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Improving circular economy by the valorization of non-conventional coal fly ashes in composite cement manufacturing

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Keywords: coal fly ash; coal combustion; spreader stoker; composite cements, eco-cement

Abstract

Spreader Stoker thermal power plants are initially used to burn bagasse during the sugarcane harvest, but also coal when the season is over. The drawback is that, compared to standard pulverized coal fly ashes, the coal fly ashes resulting from this process contain many more unburned particles. Therefore, Spreader Stoker Coal Fly Ash (SSCFA) is sent to landfill despite its potential for valorisation in construction. The main objective of this work was to evaluate the potential of laboratory manufactured composite cements incorporating SSCFA by using a variety of manufacturing methods, such as co-grinding/separate grinding of the components, and grinding of laboratory cements to equivalent global fineness. The behaviour in the fresh, hardening and hardened states was investigated to bring out the influence of Blaine specific surface and type of addition in different combinations of composite cements. Despite the high carbon content of the coal fly ash studied, the mechanical behaviour of SSCFA-cements was better than that of cement with the local pozzolan, which is the reference in Reunion Island. In addition, the use of slag and the pozzolan/SSCFA association in composite cements showed good results. An artificial neural network approach was employed to predict compressive strength in mortars with parameters such as amounts of clinker, gypsum, pozzolana, SSCFA and slag, and the Blaine specific surface. The results also enabled compressive strength response curves to be developed for mixes according to the amount of clinker in the cements.

1. INTRODUCTION

Several wastes and by-products have long been used in the manufacture of composite cements. For instance, fly ash, blast furnace slag and silica fume are used all over the world in partial replacement of clinker [1]. However, the exploitation of these by-products is usually regulated by standards, as is the case in Europe with standard EN 197-1 [2]. Currently, it is not possible to employ by-products indiscriminately and permitted ones must meet specific guidelines regarding physical and chemical properties [3].

On the one hand, local situations may exist where non-standard by-products could be used, although they do not meet all the requirements. Such is the case for Reunion Island, a small French island (2512 km²) that produces more than 30 000 tons of coal fly ash per year in its spreader stoker power plants. Despite their potential for valorization in construction having

40 been shown in previous studies [4, 5], these ashes (referred to as SSCFA for Spreader Stoker
41 Coal Fly Ashes) are currently sent to landfill because they do not comply with standard EN
42 450-1 [3] (fly ash standard) and EN 197-1 [2] (cement standard including, among others, coal
43 fly ash conform to EN 450-1), which covers only fly ashes obtained by burning pulverized
44 coal. SSCFA also contain a large amount of unburned carbon particles, far above that
45 recommended in the European Standard EN 450-1 for fly ash and EN 197-1 for the use of fly
46 ash in cements. Unburned carbon in fly ash could sometimes be detrimental to the rheology or
47 the air entrainment of the concrete [6, 7], or even responsible of some durability properties [8,
48 9]. Moreover, natural radioactivity fly ash might need to be assessed before their use for
49 cement manufacturing [10]. Although these issues must be addressed, SSCFA-based mortar
50 has shown interesting mechanical properties, with a strength activity index much higher than
51 the minimum value specified in standard EN 197-1, probably due to its high pozzolanic
52 activity.

53 On the other hand, Reunion Island has no cement plants. Clinker imported from other
54 countries is ground locally and mixed with a natural pozzolana to manufacture CEM II
55 cements. The use of fly ashes produced locally could lead to real progress in the sustainable
56 development of the island, since their rational valorization could simultaneously decrease the
57 amounts of clinker to be imported, of pozzolana exploited and of SSCFA sent to landfills.

58 This kind of by-products will probably be increasingly used in the future for the manufacture
59 of cements, in order to reduce the carbon impact of ordinary Portland cement and improve the
60 circular economy. Reducing clinker content is one of the ways possible to achieve carbon
61 neutrality, as stated in several roadmaps published in the literature (see for instance [11]).

62 The aim of this paper is thus to illustrate how a non-conventional fly ash could be used to
63 develop a composite cement. It investigates the reuse of SSCFA in such an application. The
64 first part will describe the grinding methods applied to make the laboratory composite cement.
65 Then, a brief characterization of these manufactured cements will be reported, along with the
66 evaluation of fresh, hardening and hardened properties of cement pastes and mortars. Finally,
67 an approach using Artificial Neural Networks (ANN) will be presented to predict the 28-day
68 compressive strength on mortars of the composite cements manufactured in the laboratory.

69 2. MATERIALS AND METHODS

70 2.1. Materials

71 The high carbon coal fly ashes studied were produced in a power plant located in Reunion
72 Island, which uses a spreader stoker type boiler. The power plant burns bagasse during the
73 sugarcane harvest and produces ashes that are already reused in other applications. For the
74 rest of the year, imported coal is burned instead of bagasse, producing SSCFA that are then
75 landfilled. SSCFA have been characterized in previous studies, showing many similarities

76 with standard pulverized coal fly ashes but also some differences, such as the amount of
 77 unburned carbon [4, 5]. This is why it can be related to high carbon coal fly ash.

78 Clinker, gypsum, slag and natural pozzolana used to manufacture the laboratory composite
 79 cements were the same as the local materials (constituent from commercial cements in
 80 Reunion Island, LafargeHolcim). The sand used in mortar production was normalized quartz
 81 sand conforming to EN 196-1 [12].

82 The chemical compositions, including the percentage of unburned particles (LOI: Loss On
 83 Ignition), and the physical characteristics of the materials selected for this study are detailed
 84 in Table 1. SSCFA have a composition approaching that of silico-aluminous fly ashes from
 85 pulverized coal thermal power plants, with 80 wt% of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ when the
 86 unburned content is excluded from the calculation. This unburned content is very high
 87 compared to that of class F fly ashes [4,13,14].

88

89 *Table 1: Chemical composition (wt%) and physical characteristics of materials used to*
 90 *manufacture composite cements*

Oxide wt%	Clinker	SSCFA	Pozzolana	Slag	Gypsum
SiO_2	20.9	35.9	52.3	34.5	0.6
Al_2O_3	5.1	20.6	16.0	12.6	0.2
CaO	65.7	4.3	5.5	37.5	38.0
Fe_2O_3	3.4	3.4	11.0	0.8	0.1
K_2O	0.4		2.0	0.8	0.0
Na_2O	0.2	0.2	3.8	0.3	0.0
MgO	2.0	0.9	2.4	9.6	0.0
MnO_2	0.1		0.3	0.3	
TiO_2	0.3	1.2	2.1	0.4	0.0
P_2O_5	0.1	1.8	0.4	0.0	
F	0.0	0.0	0.0	0.9	
SO_3	0.6	0.7	0.1	0.1	53.5
LOI	1.3	31.1	4.2	2.1	7.4
Specific gravity (g/cm^3)	3.19	2.16	2.66	2.85	2.32
Blaine specific surface (cm^2/g)	3600	5500	5700	4100	6100

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92 2.2. Methods

93 The chemical composition was determined by inductively coupled plasma-optical emission
 94 spectrometry (ICP-OES, Optima 7000 DV). The sample preparation used for chemical

95 analyses was based on borate fusion. A mixture of fly ash, lithium tetraborate and lithium
 96 metaborate was placed in a muffle furnace at 1100°C for 30 min. The melt was then carefully
 97 dissolved in diluted nitric acid before ICP–OES analyses. The loss on ignition was determined
 98 at 1000 °C according to EN 196-2 [15]. Specific gravity was found by hydrostatic weighing
 99 and the Blaine method was used to determine the specific surface (EN 196-6) [16]. The
 100 laboratory cements were ground in a 1L planetary ball mill (CONTROLS model D461/C)
 101 with 90 ceramic balls around 15 mm in diameter. Consistency and setting time tests were
 102 carried out on pastes with various water to binder (W/B) ratios in order to reach the same
 103 consistency [2]. The mortars were cast in 4*4*16 cm moulds according to EN 196-1. The
 104 tests on cement pastes and mortars included normalized consistency (EN 196-3) [17], setting
 105 time (EN 196-3), flowing time on mortars (NF P 15-437) [18] and compressive strength on
 106 mortars (EN 196-1). Compressive strength was measured at 7, 28 and 90 days on 4x4x16 cm
 107 prisms (loading speed of 2 400 N/s ± 200 N/s) according to EN 196-1.

108

109 2.3. Manufacture of laboratory cements

110 Several options were possible for the choice of composite cements to manufacture, according
 111 to the reference table from standard EN 197-1, which shows the current cement families [2].
 112 Table 2 gives the names and details of the composite cements manufactured for this study. In
 113 this table, the numbers represent the percentages by weight for the components concerned
 114 (these values are within the allowed range specified in EN 197-1).

115 The cements marketed in Reunion Island are essentially CEM II/A-P and CEM II/B-P, which
 116 are composite cements with natural pozzolana. In order to be consistent with the properties of
 117 cements on the market, it was thus essential to compare SSCFA versus pozzolana additions,
 118 but also go deeper into the research to suggest different types of composite cements based on
 119 slag, pozzolana and fly ashes. It should be noted that the reference cements CEM II/A-P and
 120 CEM II/B-P were manufactured in the laboratory in order to have the same conditions of
 121 production as the new cements made with SSCFA. As will be explained in the following
 122 parts, for the composite cement manufactured at a laboratory scale, three grinding methods
 123 were used, each having a specific objective.

