



HAL
open science

Optimization of concrete mix design to account for strength and hydration heat in massive concrete structures

Agathe Bourchy, Laury Barnes, Laetitia Bessette, Florian Chalencon, Aurélien Joron, Jean Michel Torrenti

► To cite this version:

Agathe Bourchy, Laury Barnes, Laetitia Bessette, Florian Chalencon, Aurélien Joron, et al.. Optimization of concrete mix design to account for strength and hydration heat in massive concrete structures. *Cement and Concrete Composites*, 2019, 103, pp. 233-241. 10.1016/j.cemconcomp.2019.05.005 . hal-02466837

HAL Id: hal-02466837

<https://hal.science/hal-02466837>

Submitted on 4 Feb 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Optimization of concrete mix design to account for strength and hydration heat in massive**
2 **concrete structures.**

3

4 Agathe Bourchy¹, Laury Barnes², Laetitia Bessette², Florian Chalencon³, Aurélien Joron³ and
5 Jean Michel Torrenti^{1*}

6

7 ¹IFSTTAR, Materials and Structures Department, 14-20 boulevard Newton, 77420 Champ-sur-
8 Marne, France

9 ²Vicat SA, 4 rue Aristide Bergès, 38080 L'Isle d'Abeau, France

10 ³Sigma Béton SA, 4 rue Aristide Bergès, 38080 L'Isle d'Abeau, France

11

12 *Corresponding author

13 Tel.: +331.81.66.84.40

14 email: jean-michel.torrenti@ifsttar.fr

15 **ABSTRACT**

16 In the case of massive concrete structures, the heat generated by cement hydration may cause
17 cracking due to thermal strains. The mix design of the concrete used for such structures has to
18 take account of mechanical properties and generated temperatures. Using experimental design
19 principles, the hydration heat and the development of compressive strength are measured in order
20 to determine how the composition of concrete and the presence of SCM influence the
21 characteristics of concrete and to create a mix design protocol. This protocol can help to
22 determine which mix design minimizes the hydration temperature for a given compressive
23 strength.

24 **KEYWORDS:** concrete, formulation, supplementary cementitious materials, hydration heat,
25 compressive strength.

26 **1. INTRODUCTION**

27 In massive structures, the exothermy of the hydration reactions of cement and the thermo-hydro-
28 mechanical behavior of early age concrete can lead, if strains are restrained, to the development
29 of compressive and tensile stresses. If the tensile stresses exceed the tensile strength, cracking
30 may occur, threatening the durability of the concrete. In order to prevent the risk of cracking as
31 well as that of Delayed Ettringite Formation (DEF), sulfate resisting cement and the use of
32 additions are recommended [1]. Mineral additions such as limestone, slag or fly ash can also be
33 added to concrete to decrease the exothermy of hydration reactions and, in the case of slag and
34 fly ash, protect against DEF.

35 The aim of this research is to obtain a tool which optimizes concrete mix design while respecting
36 classical specifications such as the compressive strength after 28 days and minimizing the
37 temperature rise in massive structures. To do this, the impact of several parameters of cement
38 (composition and fineness) and of concrete (type and percentage of additions, W/B ratio,
39 chemical admixtures) on the rheology, hydration heat and mechanical strength of concrete have
40 been studied by means of an experimental design. The influence of the different factors is
41 analyzed and a concrete mix tool is proposed. Finally, this tool is applied to the case of massive
42 concrete structures.

43

44 **2. CURRENT STATE OF KNOWLEDGE**

45 The hydration reaction of cement is exothermic and the heat that is produced can lead to DEF or
46 cracking under particular conditions and especially in massive concrete structures [2,3]. Usually,
47 mix design – cement, additions, water-to-binder ratio, chemical admixtures – is optimized with
48 reference to workability, setting time, compressive strength at early or later age (Bolomey

49 equation for compressive strength after 28 days [4]) or the hydration heat [5,6] and in order to
50 limit the risk of cracking. Depending on the notional size of the concrete structure in question, it
51 is important to optimize the concrete mix design, the hydration kinetic and the total heat release
52 which impact temperature changes in the structure.

53 Firstly, it is possible to optimize the granular skeleton in order to minimize the quantity of cement
54 paste as recommended in the standard EN 206 [7] with classical methods such as the ACI method
55 [8] or the de Larrard [5] method which take into account the size and form of the particles. The
56 standard EN 12620 gives the characteristics of aggregates which can be employed in concrete [9].
57 Then, when the granular skeleton has been optimized, it is possible to optimize the composition
58 of the paste. This involves selecting the type of cement with respect to durability and such
59 properties as carbonation, the alkali reaction or DEF: special attention is paid to the amount of
60 sulfate in the cement provided by alkaline sulfates or a setting regulator. For Byfors [10] and
61 Minard [11], coupling occurs between the anhydrous phases and for Lerch and Bogue, it is
62 possible to reduce hydration heat by reducing the quantity of highly reactive phases such as C_3A
63 and C_3S [12]. Furthermore, the more fine the cement, the faster the hydration reactions which can
64 increase the rate at which hydration heat is released [13–15].

65 The heat of hydration can be limited when mineral additions – reactive or not - are used in the
66 cement as recommended in the standard EN 197-1 [16] or by several authors [17,18], but they
67 may also be used in the concrete as described in standard EN 206 [7]. Mineral additions in
68 cementitious materials change their properties over time [19]. Even if these modifications can be
69 related to the characteristics of additions (type of fly ash, slag fineness...), several general points
70 are accepted. During hydration, mineral additions interact with hydrates and modify heat release
71 and mechanical properties. It is possible to explain this on the basis of several phenomena: a

72 granular effect which affects the material in its fresh state and its rheology and a physico-
73 chemical effect which affects the hydration and setting of the material.

74 The granular or filler effect is mainly due to fine and ultra-fine particles of materials such as
75 limestone [20–23] or silica fume [24]. For Villagran-Zaccardi, et al. [25], Lothenbach, et al. [26]
76 and Schöler, et al. [27], the fineness of mineral additions affects the hydration kinetic, especially
77 the hydration of aluminates due to a filler effect: the impact is faster for limestone and slower for
78 slag [28,29] and fly ash [30]. These particles position themselves between the cement particles
79 [31]. This effect can have a beneficial or an adverse impact on material properties in the fresh
80 state – i.e. their slump and rheology. According to Ramachandran, et al., for similar specific
81 surfaces, fly ash increases fluidity thanks to its spherical surface [32] whereas slag increases
82 viscosity due to its irregular surface which decreases the granular skeleton [33]. Their specific
83 surface areas are respectively equal to $3,800 \text{ cm}^2.\text{g}^{-1}$ and $4,200 \text{ cm}^2.\text{g}^{-1}$ for fly ash and slag. In the
84 case of silica fume, due to its very high specific surface ($150,000$ to $200,000 \text{ cm}^2.\text{g}^{-1}$) the use of a
85 superplasticizer is essential in order to obtain an acceptable level of fluidity [34]. The
86 physicochemical effect – nucleation sites and modification of hydrate morphology and secondary
87 hydration reactions – affects the interactions between additions, anhydrous and hydrates and so
88 modifies the hydration process [19,28]. Generally, the presence of additions decreases the early
89 age heat of hydration [26]. For example, limestone, being a non-reactive addition, decreases the
90 hydration heat [28] but gives higher early age compressive strengths than Portland cement thanks
91 to its role as a nucleation site [23,35], and it also improves cement hydration [26,36]. Lawrence,
92 et al. have shown that limestone in cement increases early age mechanical strength because of its
93 reactions with the C_3A and C_4AF phases (formation of aluminates and carboaluminates) but later
94 its impact becomes marginal [37,38]. As a result of their low early age reactivity [29,30,39] and

95 the increase in the length of the dormant period [40,41], slag and fly ash produce low hydration
96 heat with time. The compressive strength is lower at early age but similar to or higher than
97 compressive strength after 28 days for concretes without slag and fly ash considering an equal
98 binder content [30,42]. However, for Berodier, an increase in the percentage of slag increases the
99 hydration heat released up to a maximum value when there is not enough cement to activate the
100 slag [28]. For Schindler and Folliard, a higher percentage of fly ash in concrete does not retard
101 hydration and the production of hydration heat while a higher percentage of slag retards the
102 hydration of cement and decreases the hydration heat [43]. In contrast, silica fume, which is very
103 reactive and exothermic, gives a higher compressive strength from early age [39]. Moreover, the
104 reactions are sensitive to temperature [44–46], especially those involving slag [47] and fly ash
105 which have a high activation energy (around 65 kJ.K⁻¹) [48]. Additions are taken into account in
106 concrete mix design via the notion of equivalent binder which corresponds to the sum of the
107 quantity of cement and the quantity of addition multiplied by the activity coefficient of the
108 addition. It would be possible to estimate mechanical strengths using expressions which include
109 the equivalent binder. For instance, in the Bolomey formula, see equation (1), the equivalent
110 binder is calculated with the activity coefficient k considered as a constant. But according to Cyr,
111 et al. and Khokhar, et al., this coefficient varies according to the type of cement (C) and addition
112 (A) because of the interaction between them, but also according to the quantity of addition and
113 the age of concrete [49,50].

$$R_c = G \cdot R_{c_cement_iso} \cdot \left(\frac{C + k \cdot A}{W} - 0.5 \right) \quad (1)$$

114 where G is the granular coefficient which depends on the quality and maximum size of the
115 granular material, $R_{c_cement_iso}$ is the compressive strength of the cement after 28 days (MPa) , C ,
116 A and W the quantity of cement, addition and water (kg).

