypsum in sprayed mixes

774   leads to a faster formation of ettringite by increasing the reactivity of alkali-free

775   and alkaline accelerators. Since ettringite is the main hydrate responsible for the

776   development of initial mechanical strength, an increase in the penetration

777   resistance of mortar is achieved. The effect is more relevant in matrices produced

778   with the alkaline accelerators because they do not contain sulfates in their

779   formulation.

780

781   • The use of a proper sulfate balance (ID mixes) in the matrix is a key factor to

782   optimize the reactivity and the mechanical properties of sprayed mortars

783   containing accelerators at short and long term. A significant improvement in

784   performance may be achieved in mixes with accelerator by using cement

785   specially designed for spraying or by incorporating gypsum as an addition. In the

786   present study, the best performance was obtained for mixes with C_3A/SO_3 equal

787   to 0.66, defined according to Eq. 1.

788

789

790   • The introduction of an excess of gypsum (GE mixes) suppresses alite dissolution

791   due to the common ion (Ca^{2+}) effect. It also causes the formation of the largest

792   amount of ettringite by accelerator reaction, which fills up the pores of the matrix

793   before the onset of the main hydration peak and leads to more porous matrices.

794   Therefore, the compressive strength of mortars GE is the lowest in the period

795   analyzed.

796

797

798   • The benefits of using an optimum dose of gypsum were observed in mixes with

799   alkali-free and alkaline accelerators. They were more evident in the latter due to

800   the absence of sulfates in the formulation of alkaline accelerators. Therefore, the

801   correction of the sulfate content by the gypsum addition in the mix is especially

802   advisable in case of using this type of accelerator.

803

804

805   **Acknowledgements**

806

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