124

Table 2: List and composition of manufactured cements

Cement designation	Clinker	Slag	Pozzolana	Fly ash (SSCFA)	Gypsum
	K (wt%)	S (wt%)	P (wt%)	V (wt%)	G (wt%)
II/A-P15	83	-	13	-	4
II/A-V15	83	-	-	13	4
II/A-V20	78	-	-	18	4
II/A-M (P5-V15)	78	-	4	14	4

II/B-V25	73	-	-	23	4
II/A-M (P5-V20)	73	-	4	19	4
II/B-P30	68	-	28	-	4
II/B-V30	68	-	-	28	4
II/B-V35	63	-	-	33	4
II/A-M (P10-V25)	63	-	9	24	4
V/A-S20-V20	58	19	-	19	4
V/A-S20-P20	58	19	19	-	4
V/A-S20-P10-V10	59	19	9	9	4
V/A-S20-P10-V20	49	19	9	19	4

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2.3.1. Separate grinding

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Each ingredient (clinker, pozzolana, slag, gypsum) was ground separately before the mixture was homogenized in the mill for around 1.5 min. Specific gravity and final specific surface values are specified in Table 1 for the components of manufactured composite cements. Clinker and slag were milled to a fineness considered sufficient for good reactivity, i.e. about 3500 cm²/g for clinker and about 4000 cm²/g for slag [19-21]. Note that grindability refers to the speed and ease with which the material can be ground here. In our case, slag seemed to be more grindable than clinker, with a higher specific surface for an equivalent grinding time. However, according to the literature, slag usually presents lower grindability than clinker [19]. The pozzolana was crushed to achieve a Blaine specific surface equivalent to that of SSCFA, i.e., close to 5500 cm²/g. Considering the high grindability of gypsum, its fineness was set at 6100 cm²/g after just 5 minutes of grinding. The main advantage of this kind of grinding is the possibility of controlling the initial fineness of each constituent of the cement-

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2.3.2. Co-grinding

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The co-grinding method consists of weighing and inserting the different constituents of the cement directly into the mill and grinding them together. A co-grinding time of 35 minutes was chosen through a preliminary test carried out on the CEM II/A-P15 reference cement that was manufactured. The objective was to determine the time required to obtain a Blaine specific surface of approximately 3500 cm²/g, which is the value for the cements currently on the market in Reunion Island.

The reason for "co-grinding" materials for a fixed duration was to verify whether the use of SSCFA was more advantageous for this type of grinding in a cement plant. It allowed us to check whether better fineness and results in terms of workability and compressive strength could be obtained compared to pozzolana cement with an equivalent grinding duration. For this study, the main disadvantages of this grinding method were the difficulty of exploiting the results scientifically and making comparisons between the different cements, as only the

152 final Blaine specific surface was known. Moreover, given the grindability differences among
153 constituents (clinker, fly ash, pozzolana, slag and gypsum), the behaviour of each during the
154 grinding was difficult or impossible to identify.

155 2.3.3. Equivalent global fineness grinding

156 The last method used consisted of two steps: first, separate grinding as for the separate
157 grinding method, then co-grinding of the components in order to reach a targeted and constant
158 global fineness (Blaine specific surface) for all the composite cements tested.

159 The cement with the highest expected final Blaine specific surface value, namely cement with
160 35% SSCFA, was the first prepared using this method. This Blaine specific surface was taken
161 as the target value. This cement was chosen because it contained the largest amount of
162 SSCFA, the particles of which had a specific Blaine specific surface about twice that of the
163 ground clinker. Then, the other cements were obtained by co-grinding their respective
164 components (after the separate grinding of each component) until the target Blaine specific
165 surface value was reached. This method avoided sub-grinding constituents such as clinker,
166 while ensuring a final fineness close to the same value for all cements (that is why it is
167 referred to as equivalent global fineness grinding).

168 The interest here is to show the effect of replacing the clinker while keeping the same fineness
169 for the different cements produced. The disadvantage of this type of grinding is that,
170 depending on the co-grinding duration needed to reach the desired fineness, there is deviation
171 from the initial fineness of the different materials, especially those for which the grindability
172 is high. For example, a CEM II/A, which contains 83% clinker, 13% SSCFA and 4% gypsum,
173 requires much longer co-grinding than a CEM II/B, which contains 70% clinker and 30%
174 SSCFA (cf. part 3.2.3). This higher co-grinding duration will therefore have a direct impact
175 on gypsum and SSCFA, which have high grindability in comparison with clinker or slag (see
176 grindability of materials in Figure 1). This observation is discussed in more detail in the
177 following part.

178

179 3. RESULTS AND DISCUSSION

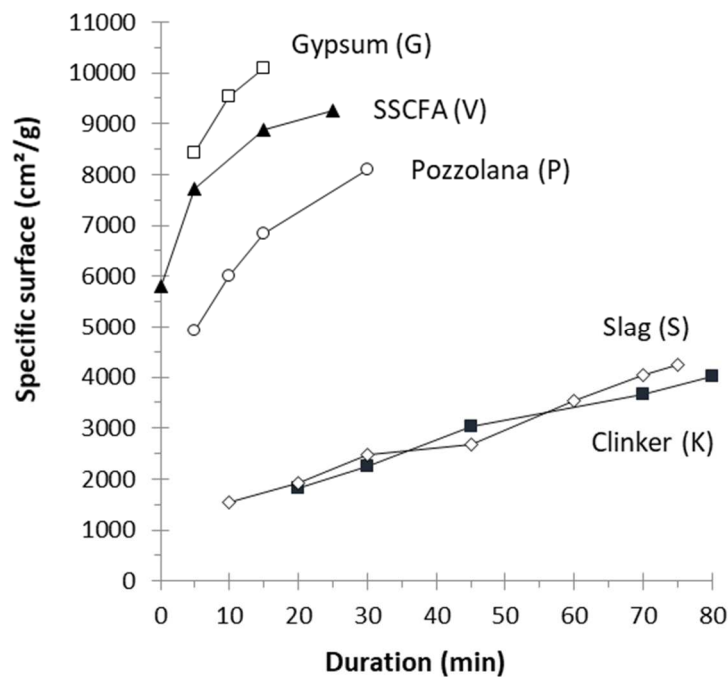
180 3.1. Influence of grinding time on fineness of binder components

181 Figure 1 shows the evolution of specific surfaces according to the duration of grinding for the
182 components tested. The mass introduced into the mill was arbitrarily fixed at 600 g in order to
183 keep the same reference value for all the components tested and ensure good repeatability.
184 After the grinding step, the specific surface of each component was evaluated according to
185 EN 196-6.

186 In order to better understand the grinding behaviour of each material used for the manufacture
187 of laboratory cements, their specific surfaces were assessed after various grinding times and

188 the grindability was assessed from the slope of the curve. From the results presented in Figure
 189 1, a much lower grindability can be observed for clinker, the main constituent of Portland
 190 cements, and for slag, which is very close. The pozzolana was brought back into the same
 191 range of fineness as the SSCFA after a few minutes of grinding. Gypsum was the material
 192 with the finest particles among the binders tested; it reached 10 000 cm²/g after 15 minutes of
 193 grinding.

194 Differences in grinding behaviour were observed in terms of both grindability and final
 195 fineness obtained. Actually, SSCFA reached a specific surface of around 8000 cm²/g after 5
 196 min of grinding, as for gypsum. However, by looking at the slopes of their respective curves
 197 between 5 and 15 min, it can be noted that the SSCFA presented slower kinetics of grinding,
 198 which seemed to decrease further for times longer than 15 min. For pozzolana, a rather linear
 199 grinding curve was observed up to 20 min, then grindability decreased after 30 min to reach a
 200 specific surface around 8000 cm²/g. The slag and the clinker showed a linear behaviour
 201 through 80 min of grinding with a specific surface reaching around 4000 cm²/g and a slightly
 202 higher grindability for the slag.



203

204

Figure 1: Specific surface versus grinding time for the materials investigated

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3.2. Impact of grinding method on cement fineness through Blaine specific surface

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3.2.1. Impact of separate grinding on fineness

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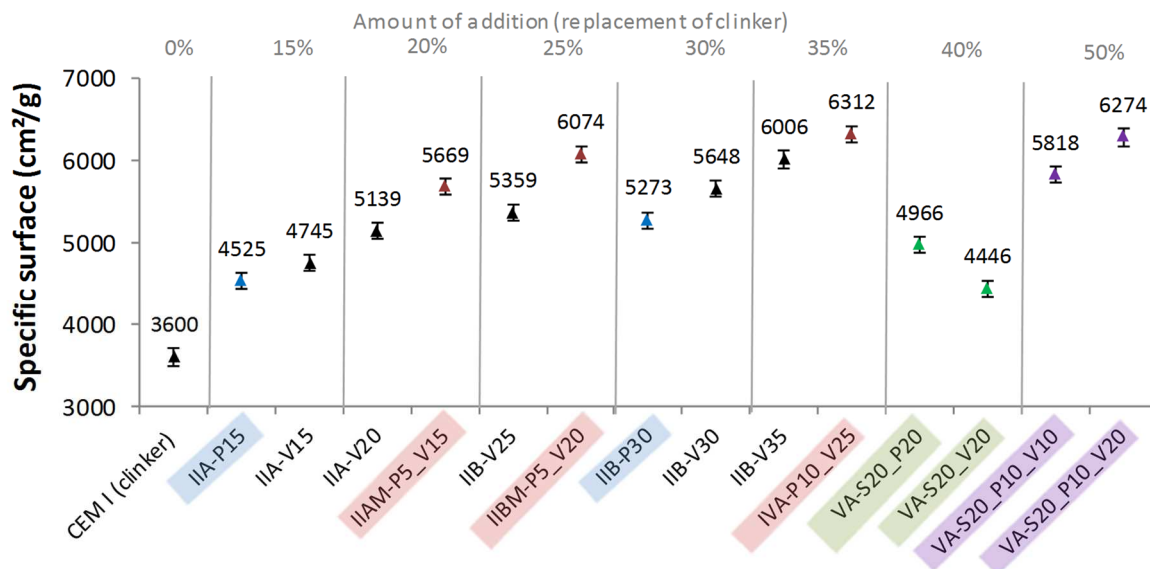
The specific surface values of the cements manufactured by the separate grinding method are shown in Figure 2. For this method, the different materials were crushed beforehand in order

210 to reach specific fineness objectives (cf. part 2.3.1). We recall that the pozzolana was ground
 211 to a fineness approaching that of SSCFA (5700 cm²/g). Clinker (3600 cm²/g), slag (4100
 212 cm²/g) and gypsum (6100 cm²/g) were ground to a specific surface value considered sufficient
 213 to obtain good reactivity in the binders investigated.