117 Hu et al. show that when the water-to-binder ratio decreases, hydration reactions are faster and
118 the hydration heat increases. If the water-to-binder ratio is higher than 0.7, the reactive materials
119 are diluted which leads to fewer hydration reactions and therefore lower hydration heat [51]. For
120 Torrenti and Benboudjema, for a cement paste, the higher the water-to-binder ratio, the longer it
121 takes for hydration to begin and the first mechanical properties to appear [52]. For Stefan, in the
122 case of mortar or concrete, the granular skeleton also plays a role in the development of the
123 mechanical characteristics at very early age [53]. On the contrary, for Hewlett, the water-to-
124 binder ratio needs to be higher for fine cement to obtain good hydration and fresh state properties
125 as well as during hardening [54]. For Kadri and Duval, the water-to-binder ratio can be optimized
126 in order to obtain low hydration heat for concrete containing silica fume [55] or, according to
127 Hani, et al. [56], in order to obtain better mechanical properties.

128 Mineral additions impact the water demand and the fluidity of concrete, especially when recycled
129 aggregates are used [57]. In order to regulate these effects, chemical admixtures can be used to
130 deflocculate fine particles and free water between these particles [58]. The use of chemical
131 admixtures makes it possible to decrease the water-to-binder ratio and thus increase the
132 mechanical strength by improving the microstructure [59]. For Huang, et al., in the case of higher
133 percentages of entrained air, chemical admixtures are more effective [60]. For Mardani-
134 Aghbaghou, et al., the chemical admixture needs to be chosen on the basis of the type of sulfates
135 present in cement, i.e. anhydrite or gypsum, because of the difference in their reactivity in the

136 presence of superplasticizers [61]. Moreover, the standard EN 934-2 states that a chemical
137 admixture can only be used in concrete if the SO_3 content is lower than 2% [62].

138 After analysis of the literature, we decided to study the impact of the type and quantity of cement,
139 the type and quantity of additions, the water-to-binder ratio and the quantity of chemical
140 admixture on the early age thermomechanical properties of concrete, and in particular to perform
141 experimental design in order to minimize heat release for a given strength. To do this, three
142 cements and three additions were selected in order to compare their effect on hydration heat and
143 mechanical properties.

144

145 **3. MATERIALS AND METHODS**

146 The materials and method are presented below. The Bolomey formula (eq. (1)) is used in the
147 experimental design.

148

149 **3.1 Materials tested**

150 3.1.1 Selected cements

151 The three cements were selected on the basis of their hydration heat and their compressive
152 strengths. They were produced in a pilot scale ball mill, and their composition varied from CEM I
153 (95 to 100 percent of cement), CEMII/A-LL (80 to 94 percent of cement and 6 to 20 percent of
154 limestone) and CEM II/B-LL (65 to 79 percent of cement and 21 to 35 percent of limestone).

155 The first selected cement, denoted by C1, was equivalent to a CEM II/B-LL and contained 35 %
156 of limestone, 5.85 % of anhydrite and had a median particle diameter of 12 μm . The second
157 cement is denoted by C2 and was equivalent to a CEM II/A-LL. It contained 20 % of limestone,
158 5.85 % of anhydrite and had a median diameter of 12 μm . Finally, the third cement (C3)

159 contained only 5 % of limestone but 7.85 % of anhydrite and had a median diameter of 9 μm .
160 This cement corresponded to a CEM I. Table 1 presents the characteristics of the selected
161 cements.

162

163 Table 1. Characteristics of selected cements.

	C1	C2	C3
D_{50} (μm)	11.2	11.4	12.0
Blaine surface area ($\text{cm}^2.\text{g}^{-1}$)	5300	4450	4270
Density ($\text{g}.\text{cm}^{-3}$)	3.00	3.06	3.13
Water demand (%)	32.0	34.0	37.0
Beginning of setting time (min)	185	170	240
End of setting time (min)	260	225	310

164

165 The water demand of our cements was measured according to the standard EN 196-3 [63] and is
166 higher than that usually obtained for cements. This is due to the way our cements were produced,
167 with a pilot ball mill rather than an industrial facility. This affects the rheology of the concretes.
168 Table 2 shows the hydration heat and mechanical characteristics of mortars made from cement
169 measured as described in the standards EN 196-9 [64] for hydration heat and EN 196-1 for
170 compressive strength [65]. The compressive strengths after 28 days varied from 40 to 60 MPa.
171 The hydration heat measurements were corrected using the method proposed in EN 196-9 [64].
172 The less limestone a cement contains, the higher is its hydration heat after 41 h, but with time the
173 cement becomes less reactive and less hydration heat is produced. After 5 days, cements C1 and
174 C2, which respectively contained 35 and 20 % of limestone, produced the same hydration heat
175 (allowing for uncertainty) of $20 \text{ J}.\text{g}^{-1}$ while cement C3, with a limestone content of only 5 %, was
176 still reactive and produced $100 \text{ J}.\text{g}^{-1}$ more than the other two after 7 days.

177 Table 2. Thermal (Langavant hydration heats Q_{41} , Q_{120} and Q_{168} measured respectively after 41,
178 120 and 168 hours) and mechanical characteristics obtained for mortars made from the three
179 selected cements.

	C1	C2	C3
Q_{41} (J.g ⁻¹)	255	296	364
Q_{120} (J.g ⁻¹)	274	302	392
Q_{168} (J.g ⁻¹)	294	303	406
Maximal heating (°C)	25.6	29.3	36.3
R_c 1 day (MPa)	8.2	13.3	15.4
R_c 2 days (MPa)	20.4	24.7	27.5
R_c 28 days (MPa)	39.4	49.0	60.2

180
181 The cement hydration products, for W/C=0.5, were studied with XRD and XF analysis at
182 different stages of maturity from 15 minutes after mixing to 28 days. Here, only results at 28 days
183 are presented. Weight loss at 500 °C was measured in order to calculate the bound water and,
184 using Rietveld calculations, the weight fractions of each crystalline phase and of total amorphous
185 was obtained.

186
187 The quantities of Portlandite, ettringite and amorphous phase after 28 days for cements C3, C2
188 and C1 are presented in Table 3.

189
190

191 Table 3. Quantities of Portlandite, ettringite and amorphous phase in cement C1, C2 and C3 after
192 28 days.

Quantity phase (%)	C1	C2	C3
Portlandite	11	16	13
Ettringite	14	13	5
Amorphous phase	60	68	28

193

194 3.1.2 Selected additions

195 The effect of three concrete additions was studied. These were: a granulated blast furnace slag,
196 with a Blaine surface area equal to $4,230 \text{ cm}^2.\text{g}^{-1}$, produced by Ecocem SA; a fly ash from
197 Carling SA, with a Blaine surface area equal to $3,360 \text{ cm}^2.\text{g}^{-1}$ and a mechanically densified silica
198 fume (FS95 DM), from Condensil SA. Because of the high silica fume fineness, it was not
199 possible to measure it thanks to Blaine equipment. According to the technical datasheet, the
200 specific surface area of the silica fume is between $150,000$ and $350,000 \text{ cm}^2.\text{g}^{-1}$. These three
201 additions were added to concrete in the usual percentages, with a variation of 50 % around this
202 value: 50 % for the slag, 25 % for the fly ash and 8 % for the silica fume.

