

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

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ABSTRACT

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

1. Introduction

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

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

2. Current state of knowledge

The hydration reaction of cement is exothermic and the heat that is produced can lead to DEF or cracking under particular conditions and especially in massive concrete structures [2,3]. Usually, mix design – cement, additions, water-to-binder ratio, chemical admixtures – is optimized with reference to workability, setting time, compressive strength at early or later age (Bolomey equation for compressive strength after 28 days [4]) or the hydration heat [5,6] and in order to limit the risk of cracking. Depending on the notional size of the concrete structure in question, it is important to optimize the concrete mix design, the hydration kinetic and the total heat release which impact temperature changes in the structure.

Firstly, it is possible to optimize the granular skeleton in order to minimize the quantity of cement paste as recommended in the standard EN 206 [7] with classical methods such as the ACI method [8] or the de Larrard [5] method which take into account the size and form of the particles. The standard EN 12620 gives the characteristics of aggregates which can be employed in concrete [9].

Then, when the granular skeleton has been optimized, it is possible to optimize the composition of the paste. This involves selecting the type of cement with respect to durability and such properties as carbonation, the alkali reaction or DEF: special attention is paid to the amount of sulfate in the cement provided by alkaline sulfates or a setting regulator. For Byfors [10] and Minard [11], coupling occurs

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between the anhydrous phases and for Lerch and Bogue, it is possible to reduce hydration heat by reducing the quantity of highly reactive phases such as C_3A and C_3S [12]. Furthermore, the more fine the cement, the faster the hydration reactions which can increase the rate at which hydration heat is released [13–15].

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

The granular or filler effect is mainly due to fine and ultra-fine particles of materials such as limestone [20–23] or silica fume [24]. For Villagran-Zaccardi et al. [25], Lothenbach, et al. [26] and Schöler et al. [27], the fineness of mineral additions affects the hydration kinetic, especially the hydration of aluminates due to a filler effect: the impact is faster for limestone and slower for slag [28,29] and fly ash [30]. These particles position themselves between the cement particles [31]. This effect can have a beneficial or an adverse impact on material properties in the fresh state – i.e. their slump and rheology. According to Ramachandran et al., for similar specific surfaces, fly ash increases fluidity thanks to its spherical surface [32] whereas slag increases viscosity due to its irregular surface which decreases the granular skeleton [33]. Their specific surface areas are respectively equal to $3800 \text{ cm}^2 \text{ g}^{-1}$ and $4200 \text{ cm}^2 \text{ g}^{-1}$ for fly ash and slag. In the 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 superplasticizer is essential in order to obtain an acceptable level of fluidity [34]. The physicochemical effect – nucleation sites and modification of hydrate morphology and secondary hydration reactions – affects the interactions between additions, anhydrous and hydrates and so modifies the hydration process [19,28]. Generally, the presence of additions decreases the early age heat of hydration [26]. For example, limestone, being a non-reactive addition, decreases the hydration heat [28] but gives higher early age compressive strengths than Portland cement thanks to its role as a nucleation site [23,35], and it also improves cement hydration [26,36]. Lawrence et al. have shown that limestone in cement increases early age mechanical strength because of its reactions with the C_3A and C_4AF phases (formation of aluminates and carboaluminates) but later its impact becomes marginal [37,38]. As a result of their low early age reactivity [29,30,39] and the increase in the length of the dormant period [40,41], slag and fly ash produce low hydration heat with time. The compressive strength is lower at early age but similar to or higher than compressive strength after 28 days for concretes without slag and fly ash considering an equal binder content [30,42]. However, for Berodier, an increase in the percentage of slag increases the hydration heat released up to a maximum value when there is not enough cement to activate the slag [28]. For Schindler and Folliard, a higher percentage of fly ash in concrete does not retard hydration and the production of hydration heat while a higher percentage of slag retards the hydration of cement and decreases the hydration heat [43]. In contrast, silica fume, which is very reactive and exothermic, gives a higher compressive strength from early age [39]. Moreover, the reactions are sensitive to temperature [44–46], especially those involving slag [47] and fly ash which have a high activation energy (around 65 kJ K^{-1}) [48]. Additions are taken into account in concrete mix design via the notion of equivalent binder which corresponds to the sum of the quantity of

cement and the quantity of addition multiplied by the activity coefficient of the addition. It would be possible to estimate mechanical strengths using expressions which include the equivalent binder. For instance, in the Bolomey formula, see equation (1), the equivalent binder is calculated with the activity coefficient k considered as a constant. But according to Cyr et al. and Khokhar et al., this coefficient varies according to the type of cement (C) and addition (A) because of the interaction between them, but also according to the quantity of addition and the age of concrete [49,50].