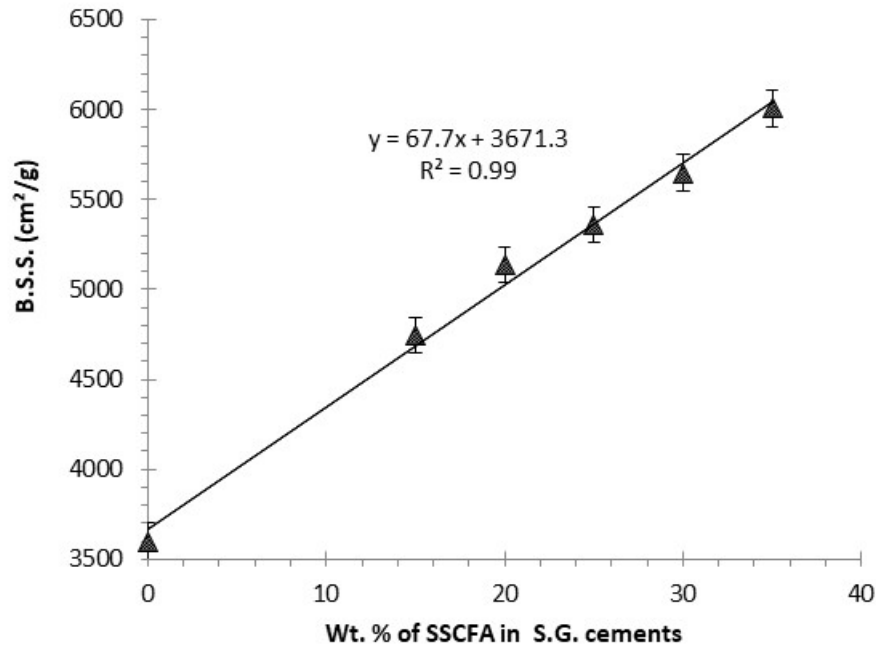
214 Good correlation was observed between the increase of specific surface and the increase of
 215 SSCFA percentage in the different compositions. As shown in Figure 2, this was true not only
 216 for binary cements (SSCFA alone, represented by the black triangles), but also for ternary
 217 cements (SSCFA/pozzolana in red triangles) and quaternary cements (slag/pozzolana/SSCFA
 218 in purple triangles). Figure 3 also highlights this correlation by showing a linear relationship
 219 between the amount of SSCFA and the specific surface of the cement ($R^2=0.99$).

220 Moreover, it can be noted that the specific surfaces of cements with SSCFA were greater than
 221 those of cements with pozzolana (for binary cements and also for ternary cements in green
 222 triangles on Figure 2), despite the fact that the initial fineness values were equivalent for these
 223 two materials. This might be explained by the homogenization step when making the mixtures
 224 (see part 3.1), during which SSCFA, more crushable than pozzolana at this stage, would lead
 225 to a greater fineness for a given duration of grinding. The larger specific surface difference
 226 between SSCFA and pozzolana cement obtained at 30% replacement (compared to 15%
 227 replacement) seems to confirm this hypothesis.

228 SSCFA/pozzolana composite cements (in red triangles) tended to have higher specific surface
 229 values than SSCFA cements (in black) for different clinker replacement rates. This could be
 230 due, as for the co-ground cements, to a better granular arrangement [19], with higher specific
 231 surface here because the materials were ground beforehand.



232
 233 *Figure 2: Blaine Specific Surface of the composite cements obtained by the separate*
 234 *grinding method*



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236
237

Figure 3: Correlation between the percentage of SSCFA and the Blaine specific surface of composite cements

238 3.2.2. Impact of co-grinding on fineness

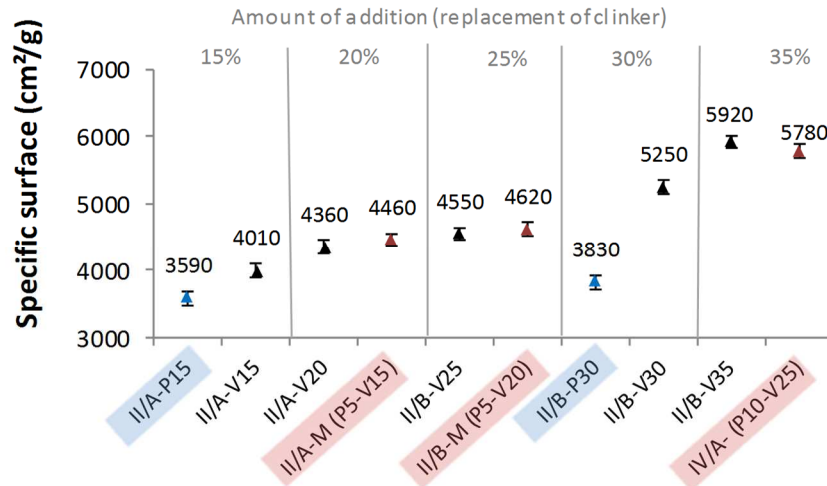
239 We recall that the main objective was to achieve the same fineness as that of the CEM II/A-
240 P15 cement commercially available on Reunion Island, which is about 3600 cm²/g. The
241 grinding time needed to reach this value was therefore assessed. Then, the grinding duration
242 obtained was imposed on all the other mixtures in order to evaluate the influence of the
243 quantity and nature of additions for a fixed grinding duration.

244 Figure 4 presents the results of the specific surfaces obtained for 10 different cements. An
245 increase in the specific surface was observed with the percentage of clinker replacement. This
246 result was expected, as the clinker was less easy to grind than the other materials tested
247 (except slag as shown in Figure 1). Therefore, its replacement during co-grinding resulted in a
248 double effect: on the one hand, a reduction of the less grindable part of the mixture and, on
249 the other hand, an increase of the material proportion that was easier to grind.

250 Higher specific surface and better grindability of cements with SSCFA (black triangles in
251 Figure 4) than with pozzolana (blue triangles in Figure 4) were noted. The difference in
252 specific surface was observed to be much higher at 30% replacement of clinker than at 15%.
253 This was due not only to the fact that SSCFA are already in powder form before grinding, but
254 probably also because their grindability is greater than that of pozzolana, as seen in Figure 1.

255 In addition, composite cements with both SSCFA and pozzolana (red triangles in Figure 4)
256 tended to have a slightly higher specific surface than those with SSCFA only. However, this
257 trend was not verified at 35% replacement of clinker. This phenomenon could be explained by
258 a better granular arrangement of the grains, reducing the permeability of the powder bed of

259 the mixtures during the measurement of specific surface [19, 21]. In fact, clinker is less
 260 crushable than pozzolana (cf. part 3.1), which itself is less crushable in this mixture than
 261 SSCFA (already in pulverulent form), a more compact distribution of particles could have
 262 been obtained as for a concrete granular skeleton [19].

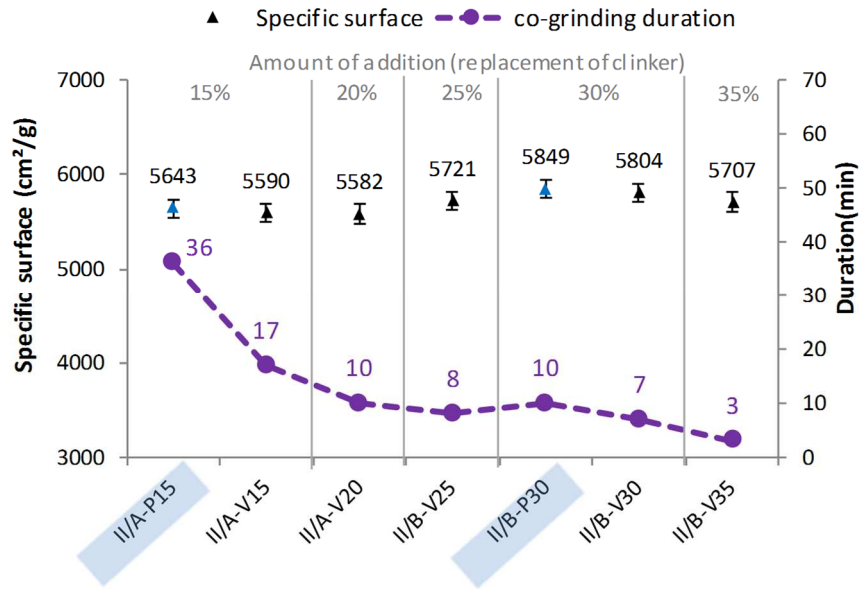


263 *Figure 4: Blaine Specific Surface of the composite cements obtained by the co-grinding*
 264 *method*
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267 3.2.3. Impact of equivalent global fineness grinding

268 For the equivalent global fineness method, the different cements were ground to equivalent
 269 specific surfaces. The slight variation observed in fineness can be explained by the difficulty
 270 of obtaining accurate specific surface values with this method. From the results shown in
 271 Figure 5, it can be observed that co-grinding duration decreases with the clinker replacement
 272 rate and is higher for pozzolana-based cements than for those with SSCFA. It can also be
 273 noted that the amount of clinker has greater influence on co-grinding duration when cements
 274 with 15% replacement (II/A-V15 versus II/A-P15) are compared with those having 30%
 275 replacement (II/B-P30 versus II/B-V30). This result confirms the ones obtained in part 3.1
 276 and shows the interest of using SSCFA instead of pozzolana for a substantial saving of
 277 grinding energy, as the grinding duration needs to be doubled for II/A-P15 compared to II/A-
 278 V15 cements.