203 Table 4 shows the physical characteristics of the three selected additions. We can see that the
204 median diameter of the silica fume was larger than that of the slag or the fly ash. This is due to
205 our method which is not powerful enough to break coagulation of silica fume particles. In
206 addition, the activity coefficients were not measured with the three selected cements but with a
207 reference cement as laid down in the standard EN 197-1 [16]. The ratios ($R_{A/C}$) between the
208 compressive strengths after 28 days (R_{100C}) for the 50-50 % slag-cement [69], the 25-75 % fly
209 ash-cement [67] and the 10-90 % silica fume-cement [34] and the 100 % cement gives the 28-day
210 activity coefficients, see equation (2). The ratio 10-90 % silica fume-cement for measuring the

211 activity coefficient is used according to the standard, even if it is slightly different to our mean
212 value (8 %).

$$k = \frac{R_{A/c} - R_{100c}}{R_{100c}} \quad (2)$$

213 These values were used in the Bolomey formula, see equation (1), as well as in the concrete mix
214 design tool presented in part 4.4.

215

216 Table 4. Physical characteristics of the three selected additions [16].

	Slag	Fly ash	Silica fume
D ₅₀ (µm)	10.8	17.2	58.2
Blaine surface area (cm ² .g ⁻¹)	4230	3360	NC
Density (g.cm ⁻³)	2.96	2.31	2.27
28-day activity coefficient	0.9	0.8	1.2

217

218 Finally, the chemical admixture used here was a MasterPolyheed 650 superplasticizer from
219 BASF.

220

221 3.2 Notation

222 A notation was applied for the concretes based on the three factors:

223 Cx_%Addition_W/B_%Admixture

- 224 - Cx which indicates the type of cement – C1, C2 or C3,
- 225 - %Addition which indicates the percentage of addition and is followed by the suffix S for
226 slag, FA for fly ash or SF for silica fume,
- 227 - W/B which indicates the water-to-binder (cement + addition) ratio,
- 228 - %Admixture which indicates the percentage of chemical admixture.

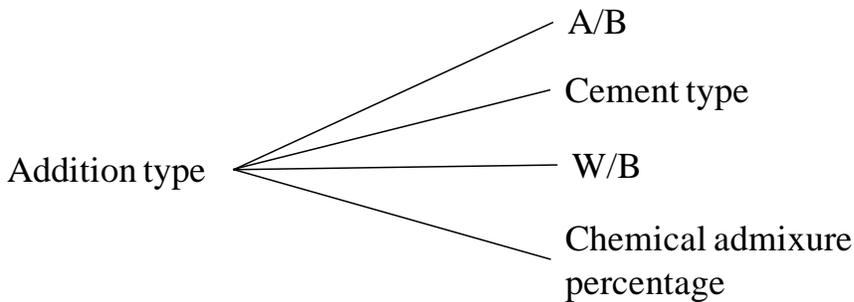
229

230 3.3 Experimental design

231 Screening experimental design was used to study the impact of parameters on hydration heat and
232 mechanical strength. To do this, and limit the number of experiments, only five parameters were
233 varied over three different levels: addition-to-binder ratio, type of cement, type and quantity of
234 additions, water-to-binder ratio and percentage of chemical admixture, see Figure 1. With this
235 type of experimental design, it is possible to observe not only the effect of each parameter, but
236 also the interaction between them. The total quantity of cement and addition was fixed at 360
237 kg.m^{-3} . Because of the variation in the quantity of the addition for each addition, the addition-to-
238 binder ratio varied by 50% around a nominal value.

239

240 Figure 1. Diagram representing the parameters studied in our concrete experimental design.



241

242

243 Considering the various cements and additions water demand, the chemical admixture percentage
244 varies more or less 15 % around a nominal value in order to obtain fluid, or at least not too dry,
245 concretes at fresh state.

246 **Erreur ! Source du renvoi introuvable.** Table 5 shows the parameters and their levels (cement
247 type, type and quantity of addition, W/B, chemical admixture).

248

249 Table 5. Levels and parameters selected for this experimental design.

Parameter	Level								
	Slag			Fly ash			Silica fume		
Addition quantity for 100kg of cement (kg/100kg of cement)	25.0	50.0	75.0	12.5	25.0	37.5	4.0	8.0	12.0
Cement type	C1			C2			C3		
W/B	0.375			0.400			0.425		
Chemical admixture (%)	0.38	0.45	0.52	0.51	0.60	0.69	0.85	1.00	1.15

250

251 The name and formulation of concretes studied in this article are presented in appendix A.

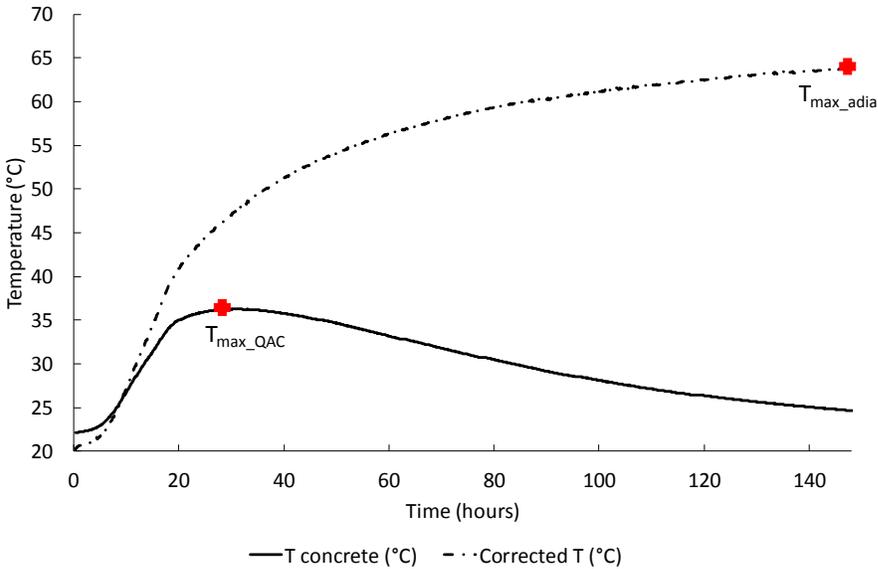
252 3.4 Analytical techniques

253 The concretes were characterized:

- 254 - in the fresh state, by measuring slump according to the standard EN 12350-2 [68],
- 255 - thermally, by measuring the hydration heat with quasi-adiabatic calorimetry QAC
256 according to the standard EN 12390-14 [69]. Figure 2 shows an example of the result of
257 such a test.
- 258 - mechanically, by measuring compressive strengths on 16x32cm cylindrical specimens
259 according to the standard EN 12390-3 [70].

260

261 Figure 2. Example of the result of quasi-adiabatic calorimetric test (QAC). Case of the concrete
262 C1_25S_0.375_0.45. T_{\max_QAC} corresponds to the maximal temperature measured during the test
263 and T_{\max_adia} to the final temperature obtained after correction due to the losses of the calorimeter
264 (and that are estimated with the method proposed by EN 12390-14).



265

266

267 4. RESULTS AND DISCUSSION

268 In this section, we shall present and discuss the results from the experimental design, especially
 269 with regard to the fresh state and changes in the hydration heat and compressive strength. The
 270 fresh state characteristics were measured but were not included in our mix design tool. The
 271 figures below present the median effects in black and the interaction between factors in blue for
 272 slag (S), red for fly ash (FA) and green for silica fume (SF). The interactions were analyzed by a
 273 comparison with the general trend. If the change was similar but with just a vertical displacement,
 274 no interaction was deemed to take place between the type of addition and the other factors. On
 275 the other hand, if the trend was reversed, there a considerable interaction was deemed to take
 276 place between the type of addition and the other factors.

277 4.1 Influence of the factors on concrete in the fresh state

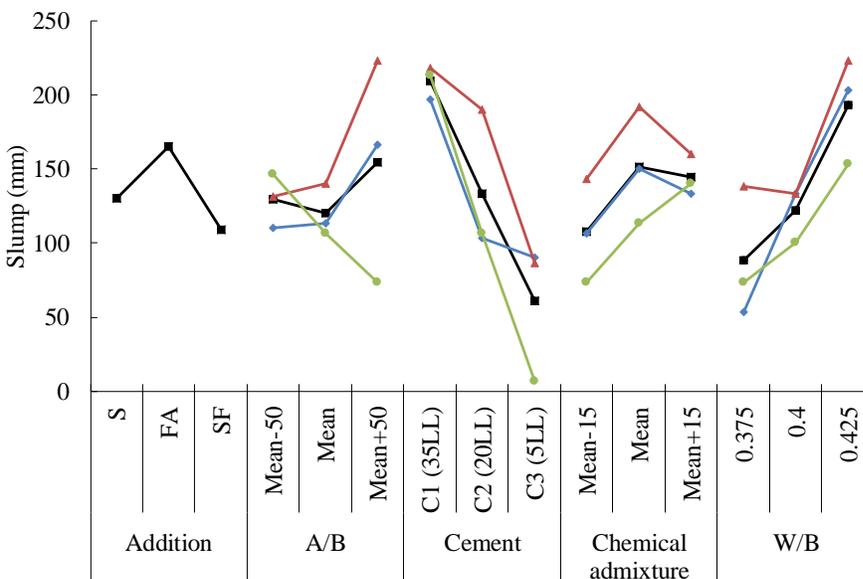
278

279 Figure 3 presents the effects of the different factors and their mutual interactions on concrete
 280 slump in the fresh state. Generally, the use of slag and fly ash in concrete leads to more slump

281 than silica fume. This is due to the clustering of silica fume which means that water is confined
 282 within it. Because of this, less water is available to increase concrete fluidity. The difference in
 283 slump between slag and fly ash concretes is explained by the fact that fly ash has a spherical
 284 specific surface [32] whereas that of slag is granular [33]. The higher the quantity of addition, the
 285 greater the slump, except when silica fume is added.