$$R_c = G \cdot R_{c_{\text{cement}_{\text{iso}}}} \cdot \left(\frac{C + k \cdot A}{W} - 0.5 \right) \quad (1)$$

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

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

Mineral additions impact the water demand and the fluidity of concrete, especially when recycled aggregates are used [57]. In order to regulate these effects, chemical admixtures can be used to deflocculate fine particles and free water between these particles [58]. The use of chemical admixtures makes it possible to decrease the water-to-binder ratio and thus increase the mechanical strength by improving the microstructure [59]. For Huang et al., in the case of higher percentages of entrained air, chemical admixtures are more effective [60]. For Mardani-Aghboghrou et al., the chemical admixture needs to be chosen on the basis of the type of sulfates present in cement, i.e. anhydrite or gypsum, because of the difference in their reactivity in the presence of superplasticizers [61]. Moreover, the standard EN 934-2 states that a chemical admixture can only be used in concrete if the SO_3 content is lower than 2% [62].

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

3. Materials and methods

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

3.1. Materials tested

3.1.1. Selected cements

The three cements were selected on the basis of their hydration heat

Table 1
Characteristics of selected cements.

	C1	C2	C3
D ₅₀ (μm)	11.2	11.4	12.0
Blaine surface area (cm ² .g ⁻¹)	5300	4450	4270
Density (g.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

Table 2

Thermal (Langavant hydration heats Q₄₁, Q₁₂₀ and Q₁₆₈ measured respectively after 41, 120 and 168 h) and mechanical characteristics obtained for mortars made from the three 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

and their compressive strengths. They were produced in a pilot scale ball mill, and their composition varied from CEM I (95–100% of cement), CEMII/A-LL (80–94% of cement and 6 to 20% of limestone) and CEM II/B-LL (65–79% of cement and 21 to 35% of limestone).

The first selected cement, denoted by C1, was equivalent to a CEM II/B-LL and contained 35% of limestone, 5.85% of anhydrite and had a median particle diameter of 12 μm. The second cement is denoted by C2 and was equivalent to a CEM II/A-LL. It contained 20% of limestone, 5.85% of anhydrite and had a median diameter of 12 μm. Finally, the third cement (C3) contained only 5% of limestone but 7.85% of anhydrite and had a median diameter of 9 μm. This cement corresponded to a CEM I. Table 1 presents the characteristics of the selected cements.

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

Table 3

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

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

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

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

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

3.1.2. Selected additions

The effect of three concrete additions was studied. These were: a granulated blast furnace slag, with a Blaine surface area equal to 4230 cm² g⁻¹, produced by Ecocem SA; a fly ash from Carling SA, with a Blaine surface area equal to 3360 cm² g⁻¹ and a mechanically densified silica fume (FS95 DM), from Condensil SA. Because of the high silica fume fineness, it was not possible to measure it thanks to Blaine equipment. According to the technical datasheet, the specific surface area of the silica fume is between 150,000 and 350,000 cm² g⁻¹. These three additions were added to concrete in the usual percentages, with a variation of 50% around this value: 50% for the slag, 25% for the fly ash and 8% for the silica fume.

Table 4 shows the physical characteristics of the three selected additions. We can see that the median diameter of the silica fume was larger than that of the slag or the fly ash. This is due to our method which is not powerful enough to break coagulation of silica fume particles. In addition, the activity coefficients were not measured with the three selected cements but with a reference cement as laid down in the standard EN 197–1 [16]. The ratios (R_{A/C}) between the compressive strengths after 28 days for the 50-50% slag-cement [66], the 25–75% fly ash-cement [67] and the 10–90% silica fume-cement [34] and the 100% cement (R_{100C}) gives the 28-day activity coefficients, see equation (2). The ratio 10–90% silica fume-cement for measuring the activity coefficient is used according to the standard, even if it is slightly different to our mean value (8%).

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

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

Finally, the chemical admixture used here was a Master Polyheed 650 superplasticizer from BASF.