279
280 *Figure 5: Blaine Specific Surface of the composite cements obtained by the equivalent*
281 *global fineness grinding method*

282

283 3.3. Fresh and hardening properties

284 3.3.1. Workability of mortars

285 The effect of the different components of composite cements on mortar workability was
286 assessed by measuring the flowing time with LCL apparatus [18]. The flowing time results for
287 mortars based on cements obtained only with the separate grinding method are shown in
288 Figure 6. The aim here is to observe the influence of addition incorporation and nature on
289 flowing time by increasing the percentage of clinker replacement from 0% to 50%. The
290 results show that the replacement of clinker by addition led to an increase in the flowing time,
291 thus reducing the workability of mortars. In fact, all the flowing times measured were longer
292 than the one obtained for the mortar composed of CEM I (2 seconds).

293 An increase of 15 to 30% of clinker replacement by pozzolana (blue) did not increase the
294 flowing time significantly. For mixtures with SSCFA (black), a large increase in the flowing
295 time was observed for a replacement rate of 30% and 35%. In terms of workability, an upper
296 limit of 25% for the use of SSCFA seems to be reasonable (7 seconds). At this point, using
297 plasticizers would be almost inevitable for proper workability.

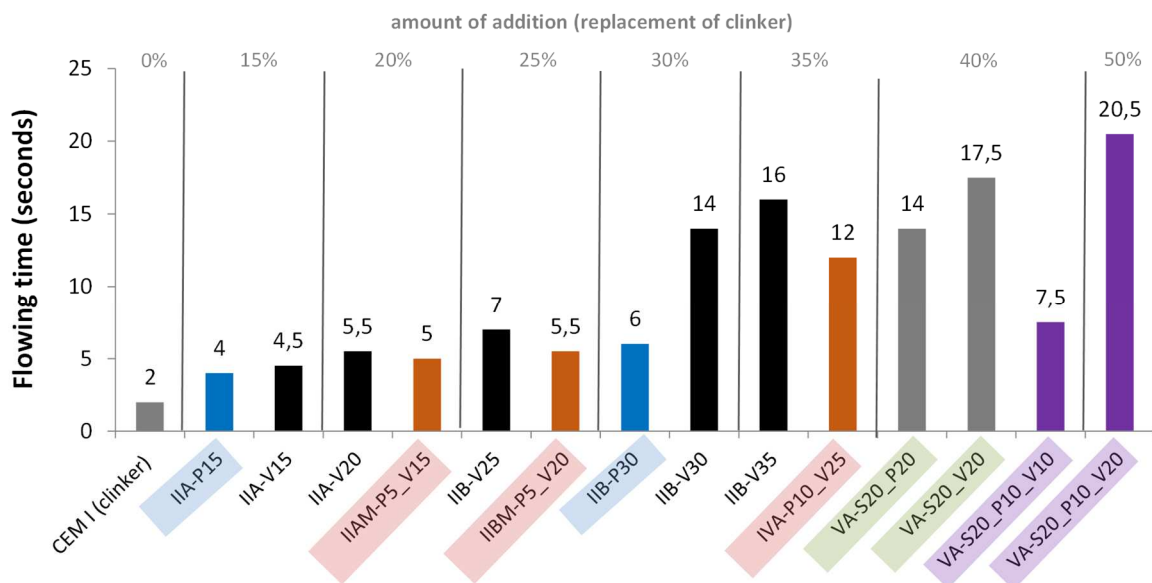
298 The incorporation of slag appears to be detrimental to workability, as the flowing time of
299 ternary binders (cement/slag/pozzolana and cement/slag/SSCFA, green) were rather high (14
300 and 17.5 seconds respectively). For these mixtures, pozzolana was seen to have a positive
301 effect on workability, compared to SSCFA, as it reduced the flowing time.

302 For the same amount of addition, the combination of pozzolana and SSCFA improved
 303 workability as it reduced the flowing time at 20%, 25%, and 35% of replacement compared to
 304 SSCFA mixtures and also at 40% compared to slag-pozzolana or slag-SSCFA mixtures.

305 From these observations the following main deductions can be drawn:

- 306 • Pozzolana had better workability than SSCFA even in composite cements with slag.
- 307 • Increasing the amount of SSCFA substantially increased the flowing time and thereby
 308 reduced workability. However, mixing pozzolana and SSCFA was a good compromise
 309 to maintain acceptable workability while raising the amount of replacement.
- 310 • When approaching an amount of 30% SSCFA, the use of plasticizers is necessary to
 311 maintain acceptable workability.

312



313

314 *Figure 6: Flowing time of mortars made with laboratory cements*

315

316 Figure 7 shows that workability (assessed through flowing time tests) is strongly correlated to
 317 the specific surface but also depends mainly on the percentage and nature of the addition
 318 (same colour code as in previous figures) used to replace clinker [20]. Actually, for the same
 319 type of addition (same colour and same shape), flowing time increases with specific surface
 320 and thus with the addition percentage, as can be seen in Figure 7. It can also be seen that
 321 green lozenges (mixes with slag) do not appear to follow the trend, with Blaine specific
 322 surface below 5000 cm²/g and flowing time above 14 seconds, showing the effect of slag
 323 combined with SSCFA or pozzolana on ternary cements. As reported in the literature [20, 22],
 324 slag behaves differently from clinker regarding the workability of cement based materials,
 325 which can explain the preceding observation.

326

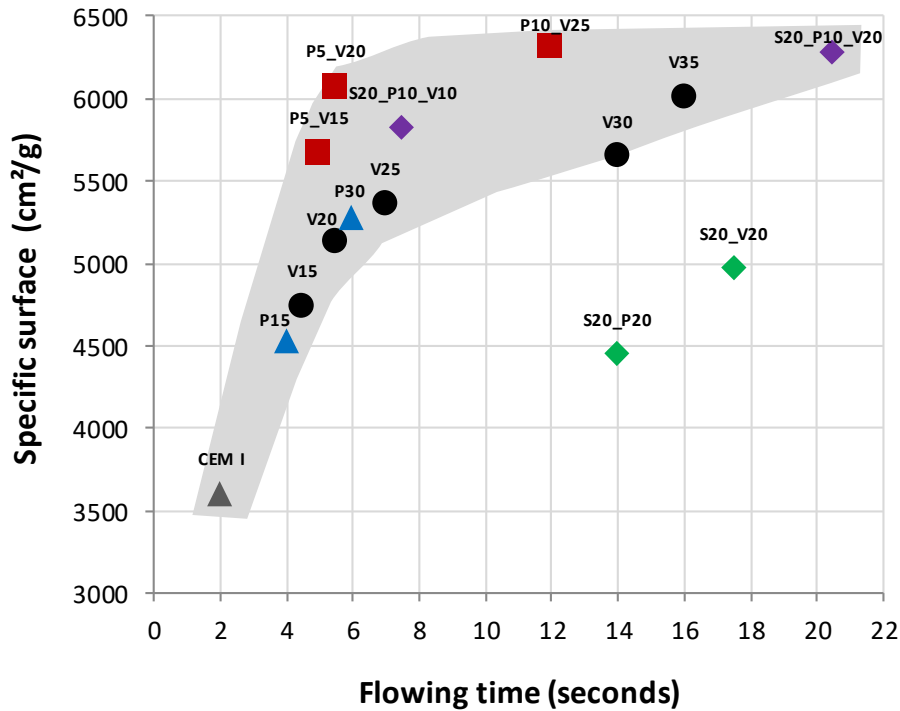


Figure 7: Blaine specific surface versus flowing time of mortars

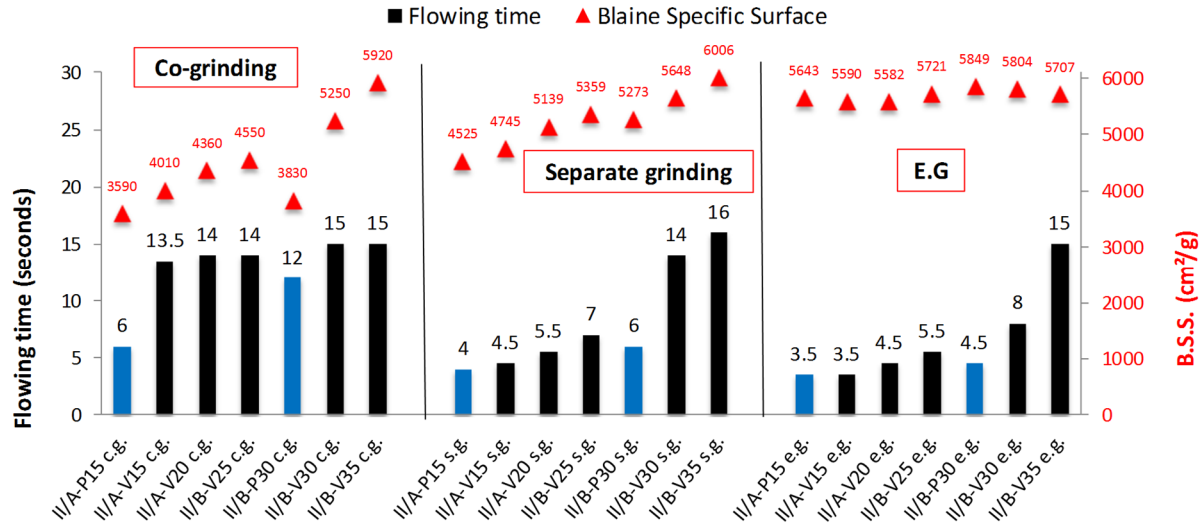
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329