286

287 Figure 3. Median effects of factors and their interactions on concrete slump.



288

289

290 The types of cement used in the concrete also had an impact on the fresh state, regardless of the
 291 type of addition, although this could increase water demand. This is due to the wide variation in
 292 the characteristics of cements, and in particular their water demand. The closer the composition
 293 of the cement was to CEM I, the higher the water demand.

294 Due to its fluidizing effect, beyond a certain quantity, the chemical admixture increased the slump
295 of the concrete. However, the full effect of chemical mixing was not achieved because the mixing
296 time was not optimized (we were close to field conditions).

297 The type of addition can interact with the chemical admixture. Bessa-Badreddine report that the
298 smaller the amount of the addition, the greater the demand for the chemical admixture [19].
299 Finally, as expected, an increase in the water-to-binder ratio increased the slump.

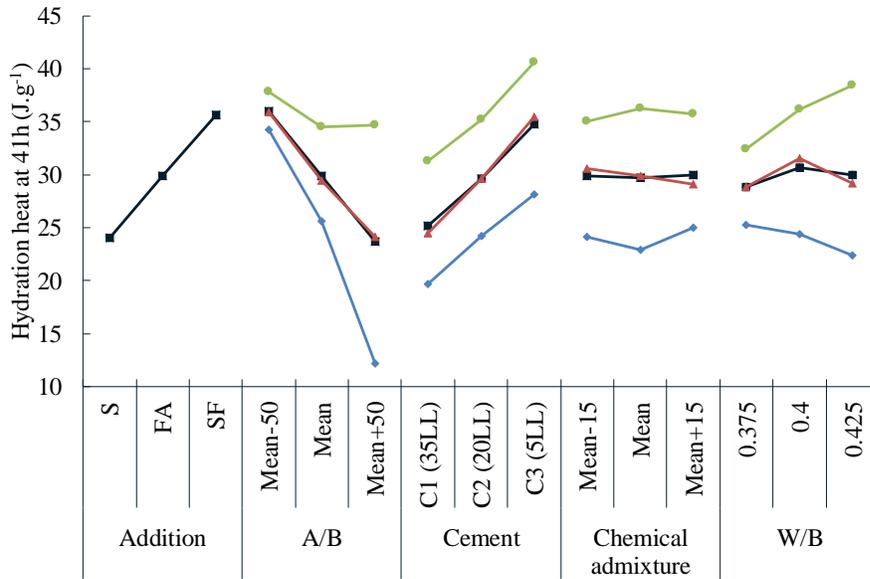
300

301 **4.2 Influence of the factors on hydration heat**

302 It is also important to study temperature rise in massive concrete structures in order to prevent the
303 risk of both DEF and cracking. To do this, the calorimetric measurement of temperature during
304 concrete hydration was analyzed, giving the hydration heat after 41h, see

305 Figure 4 and after 144h, see Figure 5. In general, we can see that concrete additions reduced the
306 hydration heat, to an extent that increased with their quantity. However, this effect was less
307 visible for silica fume, because of the lower quantity used (4 to 12 % compared to 12.5 to 37.5
308 and 25 to 75 % for fly ash and slag) and its higher reactivity. Slag and fly ash produce less heat
309 than silica fume, after both 41h and 144h. Indeed, like pozzolanic materials, they react slowly and
310 need activation, while silica fume is very reactive due to its fineness and its role as a nucleation
311 site [55]. The difference in heat flow between slag and fly ash decreased with time, and led to
312 values that were equivalent for the two, or even higher for slag than fly ash, after 144h. These
313 values agreed with the measured activity coefficients (see **Erreur ! Source du renvoi**
314 **introuvable.**).
315

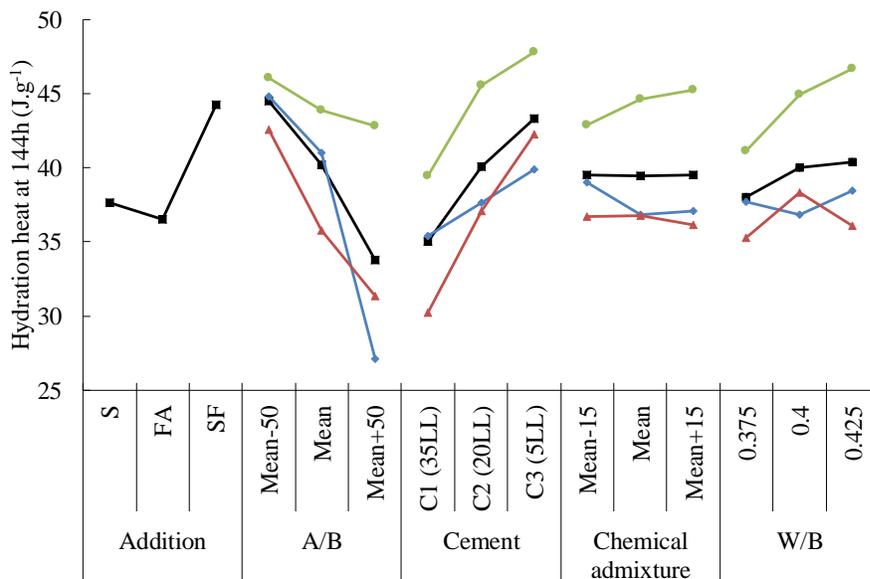
316 Figure 4. Median effects of factors and their interactions on the QAC hydration heat of concrete
 317 after 41 hours.



318

319

320 Figure 5. Median effects of factors and their interactions on the QAC hydration heat of concrete
 321 after 144 hours.



322

323

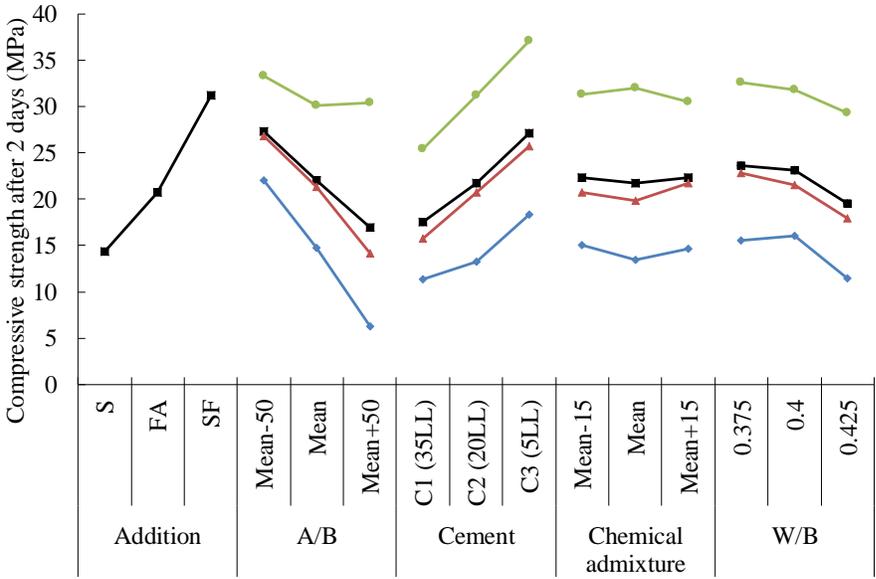
324 As in the case of slump, we could observe the effect of cement type on the hydration heat after
325 41h and 144h, whatever the type of addition. The more diluted the clinker part of the cement
326 (presence of limestone), the lower the hydration heat. However, in contrast to slump, the
327 percentage of chemical admixture did not affect hydration heat production, whatever the maturity
328 and the addition type. Finally, the water-to-binder ratio did not influence early age hydration heat
329 production and affected that after 144h very little, but our experimental design did not vary the
330 W/B ratio by a large amount. It is also possible to see a small difference between concretes with
331 silica fume when the W/B ratio increased: more water was free for hydration reactions so the
332 hydration heat produced increased with W/B ratio.