3.2. Notation

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

Cx_%Addition_W/B_%Admixture

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

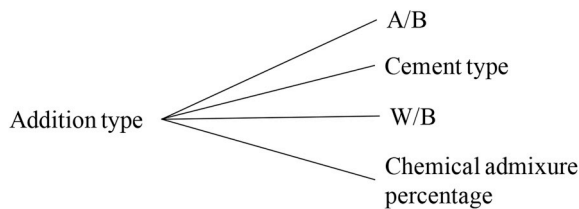


Fig. 1. Diagram representing the parameters studied in our concrete experimental design.

3.3. Experimental design

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

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

Table 5 shows the parameters and their levels (cement type, type and quantity of addition, W/B, chemical admixture).

3.4. Analytical techniques

The concretes were characterized:

- in the fresh state, by measuring slump according to the standard EN 12350-2 [68],
- thermally, by measuring the hydration heat with quasi-adiabatic calorimetry QAC according to the standard EN 12390-14 [69]. Fig. 2 shows an example of the result of such a test.
- mechanically, by measuring compressive strengths on 16 × 32cm cylindrical specimens according to the standard EN 12390-3 [70].

4. Results and discussion

In this section, we shall present and discuss the results from the experimental design, especially with regard to the fresh state and changes in the hydration heat and compressive strength. The fresh state characteristics were measured but were not included in our mix design tool. The figures below present the median effects in black and the interaction between factors in blue for slag (S), red for fly ash (FA) and

Table 5
Levels and parameters selected for this experimental design.

Parameter	Slag			Fly ash			Silica fume		
Addition type	Slag			Fly ash			Silica fume		
Addition quantity for 100 kg of cement (kg/100 kg 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

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

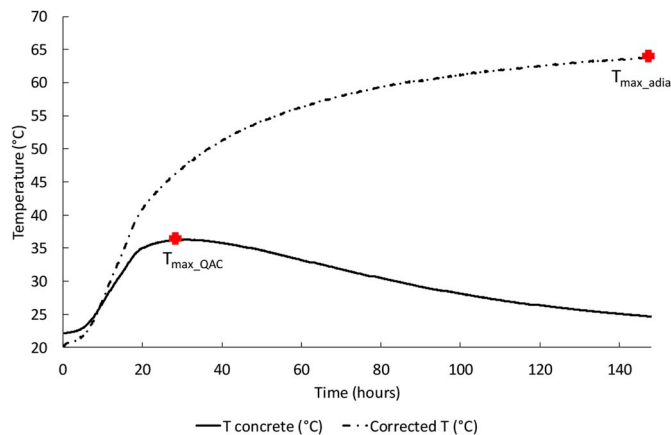


Fig. 2. Example of the result of quasi-adiabatic calorimetric test (QAC). Case of the concrete C1_25S_0.375_0.45. T_{max_QAC} corresponds to the maximal temperature measured during the test and T_{max_adia} to the final temperature obtained after correction due to the losses of the calorimeter (and that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

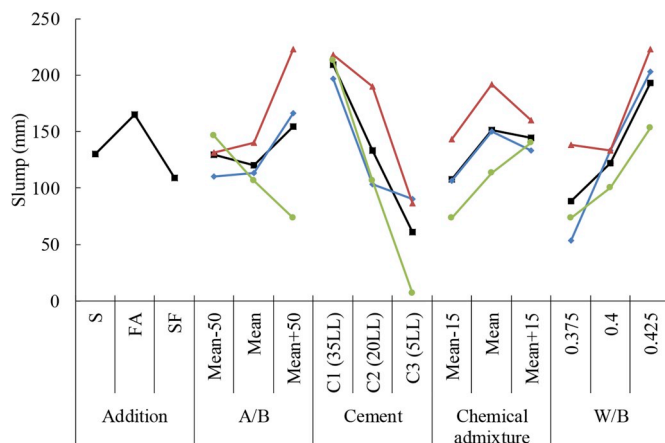


Fig. 3. Median effects of factors and their interactions on concrete slump.

green for silica fume (SF). The interactions were analyzed by a comparison with the general trend. If the change was similar but with just a vertical displacement, no interaction was deemed to take place between the type of addition and the other factors. On the other hand, if the trend was reversed, there a considerable interaction was deemed to take place between the type of addition and the other factors.