330 The flowing times of different cements from different grinding methods are compared in
331 Figure 8, where the specific surface of each cement is also plotted.

332 It can be noted that results with the co-grinding method are difficult to interpret due to the
333 unknown fineness of particulate components (especially clinker and pozzolana). Despite the
334 fact that an increase of SSCFA causes an augmentation of specific surface in cements (black
335 filled), the flowing times are nearly the same. However, it can be seen that cements with
336 pozzolana (blue filled), even up to 30% of clinker replacement, have less impact on
337 workability than SSCFA does.

338 The equivalent grinding method shows that the type and amount of addition replacing clinker
339 has more influence on flowing time than the specific surface of global cement. However, due
340 to the different co-grinding durations used to obtain the final specific surface (cf. Figure 5), it
341 can be supposed that the components' fineness (clinker, pozzolana, SSCFA and gypsum)
342 differs from one cement to another, so interpretations cannot be linked to known components'
343 specific surfaces. For example, II/A-V15 cement has a co-grinding duration of 17 minutes,
344 versus 36 minutes for II/A-P15 in Figure 5; we can suppose that clinker particles will not have
345 the same fineness in these cements.

346 The separate grinding method appears to be the one that can be used to identify the influence
347 of addition ratio and addition nature on the flowing time linked to the specific surface. The
348 principal advantage is that all parameters are controlled beforehand and known for all
349 composite cements.



350

351 *Figure 8: Comparison of flowing time for mortars based on cements obtained from*
 352 *different types of grinding methods (C.G= co-grinding; S.G= separate grinding; E.G=*
 353 *equivalent grinding) and Blaine Specific Surface (B.S.S.) values of cements*

354

355 3.3.2. Setting time on cement pastes

356 Figure 9 presents the results of water/cement (W/C) ratio to achieve standard consistency (left
 357 y-axis) and setting time (right y-axis) in tests according to EN 196-3. When comparing
 358 pozzolana (blue triangles) with SSCFA (black dots), it is noted that, to achieve a standardized
 359 consistency, the SSCFA require more water than pozzolana, which is in accordance with
 360 previous results (cf. part 3.3). It is also in accordance with part 3.3 that slag appears to
 361 consume less water than the SSCFA, as there is a lower standardized consistency for ternary
 362 cements (in green) containing 40% replacement than for II/B-V30 (30% replacement).

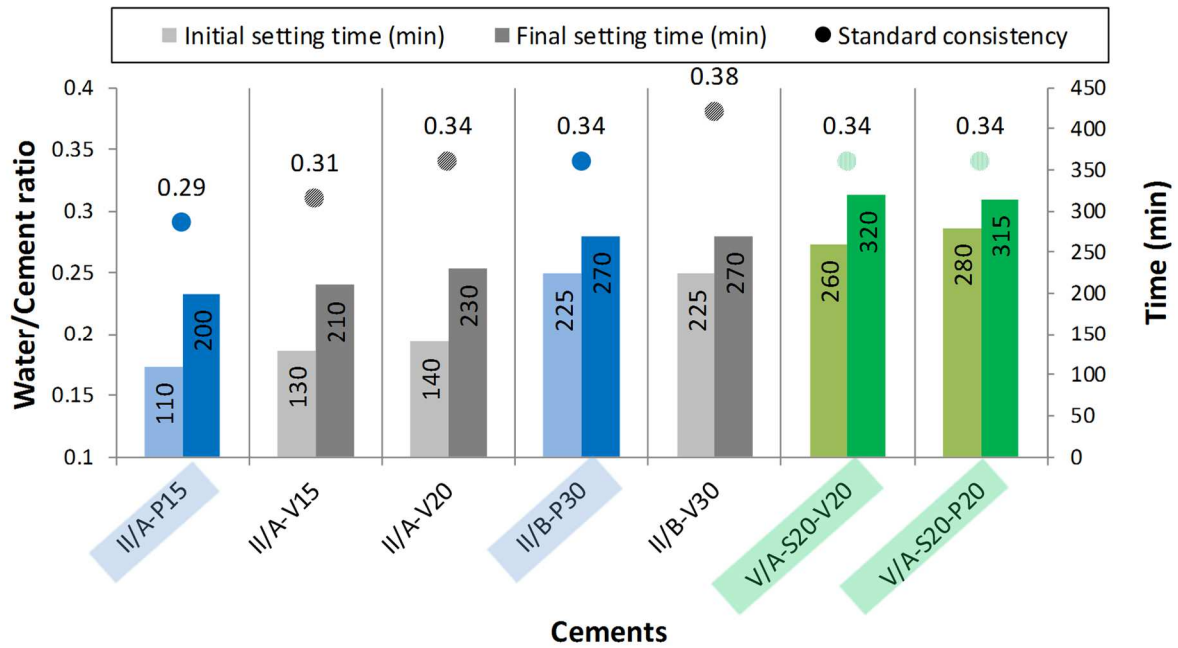
363 An increase in setting time is observed following the decrease in clinker content, which could
 364 be explained by:

- 365 - a dilution effect on the cement since the pastes with composite cements have less
 366 cement than the reference, resulting in a decrease in the quantity of hydrates formed in
 367 the first few hours [14, 23];
- 368 - an increase of the water-cement ratio due to the higher water demand of cement with
 369 more addition, known to have an effect on the setting time [13, 14, 23];
- 370 - a harmful effect of the ashes themselves, maybe due to the presence of minor elements
 371 (e.g. P, Zn, etc.) perturbing the hydration of the cement [24].

372

373 There is a sharp increase of initial setting time at 30% replacement regardless of the substitute
 374 material. SSCFA compared to pozzolana, at this replacement rate, do not cause an increase in
 375 setting time despite the increase in W/C ratio; the cement dilution effect seems to be the
 376 overriding factor. However, this phenomenon could be also explained by the effect of small
 377 particles of SSCFA on the nucleation sites for hydrates, helping to increase the global

378 hydration of cement particles and thus compensating for the delay in setting time despite the
 379 higher W/C [23, 25].
 380 If we compare the V/A-S20V20 paste with II/A-V20, a strong increase in setting time is
 381 observed. The use of slag to replace 20% of clinker almost doubles the initial setting time,
 382 although there is no increase in water demand to achieve standard consistency. Slag appears
 383 to cause an additional delay in setting time in accordance with the literature [20-22].
 384 Measuring pH values could also be a way to assess the role of the slag in these cements.
 385

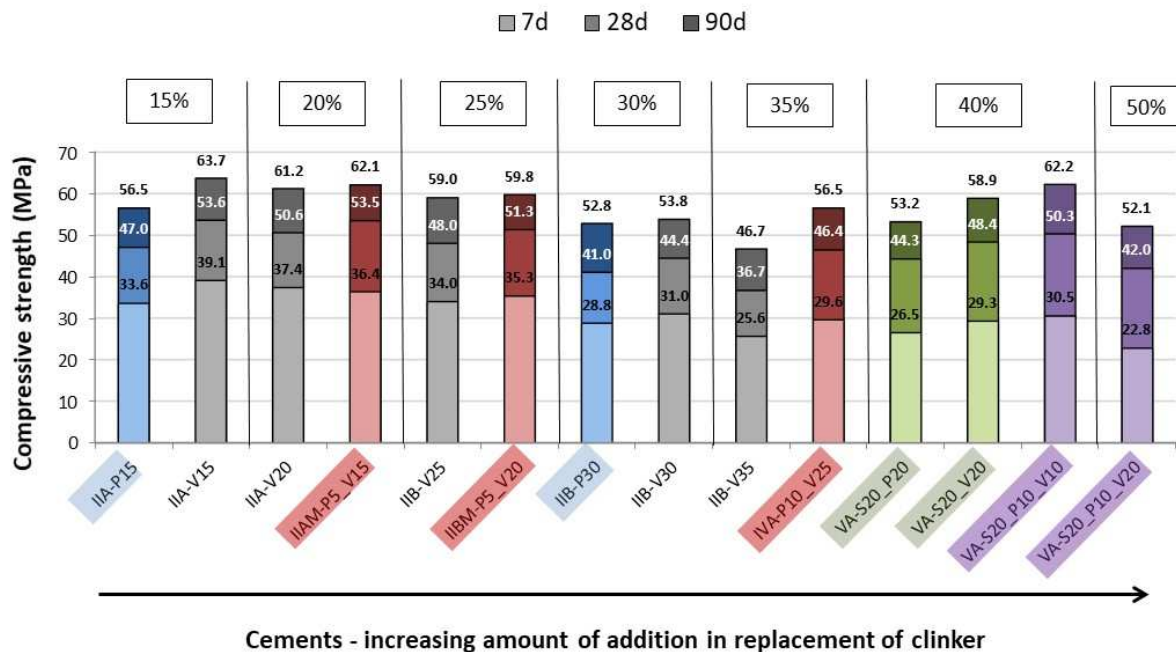


386
 387 *Figure 9: W/C ratio at normal consistency and setting time values obtained for cement*
 388 *pastes according to EN 196-3*