333 **4.3 Influence of the factors on compressive strength**

334 Figure 6 and Figure 7 respectively show the median effect and interactions of the factors on the
335 compressive strength of the concrete after 2 and 28 days. It is possible to draw a parallel between
336 the median effects of factors and their interactions with regard to hydration heat and compressive
337 strength. Silica fume gives higher compressive strength than fly ash and slag after 2 and 28 days,
338 which agrees with their activity coefficients. Moreover, as Pertué has reported, such differences
339 in early age strength can be explained by the difference between the kinetic of hydration
340 reactions, as evidenced by heat measurements [71]. However, the compressive strengths of
341 concrete with slag are lower than with fly ash because of the higher percentage of slag (less
342 cement). Even if at early age, it is difficult to see an interaction between the cement and the type
343 of addition, the strengths with greater maturity show such an interaction, predominantly for slag
344 and silica fume.

345

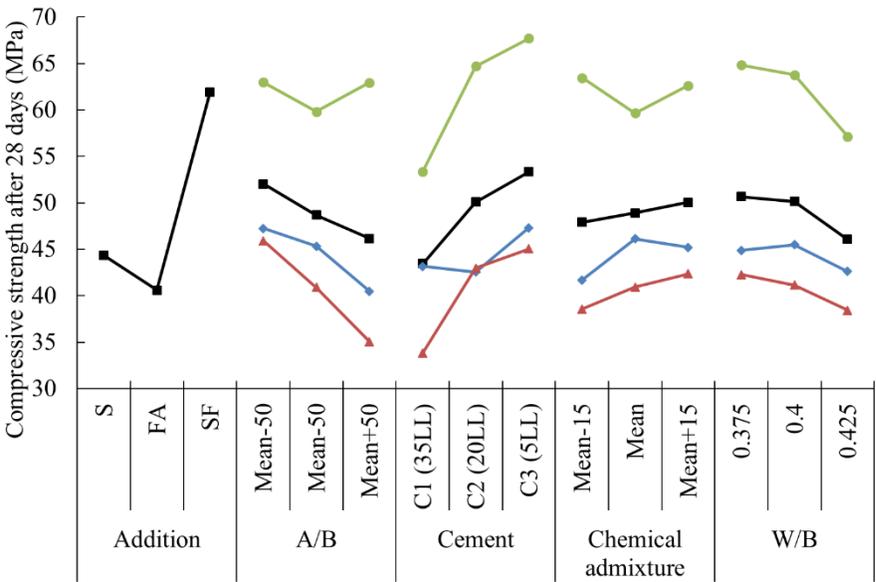
346 Figure 6. Median effects of factors and their interactions on the 2-day compressive strength of
 347 concrete.



348

349

350 Figure 7. Median effects of factors and their interactions on the 28-day compressive strength of
 351 concrete.



352

353

354 Compressive strength decreased with the quantity of additions. Interaction with the type of
355 addition was low, except for silica fume due to its high water demand and reactivity. The
356 chemical admixture had no effect on strength, irrespective of the type and quantity of additions.
357 Lastly, a small effect, resulting from a small variation in the water-to-binder ratio, on compressive
358 strength is visible, with no interaction with the type of addition.

359 **4.4 Concrete mix design tool**

360 The above analysis of the median effects and interactions provides the opportunity to create a
361 model for several answers according to each factor. The percentage of chemical admixture is not
362 taken into account in this model because of its minor impacts on the characteristics of concrete.
363 Combining these model equations provides us with a concrete mix design tool that enables
364 specified requirements to be met. Generally, the answer X is calculated using equation (3) and
365 corresponds to the sum of the median value of the answer X for the addition A \bar{X}_A , the variation
366 generated by the percentage of addition $\Delta X_{\%A}$, the variation resulting from the W/B ratio $\Delta X_{\frac{W}{B}}$
367 and the variation arising from the cement type C ΔX_C .

$$X = \bar{X}_A + \Delta X_{\%A} + \Delta X_{\frac{W}{B}} + \Delta X_C \quad (3)$$

368 Equations (4), (5) and (6) correspond respectively to the variations resulting from the cement
369 type, the W/B ratio and the percentage of additions. These variations correspond to the difference
370 between the median value of the answer X for addition A \bar{X}_A and cement C \bar{X}_C , see equation (4),
371 and the function $f_x(\%A)$ and $f_x\left(\frac{W}{B}\right)$ – obtained from the effect and interaction analyze for the
372 answer X – and the median value of the answer X for addition A, see equations (5) and (6).

$$\Delta X_C = \bar{X}_C - \bar{X}_A \quad (4)$$

$$\Delta X_{\frac{W}{B}} = f_x \left(\frac{W}{B} \right) - \bar{X}_A \quad (5)$$

$$\Delta X_{\%A} = f_x (\%A) - \bar{X}_A \quad (6)$$

373 Table 6 presents the equations and the data used to calculate the maximum temperature in the
 374 calorimeter measured during concrete hydration (T_{\max_QAC}), the maximum adiabatic temperature
 375 ($T_{\text{adia_max}}$) and the compressive strength after 2 and 28 days (R_c 2 and R_c 28). With finite element
 376 modelling of the quasi-adiabatic test [72], it has been established that T_{\max_QAC} corresponds to the
 377 temperature measured in a concrete structure with a notional size of 40 cm while $T_{\text{adia_max}}$
 378 corresponds to the temperature measured in massive concrete structures with a notional size of
 379 several meters.

380

381 Table 6. Equations and data used for the concrete mix design tool.

		\bar{X}_A	Addition (%)	Ratio $\frac{W}{B_{tot}}$	\bar{X}_{C1}	\bar{X}_{C2}	\bar{X}_{C3}
T_{\max_QAC} (°C)	S	34.3	$-0.19.\%A + 9.39$	$0.67.\frac{W}{B_{tot}} + 3.32$	31.8	34.4	36.8
	FA	37.0	$-0.26.\%A + 6.39$	$-32.00.\frac{W}{B_{tot}} + 9.02$	34.8	37.5	41.5
	SF	41.6	$-0.16.\%A + 1.31$	$51.33.\frac{W}{B_{tot}} - 20.54$	38.6	41.4	44.7
$T_{\text{adia_max}}$ (°C)	S	57.9	$-0.37.\%A + 17.98$	$-74.02.\frac{W}{B_{tot}} + 29.61$	53.2	59.0	61.5
	FA	65.2	$-0.46.\%A + 11.50$	$-1.95.\frac{W}{B_{tot}} + 0.79$	51.5	58.5	63.9
	SF	66.0	$-0.42.\%A + 3.47$	$92.23.\frac{W}{B_{tot}} - 36.89$	61.0	67.3	69.7

R _c 2 days (MPa)	S	14.3	-0.31.%A + 15.417	$-79.50 \cdot \frac{W}{B_{tot}} + 31.83$	11.4	13.3	18.4
	FA	20.8	-0.44.%A + 10.86	$98.00 \cdot \frac{W}{B_{tot}} + 39.20$	15.7	20.8	25.8
	SF	31.3	-0.35.%A + 2.92	$-66.00 \cdot \frac{W}{B_{tot}} + 26.06$	25.4	31.2	37.1
R _c 28 days (MPa)	S	44.4	-0.14.%A + 6.64	$-45.33 \cdot \frac{W}{B_{tot}} + 18.04$	44.3	42.6	47.3
	FA	40.6	-0.43.%A + 10.74	$-76.67 \cdot \frac{W}{B_{tot}} + 30.45$	33.9	43.0	45.0
	SF	61.9	-0.004.%A + 0.03	$-154.33 \cdot \frac{W}{B_{tot}} + 61.18$	53.4	64.7	67.7

382

383 4.5 Application

384 In this section, the application of this mix design tool to meet specified requirements (Table 7)
 385 and to minimize the maximum temperature in a structure with a notional size of 40 cm is
 386 presented.