389
 390 **3.4. Mortar compressive strengths**

391 The compressive strength results of mortars made with composite cements are reported in
 392 Figure 10. We recall that, in all cements, the clinker had a Blaine specific surface around 3600
 393 cm²/g and the pozzolana had nearly the same Blaine specific surface as the SSCFA (around
 394 5700 cm²/g). From the results obtained, various observations can be made.
 395 First, all the compressive strength values (at 7, 28 and 90 days) of SSCFA mortars (grey
 396 colour) are higher than those of pozzolana mortars (blue colour) with equivalent amounts of
 397 clinker replacement. This could be explained by the high water absorption of SSCFA
 398 particles, which reduces the W/B ratio and thus improves the mechanical performance while it
 399 deteriorates mortars in the fresh state. Replacing pozzolana by SSCFA also has a positive
 400 impact in ternary cement (green colour). However, increasing the amount of SSCFA reduces
 401 the compressive strength significantly when the replacement rate exceeds 30%.

402 The mix of pozzolana and SSCFA seems to improve compressive strength values, for 20%,
 403 25% and 35% of clinker replacement, as the composite cements with pozzolana + SSCFA
 404 (red colour) always present higher compressive strengths. Observations of the strength of
 405 cements with a quantity of SSCFA set at 20% revealed that the replacement of 20% clinker by
 406 slag (II/A-S20_V20) or 5% of clinker by pozzolana (IIBM-P5_V20) kept the strength in the
 407 same order of magnitude as for II/A-V20.
 408 Thus, the use of the slag definitely seems to be a good solution to reduce the amount of
 409 clinker while maintaining good mechanical strength. The delay observed in setting times did
 410 not seem to have a significant effect on later age strength. Compared to compressive strengths
 411 at 28 days, the trends for the other ages were almost the same.



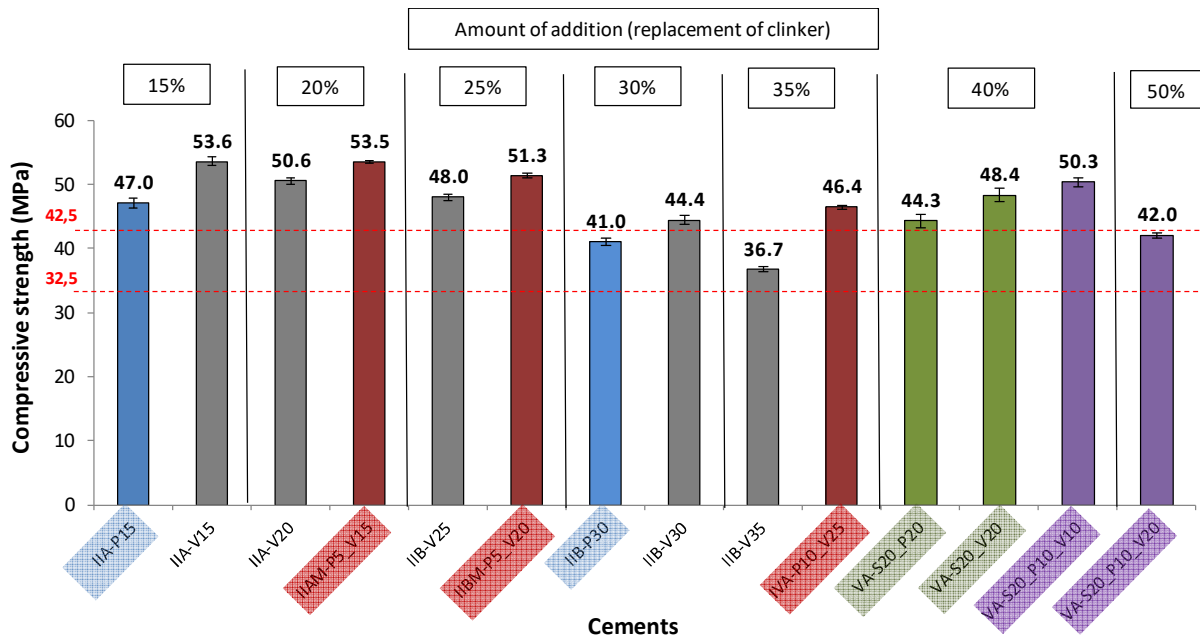
412

413 *Figure 10: Compressive strength of mortars made with the manufactured cements at 7, 28*
 414 *and 90 days*

415 The 28-day compressive strength results in Figure 11 show that mortars made with cements
 416 containing up to 25% of SSCFA in replacement of clinker have better compressive strength
 417 than mortars with cement II-A/P15 (taken as the reference). These cements could be classified
 418 in the 42.5 category according to EN 197-1, as the compressive strengths are well above 42.5
 419 MPa.

420 The benefits of SSCFA are also observed in cements containing 30% and more of clinker
 421 replacement. Only IIB-V35 presents a lower compressive strength than the reference, IIB-
 422 P30, but it could still be considered as a cement of class 32.5 according to EN 197-1. This
 423 reduction in strength may have been caused by settlement problems (mortar not enough fluid
 424 to be perfectly set in the mould) in the fresh state because of excessive water consumption by
 425 the increasing amount of unburned SSCFA particles present when exceeding 30%, as no
 426 plasticizer was used in this study. This settlement issue probably induced additional porosity
 427 in the mortar samples.

428 It is also notable that mixing SSCFA with pozzolana and/or slag enables the 42.5 MPa class
 429 of compressive strength to be achieved with up to 40% of clinker replacement.
 430

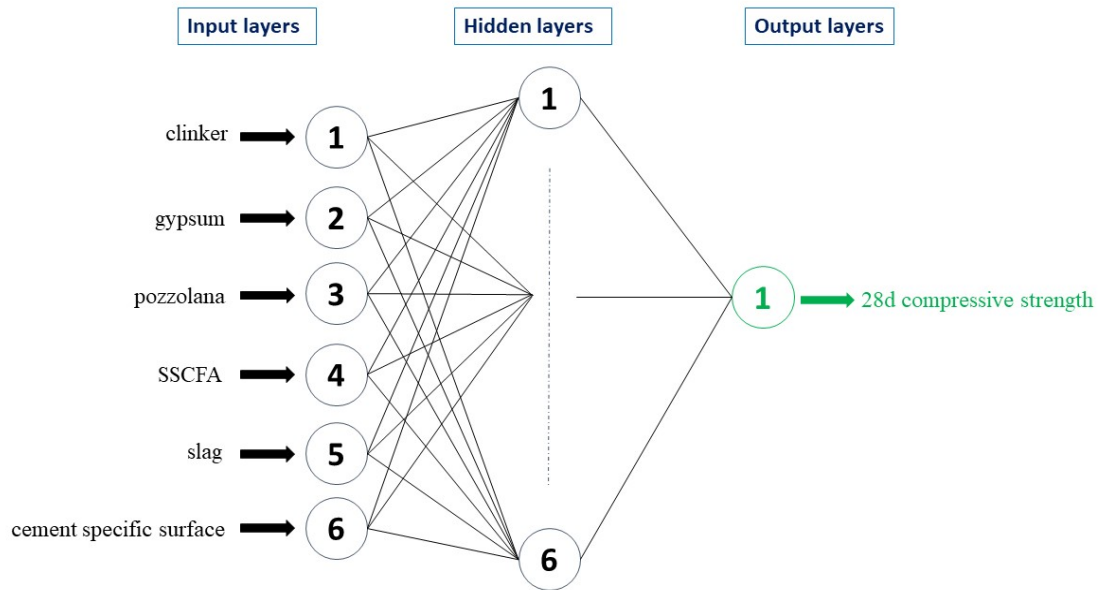


431
 432 *Figure 11: Compressive strength of mortars at 28 days*

433 3.5. Predictive approach using artificial neural networks

434 A predictive approach to manufactured mortar compressive strength data was set up by
 435 implementing artificial neural networks. The composition and calculation principle of
 436 Artificial Neural Networks (ANN) based on the multilayer feed-forward type of neural
 437 networks (cf. Figure 12) can be found in the literature [26-28]. The objective of this approach
 438 was to be able to predict characteristics such as the 28-day compressive strength of composite
 439 cements without having to manufacture them.
 440

441 The database used for this study contained 31 cements: 19 for the learning (training) database
 442 and 12 for the validation base. As shown in Figure 12, the input layer parameters were the
 443 weight ratios of clinker, gypsum, pozzolana, SSCFA and slag, and the cement specific
 444 surface. The compressive strength at 28 days was the output layer. Because of the difference
 445 of scale and units for the input and output layers, all the parameters were normalized to values
 446 between 0 and 1 by adjusting the maximum value for each parameter to 1 and the minimum
 447 value to 0, and then proceeding by simple calculation for the intermediate values.
 448



449

450

Figure 12: Structure of ANN used to predict 28-day compressive strength

451

452 Figure 13 illustrates the correlation between predicted 28-day compressive strength values
 453 and actual ones. The results show that the proposed neural network was successful in learning
 454 the relation between the different input parameters and the output parameter via compressive
 455 mortar strength.