387

388 Table 7. Specific requirements.

Addition percentage according to standard EN 206/CN NAF 1	0 < S < 0.4 0 < FA < 0.3 0 < SF < 0.1
W/B	0.3 < W/B < 0.6
B _{eq} (kg)	280 < B _{eq} < 400
Volume of paste (L)	V _{paste} ≥ 250
T _{max_QAC} (°C)	minimal
R _c 28 days for C30 (MPa)	38 MPa

389

390 Equation (7) is used to calculate the volume of paste V_{paste} considering the water to binder ratio

391 $\frac{W}{B}$, the total binder B_{tot} , the addition mass m_{add} and density ρ_{add} and the cement density ρ_c .

$$V_{paste} = \frac{W}{B} \cdot B_{tot} + \frac{m_{add}}{\rho_{add}} + \frac{B_{tot} - m_{add}}{\rho_c} \quad (7)$$

392 The parameters in this mix design tool are the type and quantity of cement, of addition and the
 393 quantity of water. The working limits were defined on the basis of the standard
 394 EN 206 NAF 1 [7] for an XC4 exposure grade (corrosion by carbonation and variable presence of
 395 water) and presented in **Erreur ! Source du renvoi introuvable.**

396 . Note that, like the experimental design, the mix design tool has been created for concrete with a
 397 fixed granular skeleton. The equivalent binder B_{eq} corresponds to the sum of the quantity of
 398 cement C and the activity coefficient k of the addition multiplied by the addition quantity A as
 399 defined in equation (8).

$$B_{eq} = C + k \cdot A \quad (8)$$

400 Table 8 presents the nine optimized mix designs (3 different cements with 3 different additions).
 401 Firstly, we can see that the 28-day compressive strength of the concretes was above 38 MPa when
 402 silica fume was used (mix designs 7 to 9). Three mix designs gave compressive strengths
 403 between 38 and 40MPa (mix designs 2, 4 and 5). As we have already seen, slag leads to higher
 404 QAC hydration heat and temperature than fly ash (more than 10°C difference between concretes
 405 with slag and those with fly ash). For the two last concretes (mix designs 4 and 5), it was the high
 406 amount of limestone in C1 that limited the temperature rise (28.4 °C) while both reach 38MPa
 407 after 28 days.

408 Table 8. Tested concrete mix designs.

Mix design number	1	2	3	4	5	6	7	8	9
Addition type	S			FA			SF		
Cement type	C1	C2	C3	C1	C2	C3	C1	C2	C3
Equivalent binder (kg)	389	387	390	364	390	280	395	400	395
A/B	0.40	0.40	0.40	0.30	0.30	0.30	0.10	0.10	0.10
W/B _{eq}	0.30	0.30	0.30	0.47	0.47	0.60	0.30	0.30	0.32
T _{max_QAC} (°C)	37.1	40.1	43.9	28.2	31.3	31.3	31.9	36.6	40.7
T _{adia_max} (°C)	65.0	70.7	73.2	49.1	56.1	61.3	51.9	58.2	62.3
R _c 2 days (MPa)	23.5	25.3	30.5	10.3	15.3	8.3	30.5	36.3	42.1
R _c 28 days (MPa)	49.3	40.4	59.5	38.1	38.1	50.5	60.7	58.7	80.0

409
 410 A further condition was then added to the specified requirements, namely a minimum 2-day
 411 compressive strength of 20 MPa. The mix designs are presented in Table 9. Concretes 1 to 3 and
 412 7 to 9 already met the two compressive strength conditions and have therefore not been modified.

413
 414 Table 9. Tested concrete mix design meeting the specified requirements with a minimum
 415 temperature in the QAC test and a 2-day compressive strength of at least 20 MPa.

Mix design number	1	2	3	4	5	6	7	8	9
Addition type	S			FA			SF		
Cement type	C1	C2	C3	C1	C2	C3	C1	C2	C3
Equivalent binder (kg)	389	387	390	388	400	400	395	400	395
A/B	0.40	0.40	0.40	0.30	0.30	0.30	0.10	0.10	0.10
W/B _{eq}	0.30	0.30	0.30	0.36	0.42	0.47	0.30	0.30	0.32
T _{max_QAC} (°C)	37.1	40.1	43.9	31.4	32.8	35.1	31.9	36.6	40.7
T _{adia_max} (°C)	64.8	70.6	73.1	49.3	56.2	61.5	51.9	58.2	62.3
R _c 2 days (MPa)	23.5	25.3	30.5	20.0	20.0	20.0	30.5	36.3	42.1
R _c 28 days (MPa)	49.3	40.4	59.5	45.7	41.8	59.6	60.7	58.7	80.0

417 This time, we can see that all the concretes have a 2-day compressive strength of at least 20 MPa
418 and that the maximum temperature in the quasi-adiabatic test stays below 44 °C. With regard to
419 this temperature, fly ash concretes are not the only ones to exhibit a low temperature rise. Indeed,
420 mix designs 7 and 8 – made with silica fume - generate the same heat as fly ash concretes (mix
421 designs 4 to 6), and even less heat than concretes with slag (mix designs 1 to 3). Contrary to what
422 was expected, slag concretes are more exothermic and have lower 2-day compressive strengths
423 than silica fume concretes.

424 Otherwise, when considering larger concrete structures, the temperature is closer to the adiabatic
425 temperature. For at least 7 mix designs, the adiabatic temperature is close to 65 °C, and
426 sometimes 75 °C for slag concrete. Such high adiabatic temperatures can increase the risk of
427 cracking. Lower temperatures than with slag concretes can be obtained with mix designs
428 containing fly ash followed by designs containing silica fume. This could be explained by two
429 things: firstly, fly ash is slightly less reactive than slag, and secondly, silica fume concrete mix
430 designs may be optimized with reference to the minimum temperature in the quasi-adiabatic test
431 but if this is the case, the water-to-binder ratio is very low. This means the cement and silica fume
432 have a low level of hydration and therefore a lower adiabatic temperature compared to slag
433 concrete. It is possible to have a water-to-binder ratio equal to 0.3 for silica fume concrete but
434 due to higher water demand, a large amount of superplasticizer is needed. If a higher water-to-
435 binder ratio is used, the cement and the silica fume will be more hydrated leading to higher
436 temperatures in massive concrete structures.

437 When heat release is considered in this mix design tool, the importance of the size of the structure
438 is apparent: mix design can only be optimized on the basis of the size of the structure matching
439 with the environment temperature or construction procedure.

440

441 **5. CONCLUSION**

442 This study has allowed us to show the effect of the type and percentage of additions, cement
443 composition, water-to-binder ratio and the quantity of chemical admixture on concrete in the
444 fresh state and later on hydration heat and compressive strength. Concrete slump is influenced by
445 the cement-addition combination and by the quantity of water and chemical admixture, which
446 deflocculates particles and provides free water for fluidity and concrete hydration. As a general
447 rule, concrete slump increases with the amount of addition, except when silica fume is used as an
448 addition.

449 After setting, the water-to-binder ratio and the amount of chemical admixture have little effect on
450 the hydration heat compared to the type of cement and addition. The greater the amount of
451 addition, the lower the heat flow. The hydration kinetic is faster for concrete with silica fume than
452 for concrete with slag or fly ash. As far as compressive strength is concerned, both at early age or
453 later, it is the cement-addition combination that is important, in addition to the activity coefficient
454 of the addition.

455 Finally, this study has enabled us to develop a concrete mix design tool that enables specified
456 requirements to be met. For example, this tool allows the optimization of concrete mix design
457 when certain temperatures during hydration or certain mechanical strengths are needed for a
458 given environmental exposition and shows how important the size of the considered structure is
459 in order to optimize the mix design. Of course, our tool does not take account of other factors that
460 should also be considered during concrete mix design, such as durability, environmental impact
461 and cost.

462 **REFERENCES**

- 463 [1] IFSTTAR, Recommendations for preventing disorders due to Delayed Ettringite Formation
 464 - Technical Guide, 2018.
- 465 [2] M. Al Shamaa, S. Lavaud, L. Divet, G. Nahas, J.M. Torrenti, Influence of relative humidity
 466 on delayed ettringite formation, *Cem. Concr. Compos.* 58 (2015) 14–22.
 467 doi:<http://dx.doi.org/10.1016/j.cemconcomp.2014.12.013>.
- 468 [3] H.Y. Ghorab, E.A. Kishar, Studies on the stability of the calcium sulfoaluminate hydrates.
 469 Part 1: Effect of temperature on the stability of ettringite in pure water, *Cem. Concr. Res.* 15
 470 (1985) 93–99.
- 471 [4] G. De Schutter, L. Taerwe, Degree of hydration-based description of mechanical properties
 472 of early age concrete, *Mater. Struct.* 29 (1996) 335–344.
- 473 [5] F. de Larrard, *Concrete Mixture Proportioning: A Scientific Approach* - CRC Press Book,
 474 1999.
- 475 [6] G. Arliguie, H. Hornain, *GranDuBé: grandeurs associées à la durabilité des bétons*, Presses
 476 de l'École nationale des ponts et chaussées, 2007.
 477 <http://books.google.fr/books?id=0hUQMCIJG9q0C> (in French).
- 478 [7] AFNOR, NF EN 206-1/CN Béton. Spécification, performance, production et conformité -
 479 Complément national à la norme NF EN 206-1, 2012 (in French).
- 480 [8] ACI R 211.1, Standard practice for selecting proportions for normal, heavyweight, and mass
 481 concrete. *ACI Manual of Concrete Practice*, Part 1, Concrete Institute, Farmington hills, MI,
 482 2005.
- 483 [9] EN 12620 Aggregates for concrete, 2008.
- 484 [10] J. Byfors, Plain concrete at early age, Swedish Cement and Concrete Research Institute,
 485 1980.
- 486 [11] H. Minard, Etude intégrée des processus d'hydratation, de coagulation, de rigidification et
 487 de prise pour un système C3S-C3A-sulfates-alcalins, PhD Thesis, Université de Bourgogne,
 488 2003 (in French).
- 489 [12] W. Lerch, R.H. Bogue, Heat of hydration of portland cement pastes, *J. Res. Natl. Bur. Stand.*
 490 12 (1934) 645–664.
- 491 [13] D.P. Bentz, E.J. Garboczi, C.J. Haecker, O.M. Jensen, Effects of cement particle size
 492 distribution on performance properties of Portland cement-based materials, *Cem. Concr.*
 493 *Res.* 29 (1999) 1663–1671. doi:[http://dx.doi.org/10.1016/S0008-8846\(99\)00163-5](http://dx.doi.org/10.1016/S0008-8846(99)00163-5).
- 494 [14] D.P. Bentz, Blending different fineness cements to engineer the properties of cement-based
 495 materials, *Mag. Concr. Res.* 62 (2010) 327–338.
- 496 [15] M.M. Costoya Fernandez, Effect of particle size on the hydration kinetics and
 497 microstructural development of tricalcium silicate, Thesis, Thèse de l'École Polytechnique
 498 Fédérale de Lausanne, 2008.
- 499 [16] EN 197-1 Cement - Part 1: Composition, specifications and conformity criteria for common
 500 cements, 2012.
- 501 [17] E. Gartner, Industrially interesting approaches to “low-CO₂” cements, *Cem. Concr. Res.* 34
 502 (2004) 1489–1498.
- 503 [18] H.F. Taylor, *Cement Chemistry*, 2nd Edition, Thomas Telford, London, 1997.
- 504 [19] A. Bessa-Badreddine, Etude de la contribution des additions minérales aux propriétés
 505 physiques, mécaniques et de durabilité des mortiers, PhD Thesis, Université de Cergy-
 506 Pontoise, 2004 (in French).

- 507 [20] I. Joudi-Bahri, A. Lecomte, M.B. Ouezdou, T. Achour, Use of limestone sands and fillers in
508 concrete without superplasticizer, *Cem. Concr. Compos.* 34 (2012) 771–780.
509 doi:<https://doi.org/10.1016/j.cemconcomp.2012.02.010>.
- 510 [21] P. Diederich, Contribution à l'étude de l'influence des propriétés des fillers calcaires sur le
511 comportement autoplaçant du béton, PhD Thesis, Université Toulouse III - Paul Sabatier,
512 2010 (in French).
- 513 [22] M.R. Jones, L. Zheng, M.D. Newlands, Estimation of the filler content required to minimise
514 voids ratio in concrete, *Mag. Concr. Res.* 55 (2003) 193–202.
- 515 [23] E. Berodier, K. Scrivener, Understanding the Filler Effect on the Nucleation and Growth of
516 C-S-H, *J. Am. Ceram. Soc.* 97 (2014) 3764–3773. doi:10.1111/jace.13177.
- 517 [24] H. Justnes, I. Meland, J.O. Bjoergum, J. Krane, The mechanism of silica fume action in
518 concrete studied by solid state ²⁹Si NMR, in: *NMR-Semin.*, 1992.
- 519 [25] Y. Villagran-Zaccardi, E. Gruyaert, N. Alderete, N. De Belie, Influence of particle size
520 ditribution of slag, limestone and fly ash on early hydration of cement assessed by
521 isothermal calorimetry, in: *Int. RILEM Conf. Mater. Syst. Struct. Civ. Eng. Concr. Suppl.*
522 *Cem. Mater.*, 2016.
- 523 [26] B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials, *Cem.*
524 *Concr. Res.* 41 (2011) 1244–1256. doi:<http://dx.doi.org/10.1016/j.cemconres.2010.12.001>.
- 525 [27] A. Schöler, B. Lothenbach, F. Winnefeld, M.B. Haha, M. Zajac, H.-M. Ludwig, Early
526 hydration of SCM-blended Portland cements: A pore solution and isothermal calorimetry
527 study, *Cem. Concr. Res.* 93 (2017) 71–82.
528 doi:<https://doi.org/10.1016/j.cemconres.2016.11.013>.
- 529 [28] E. Berodier, Impact of the supplementary cementitious materials on the kinetics and
530 microstructural development of cement hydration, Thesis, Thèse de l'Ecole Polytechnique
531 Fédérale de Lausanne, 2015.
- 532 [29] G. Van Rompaey, Etude de la réactivité des ciments riches en laitier, à basse température et
533 à court temps, sans ajout chloruré, PhD Thesis, Université libre de Bruxelles, 2006 (in
534 French).
- 535 [30] F. Massazza, M. Diamon, Chemistry of hydration of cements and cementitious systems, in:
536 9th Int. Congr. Chem. Cem., 1992: pp. 383–429.
- 537 [31] M. Cyr, P. Lawrence, E. Ringot, Efficiency of mineral admixtures in mortars, Quantification
538 of physical and chemical effects of fines admixtures in relation with compressive strength,
539 *Cem. Concr. Res.* 36 (2006) 264–277.
- 540 [32] R.V. Ramachandran V. S. Mortel N., *Concrete admixtures Handbook*, Prop. Sci. Technol.
541 (1995).
- 542 [33] A. Boudchicha, Utilisation des additions minérales et des adjuvants fluidifiants pour
543 l'amélioration des propriétés rhéologiques et mécaniques des bétons, PhD Thesis, Université
544 Mentouri Constantine, 2007 (in French).
- 545 [34] NF EN 13263-1+A1 Fumée de silice pour béton. Partie 1 : définition, exigences et critères
546 de conformité, 2009 (in French).
- 547 [35] W.A. Gutteridge, J.A. Dalziel, Filler cement: The effect of the secondary component on the
548 hydration of Portland cement: Part I. A fine non-hydraulic filler, *Cem. Concr. Res.* 20 (1990)
549 778–782. doi:[http://dx.doi.org/10.1016/0008-8846\(90\)90011-L](http://dx.doi.org/10.1016/0008-8846(90)90011-L).
- 550 [36] K. Scrivener, W. Wieker, Advances in hydration at low, ambient and elevated temperatures,
551 in: 9th Int. Congr. Chem. Cem., 1992: pp. 1449–1482.

- 552 [37] R. Talero, C. Pedrajas, M. González, C. Aramburo, A. Blázquez, V. Rahhal, Role of the filler
553 on Portland cement hydration at very early ages: Rheological behaviour of their fresh
554 cement pastes, *Constr. Build. Mater.* 151 (2017) 939–949.
555 doi:<https://doi.org/10.1016/j.conbuildmat.2017.06.006>.
- 556 [38] P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars: Effet of type, amount and
557 fineness of fine constituent on compressive strength, *Cem. Concr. Res.* 35 (2005) 1092–
558 1105.
- 559 [39] V. Waller, Relation entre composition des bétons, exothermie en cours de prise et résistance
560 en compression, PhD Thesis, Ecole Nationale des Ponts et Chaussées, 1999 (in French).
- 561 [40] F. Han, X. He, Z. Zhang, J. Liu, Hydration heat of slag or fly ash in the composite binder at
562 different temperatures, *Thermochim. Acta.* 655 (2017) 202–210.
563 doi:<http://dx.doi.org/10.1016/j.tca.2017.07.002>.
- 564 [41] B. Klemczak, M. Batog, Heat of hydration of low-clinker cements, *J. Therm. Anal. Calorim.*
565 123 (2016) 1351–1360. doi:10.1007/s10973-015-4782-y.
- 566 [42] V. Kocaba, Development and evaluation of methods to follow microstructural development
567 of cementitious systems including slags, PhD Thesis, Ecole polytechnique fédérale de
568 Lausanne, 2009.
- 569 [43] S. Schindler, K.J. Folliard, Heat of hydration models for cementitious materials, *ACI Mater.*
570 *J.* 102 (2005) 24–33.
- 571 [44] S. Arrhénius, Quantitative laws in biological chemistry, G. Bell and Sons Ed., London,
572 1915.
- 573 [45] G.J. Verbeck, Chemistry of hydration of Portland cement - III. Energetics of the hydration of
574 Portland cement, in: 4th Int. Symp. Chem. Cem., 1960: pp. 1453–1465.
- 575 [46] A.K. Schindler, Effect of temperature on hydration of cementitious materials, *Mater. J.* 101
576 (2004) 72–81.
- 577 [47] L. D’Aloia, G. Chanvillard, Determining the “apparent” activation energy of concrete: Ea—
578 numerical simulations of the heat of hydration of cement, *Cem. Concr. Res.* 32 (2002)
579 1277–1289. doi:[http://dx.doi.org/10.1016/S0008-8846\(02\)00791-3](http://dx.doi.org/10.1016/S0008-8846(02)00791-3).
- 580 [48] M. Maage, Strength and heat development in concrete: influence of fly ash and condensed
581 silica fume, in: 2nd CANMETACI Int. Conf. Fly Ash Silica Fume Slag Nat. Pozzolans
582 *Concr.*, 1986.
- 583 [49] M. Cyr, P. Lawrence, E. Ringot, A. Carles-Gibergues, Variability of efficiency factors
584 characterising mineral admixtures, *Mater. Struct.* 33 (2000) 466. doi:10.1007/bf02480667.
- 585 [50] M.I.A. Khokhar, E. Roziere, P. Turcry, F. Grondin, A. Loukili, Mix design of concrete with
586 high content of mineral additions: Optimisation to improve early age strength, *Cem. Concr.*
587 *Compos.* 32 (2010) 377–385. doi:<http://doi.org/10.1016/j.cemconcomp.2010.01.006>.
- 588 [51] J. Hu, Z. Ge, K. Wang, Influence of cement fineness and water-to-cement ratio on mortar
589 early-age heat of hydration and set times, *Constr. Build. Mater.* 50 (2014) 657–663.
590 doi:<http://dx.doi.org/10.1016/j.conbuildmat.2013.10.011>.
- 591 [52] J.M. Torrenti, F. Benboudjema, Mechanical threshold of cimentitious materials at early age,
592 *Mater. Struct.* 38 (2005) 299–304.
- 593 [53] L. Stefan, Étude expérimentale et modélisation de l’évolution des propriétés mécaniques au
594 jeune âge dans les matériaux cimentaires, PhD Thesis, Ecole Normale Supérieure de Cachan
595 et Université de Laval, 2009 (in French).
- 596 [54] P.C. Hewlett, *Lea’s Chemistry of Cement and Concrete*, 4th Edition, Elsevier, 1998.