456 Figure 14 shows the deviation in MPa between the predicted and measured values. A fair
 457 prediction of the 28-day compressive strength could be seen, with deviations for all the results
 458 not exceeding ± 2 MPa and more than two thirds of the results presenting an error of less than
 459 1 MPa.

460

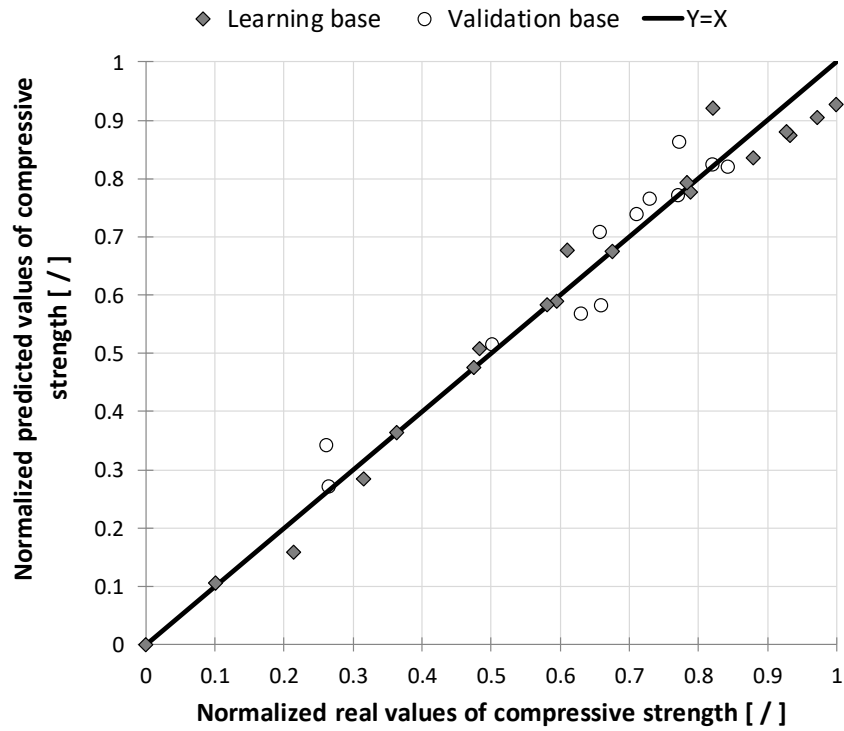
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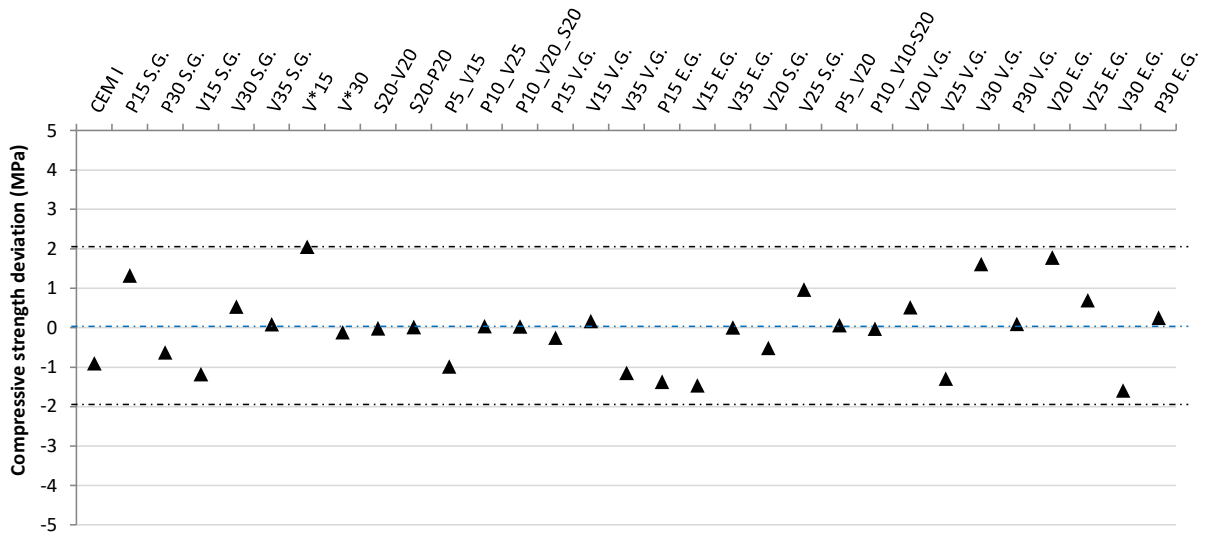
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Figure 13: Correlation between predicted compressive strength and actual values



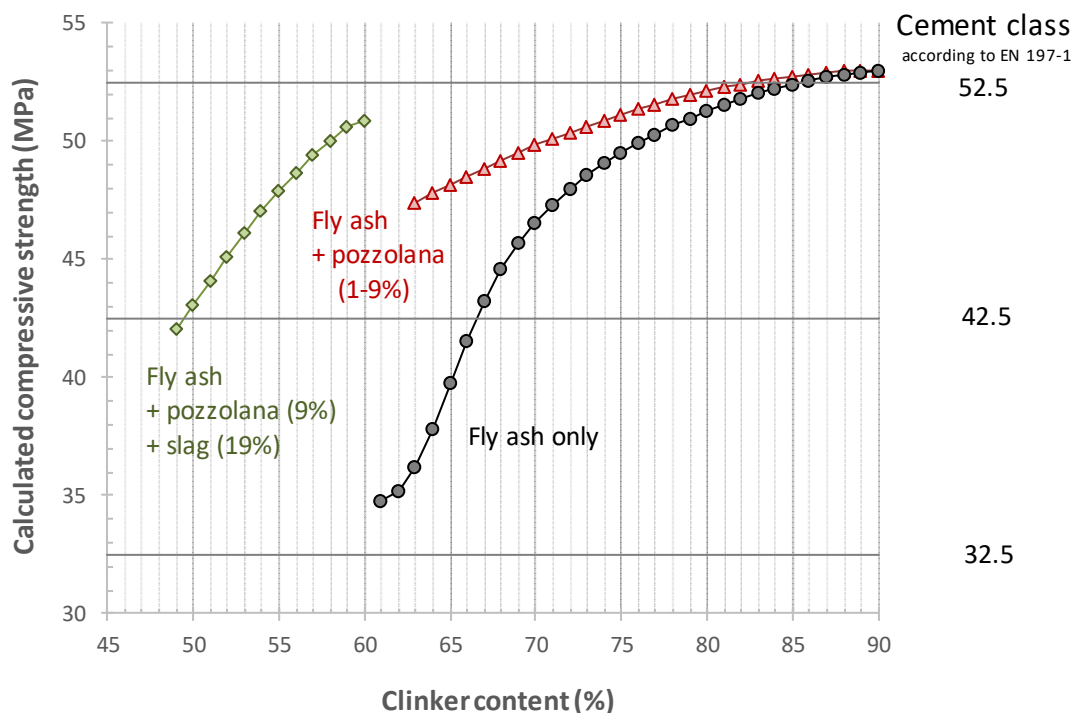
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Figure 14: Deviation in MPa between predicted and actual values of 28-day compressive strength for mortars

This approach permitted the development of response curves predicting the 28-day compressive strength of mortars with three kinds of compositions according to the clinker content, as shown in Figure 15. It can be seen that:

- 477 - With fly ash alone in replacement of clinker, there is a marked fall of compressive
- 478 strength following the reduction of clinker.
- 479 - The mix of fly ash with pozzolana in ternary cements limits the fall of compressive
- 480 strength when the amount of clinker in the mix is reduced.
- 481 - The amount of clinker can be lowered by using slag and keeping the amount of fly ash
- 482 the same, at almost 20%.

483 The response curves presented in Figure 15 also enable a class of cements (compressive
 484 strength) to be targeted according to the type of mix and amount of clinker replacement.



485
 486 *Figure 15: Response curve for 28-day compressive strength of cements with fly ash only,*
 487 *fly ash + pozzolana (1-9%) and fly ash + pozzolana (9%) + slag (19%) following clinker*
 488 *content*

489
 490 **4. CONCLUSIONS**

491 The main objective of this paper was to illustrate how circular economy could be applied in
 492 the development of cement-based matrices with Spreader Stoker coal fly ash. **In this context,**
 493 **the first step was to evaluate, from a technological point of view, the advantages or**
 494 **disadvantages compared to natural pozzolana, which is currently the only material used**
 495 **as a replacement for clinker in cement manufacturing on Reunion Island.** Ternary and
 496 quaternary cements were also made to evaluate some combinations between ashes, natural
 497 pozzolana, and blast furnace slag.