- 597 [55] E.-H. Kadri, R. Duval, Hydration heat kinetics of concrete with silica fume, *Constr. Build.*
598 *Mater.* 23 (2009) 3388–3392. doi:<https://doi.org/10.1016/j.conbuildmat.2009.06.008>.
- 599 [56] N. Hani, O. Nawawy, K.S. Ragab, M. Kohail, The effect of different water/binder ratio and
600 nano-silica dosage on the fresh and hardened properties of self-compacting concrete, *Constr.*
601 *Build. Mater.* 165 (2018) 504–513. doi:<https://doi.org/10.1016/j.conbuildmat.2018.01.045>.
- 602 [57] M.B. Bizinotto, F. Faleschini, C.G.J. Fernández, D.F.A. Hernández, Effects of chemical
603 admixtures on the rheology of fresh recycled aggregate concretes, *Constr. Build. Mater.* 151
604 (2017) 353–362. doi:<https://doi.org/10.1016/j.conbuildmat.2017.06.111>.
- 605 [58] E.H. Kadri, Contribution à l'étude de l'influence de la fumée de silice sur les
606 caractéristiques des bétons à hautes performances, PhD Thesis, Université de Cergy
607 Pontoise, 1998 (in French).
- 608 [59] H. Huang, C. Qian, F. Zhao, J. Qu, J. Guo, M. Danzinger, Improvement on microstructure of
609 concrete by polycarboxylate superplasticizer (PCE) and its influence on durability of
610 concrete, *Constr. Build. Mater.* 110 (2016) 293–299.
611 doi:<https://doi.org/10.1016/j.conbuildmat.2016.02.041>.
- 612 [60] F. Huang, H. Li, Z. Yi, Z. Wang, Y. Xie, The rheological properties of self-compacting
613 concrete containing superplasticizer and air-entraining agent, *Constr. Build. Mater.* 166
614 (2018) 833–838. doi:<https://doi.org/10.1016/j.conbuildmat.2018.01.169>.
- 615 [61] A. Mardani-Aghabaglou, O.C. Boyaci, H. Hosseinnezhad, B. Felekoglu, K. Ramyar, Effect
616 of gypsum type on properties of cementitious materials containing high range water
617 reducing admixture, *Cem. Concr. Compos.* 68 (2016) 15–26.
- 618 [62] EN 934-2 Admixtures for concrete, mortar and grout - Part 2 : concrete admixtures -
619 Definitions, requirements, conformity, marking and labelling, 2012.
- 620 [63] NF EN 196-3+A1 Méthodes d'essais des ciments. Partie 3 : détermination du temps de prise
621 et de la stabilité, 2009 (in French).
- 622 [64] EN 196-9 Methods of testing cement - Part 9 : heat of hydration - Semi-adiabatic method,
623 2010.
- 624 [65] EN 196-1 Methods of testing cement - Part 1 : determination of strength, 2016.
- 625 [66] NF EN 15167-1 Laitier granulé de haut-fourneau moulu pour utilisation dans le béton,
626 mortier et coulis. Partie 1 : définitions, exigences et critères de conformité, 2006 (in French).
- 627 [67] NF EN 450-1 Cendres volantes pour béton Partie 1 : Définition, spécification et critères de
628 conformité, 2012 (in French).
- 629 [68] EN 12350-2 Testing fresh concrete - Part 2 : slump test, 2012.
- 630 [69] EN 12390-14 Testing hardened concrete - Part 14 : semi-adiabatic method for the
631 determination of heat released by concrete during its hardening process, 2018.
- 632 [70] EN 12390-3 Testing hardened concrete - Part 3: compressive strength of test specimens,
633 2012.
- 634 [71] A. Pertué, Etude expérimentale du retrait endogène, du fluage propre et de la fissuration des
635 matrices cimentaires aux jeune et très jeune âges, Thesis, Thèse de l'Université de Nantes,
636 2008.
- 637 [72] A. Bourchy, Relation chaleur d'hydratation du ciment - montée en température et contraintes
638 générées au jeune âge du béton, PhD thesis, Université Paris-Est, 2018 (in French)
- 639

640

641 Appendix A. Concretes name and formulation.

Concrete name	Factors				
	Cement type	A/B	Addition	W/B	Chemical admixture
C1_25S_0.375_0.45	C1	25	S	0.375	0.45
C1_25S_0.4_0.38	C3	25	S	0.4	0.38
C1_25S_0.425_0.52	C2	25	S	0.425	0.52
C1_50S_0.425_0.38	C1	50	S	0.425	0.38
C1_250S_0.375_0.52	C3	50	S	0.375	0.52
C1_50S_0.4_0.45	C2	50	S	0.4	0.45
C1_75S_0.4_0.52	C1	75	S	0.4	0.52
C1_75S_0.425_0.45	C3	75	S	0.425	0.45
C1_75S_0.375_0.38	C2	75	S	0.375	0.38
C1_12.5FA_0.375_0.60	C1	12.5	FA	0.375	0.60
C1_12.5FA_0.4_0.51	C3	12.5	FA	0.4	0.51
C1_12.5FA_0.425_0.69	C2	12.5	FA	0.425	0.69
C1_25FA_0.425_0.51	C1	25	FA	0.425	0.51
C1_25FA_0.375_0.69	C3	25	FA	0.375	0.69
C1_25FA_0.4_0.60	C2	25	FA	0.4	0.60
C1_37.5FA_0.4_0.69	C1	37.5	FA	0.4	0.69
C1_37.5FA_0.425_0.60	C3	37.5	FA	0.425	0.60
C1_37.5FA_0.375_0.51	C2	37.5	FA	0.375	0.51
C1_4SF_0.375_1.00	C1	4	SF	0.375	1.00
C1_4SF_0.4_0.85	C3	4	SF	0.4	0.85
C1_4SF_0.425_1.15	C2	4	SF	0.425	1.15
C1_8SF_0.425_0.85	C1	8	SF	0.425	0.85
C1_8SF_0.375_1.15	C3	8	SF	0.375	1.15
C1_8SF_0.4_1.00	C2	8	SF	0.4	1.00
C1_12SF_0.4_1.15	C1	12	SF	0.4	1.15
C1_12SF_0.425_1.00	C3	12	SF	0.425	1.00
C1_12SF_0.375_0.85	C2	12	SF	0.375	0.85
C1_0.4_0.6	C1	-	-	0.4	0.6
C1_0.4_0.9	C2	-	-	0.4	0.9
C1_0.4_0.6Tempo10	C3	-	-	0.4	0.6 with Tempo 10

642

643