498 The main conclusions that can be drawn from these results are:

499 - **Making cement is easier with SSCFA than with pozzolana.** Since SSCFA are already in
500 pulverulent form, they make it possible to save on grinding duration and gain in overall
501 fineness of the cement manufactured. **They could also be used as a grinding agent in the**
502 **case of co-grinding with clinker, which would represent a significant economic**
503 **advantage.**

504 - Three types of grinding methods have been investigated: separate grinding, co-grinding and
505 a combination of these two, in order to understand their effects in manufactured cements.
506 Separate grinding is the method that gives the best understanding of the effects of individual
507 components because it provides the capacity to control the initial fineness of each constituent
508 of the cement. It was therefore the method investigated for cement paste and mortar results in
509 order to analyse the effects of components in the laboratory-manufactured cements.

510 - In the fresh state, SSCFA degrade the rheological properties of cement-based matrices with
511 respect to the properties obtained with pozzolana. This degradation is, however, less marked
512 when the clinker replacement rates are lower than 30%.

513 - In the hardening state, the lengthened setting time also seems to be an effect induced by
514 SSCFA rather than a clinker dilution effect.

515 - **SSCFA showed better mechanical performance than pozzolana.** The results also showed
516 good interaction between the fly ashes and slag, making it possible to replace up to 40% of
517 clinker while improving the mechanical strengths compared to mixtures with 30%
518 replacement. **There was also good interaction between SSCFA and pozzolana, which**
519 **could be a good compromise to limit the negative effects of SSCFA on rheology while**
520 **maintaining a replacement rate of over 30%.**

521 - **A predictive computing approach with artificial neural networks provided good**
522 **predictions of 28-day compressive strength values of laboratory-made cements** with
523 known compositions and components finenesses and permitted response curves to be drawn
524 for mixes according to clinker content, in order to target a class of cement as defined in EN
525 197-1.

526

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529

530

531 **REFERENCES**

- 532 [1] F. Massazza, Pozzolana and Pozzolanitic Cements, In: P. Hewlett, Ed., *Lea's Chemistry*
 533 *of Cement and Concrete*, Arnold, London, 1998, pp. 471-631.
- 534 [2] EN 197-1, *Cement. Composition, specifications and conformity criteria for common*
 535 *cements*, 2011.
- 536 [3] EN 450-1, *Fly Ash for Concrete—Definition, Specifications and Conformity Criteria*,
 537 2012.
- 538 [4] M. Sow, J. Hot, C. Tribout, M. Cyr, *Characterization of Spreader Stoker Coal Fly Ashes*
 539 *(SSCFA) for their use in cement-based applications*”, *Fuel*, 162 (2015) 224-233.
 540 <https://doi.org/10.1016/j.fuel.2015.09.017>.
- 541 [5] J. Hot, M. Sow, C. Tribout, M. Cyr, *An investigation of the leaching behavior of trace*
 542 *elements from Spreader Stoker Coal Fly Ashes-based systems*, *Constr. Build. Mater.*,
 543 110 (2016) 218-226. <https://doi.org/10.1016/j.conbuildmat.2016.02.018>.
- 544 [6] E. Freeman, Y-M. Gao, R. Hurt, E. Suuberg, *Interactions of carbon-containing fly ash*
 545 *with commercial air-entraining admixtures for concrete*, *Fuel*, 76 (1997) 761-765.
 546 [https://doi.org/10.1016/S0016-2361\(96\)00193-7](https://doi.org/10.1016/S0016-2361(96)00193-7).
- 547 [7] E. Ghafari, S. Ghahari, D. Feys, K. Khayat, A. Baig, R. Ferron, *Admixture*
 548 *compatibility with natural supplementary cementitious materials*, *Cement and Concrete*
 549 *Composites*, 112 (2020) 103683. <https://doi.org/10.1016/j.cemconcomp.2020.103683>.
- 550 [8] T.H. Ha, S. Muralidharan, J.H. Bae, Y.C. Ha, H.G. Lee, K.W. Park, and D.K. Kim,
 551 *Effect of unburnt carbon on the corrosion performance of fly ash cement mortar*,
 552 *Construction and Building Materials*, 19 (2005) 509-515.
 553 <https://doi.org/10.1016/j.conbuildmat.2005.01.005>.
- 554 [9] S. Lim, W. Lee, H. Choo, C. Lee, *Utilization of high carbon fly ash and copper slag in*
 555 *electrically conductive controlled low strength material*, *Construction and Building*
 556 *Materials*, 157 (2017) 42-50. <https://doi.org/10.1016/j.conbuildmat.2017.09.071>.
- 557 [10] M.A. Sanjuán, J.A. Suárez-Navarro, C. Argiz, P. Mora, *Assessment of natural*
 558 *radioactivity and radiation hazards owing to coal fly ash and natural pozzolan Portland*
 559 *cements*, *J Radioanal Nucl Chem*, 325 (2020) 381-390. [https://doi.org/10.1007/s10967-](https://doi.org/10.1007/s10967-020-07263-w)
 560 [020-07263-w](https://doi.org/10.1007/s10967-020-07263-w).
- 561 [11] M.A. Sanjuán, C., Argiz, P., Mora, A. Zaragoza, *Carbon Dioxide Uptake in the*
 562 *Roadmap 2050 of the Spanish Cement Industry*, *Energies* 13 (2020) 3452.
 563 <https://doi.org/10.3390/en13133452>.
- 564 [12] EN 196-1, *Methods of testing cement—Part 1: Determination of strength*, 2005.
- 565 [13] A. A. Ramezani-pour, *Fly Ash*, in: *Cement Replacement Materials: Properties,*
 566 *Durability, Sustainability*, A. A. Ramezani-pour, Ed. Berlin, Heidelberg: Springer,
 567 2014, pp. 47-156.
- 568 [14] E. E. Berry and V. M. Malhotra, *Fly Ash for Use in Concrete - A Critical Review*, *ACI*
 569 *Journal Proc.*, 77 (1980) 59-73. <https://doi.org/10.14359/6991>.
- 570 [15] EN 196-2, *Methods of testing cement - Part 2: Chemical analysis of cement*, 2005.
- 571 [16] EN 196-6, *Methods of Testing Cement. Determination of fineness*, 2010.
- 572 [17] EN 196-3, *Methods of testing cement, Determination of setting time and soundness*,
 573 2005.
- 574 [18] NF P15-437, *Liants hydrauliques - Technique des essais - Caractérisation des ciments*
 575 *par mesure de la fluidité sous vibration des mortiers*, 1987.

- 576 [19] L.O. Opoczky, S. Verdes, K. M. Török, Grinding technology for producing high-
577 strength cement of high slag content, *Powder Technol.*, 48 (1) (1986) 91-98.
578 [https://doi.org/10.1016/0032-5910\(86\)80069-9](https://doi.org/10.1016/0032-5910(86)80069-9).
- 579 [20] A. M. Rashad, An overview on rheology, mechanical properties and durability of high-
580 volume slag used as a cement replacement in paste, mortar and concrete, *Constr. Build.*
581 *Mater.*, 187 (2018) 89-117. <https://doi.org/10.1016/j.conbuildmat.2018.07.150>.
- 582 [21] T. Miura, I. Iwaki, Strength development of concrete incorporating high levels of
583 ground granulated blast-furnace slag at low temperatures, *ACI Mater. J.*, 97 (1) (2000)
584 66-70. <https://doi.org/10.14359/807>.
- 585 [22] C.-L. Hwang, D.-H. Shen, The effects of blast-furnace slag and fly ash on the hydration
586 of portland cement, *Cem. Concr. Res.*, 21 (4) (1991) 410-425.
587 [https://doi.org/10.1016/0008-8846\(91\)90090-5](https://doi.org/10.1016/0008-8846(91)90090-5).
- 588 [23] A. A. Ramezani pour, The role of supplementary cementing materials on sustainable
589 development, in: *Cement Replacement Materials: Properties, Durability, Sustainability*,
590 A. A. Ramezani pour, Ed. Berlin, Heidelberg: Springer, 2014, pp. 327-336.
- 591 [24] G. Arliguie, J. P. Ollivier, J. Grandet, Etude de l'effet retardateur du zinc sur
592 l'hydratation de la pâte de ciment Portland, *Cem. Concr. Res.*, 12 (1) (1982) 79-86.
593 [https://doi.org/10.1016/0008-8846\(82\)90101-6](https://doi.org/10.1016/0008-8846(82)90101-6).
- 594 [25] M. Coutand, M. Cyr, P. Clastres, Use of sewage sludge ash as mineral admixture in
595 mortars, *Proc. Inst. Civ. Eng. - Constr. Mater.*, 159 (4) (2006) 153-162.
596 <https://doi.org/10.1680/coma.2006.159.4.153>.
- 597 [26] I.-C. Yeh, Modeling of strength of high-performance concrete using artificial neural
598 networks, *Cem. Concr. Res.*, 28 (12) (1998) 1797-1808. [https://doi.org/10.1016/S0008-8846\(98\)00165-3](https://doi.org/10.1016/S0008-8846(98)00165-3).
- 600 [27] İ. B. Topçu, M. Sarıdemir, Prediction of compressive strength of concrete containing fly
601 ash using artificial neural networks and fuzzy logic, *Comput. Mater. Sci.*, 41 (3) (2008)
602 305-311. <https://doi.org/10.1016/j.commatsci.2007.04.009>.
- 603 [28] H. Eskandari-Naddaf, R. Kazemi, ANN prediction of cement mortar compressive
604 strength, influence of cement strength class, *Constr. Build. Mater.*, 138 (2017) 1-11.
605 <https://doi.org/10.1016/j.conbuildmat.2017.01.132>.