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

Fig. 3 presents the effects of the different factors and their mutual

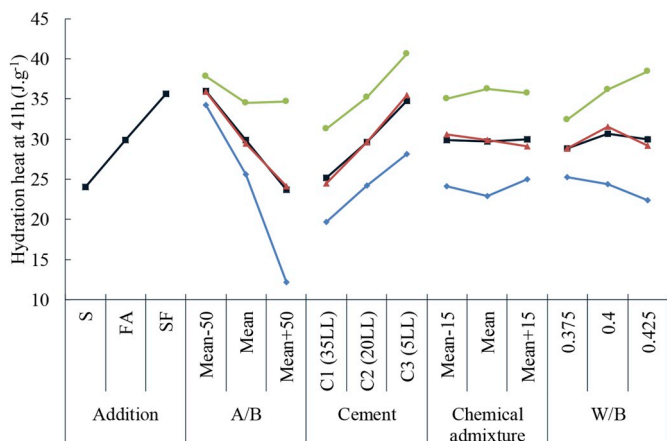


Fig. 4. Median effects of factors and their interactions on the QAC hydration heat of concrete after 41 h.

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

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

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

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

4.2. Influence of the factors on hydration heat

It is also important to study temperature rise in massive concrete

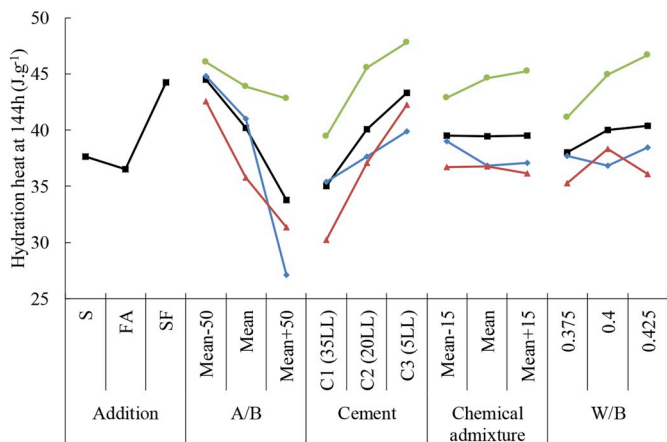


Fig. 5. Median effects of factors and their interactions on the QAC hydration heat of concrete after 144 h.

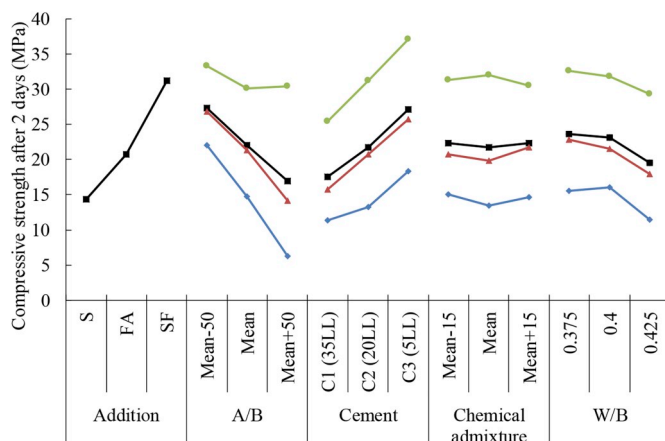


Fig. 6. Median effects of factors and their interactions on the 2-day compressive strength of concrete.

structures in order to prevent the risk of both DEF and cracking. To do this, the calorimetric measurement of temperature during concrete hydration was analyzed, giving the hydration heat after 41 h, see Fig. 4 and after 144 h, see Fig. 5. In general, we can see that concrete additions reduced the hydration heat, to an extent that increased with their quantity. However, this effect was less visible for silica fume, because of the lower quantity used (4–12% compared to 12.5 to 37.5 and 25–75% for fly ash and slag) and its higher reactivity. Slag and fly ash produce less heat than silica fume, after both 41 h and 144 h. Indeed, like pozzolanic materials, they react slowly and need activation, while silica fume is very reactive due to its fineness and its role as a nucleation site [55]. The difference in heat flow between slag and fly ash decreased with time, and led to values that were equivalent for the two, or even higher for slag than fly ash, after 144 h. These values agreed with the measured activity coefficients (see Table 4).

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

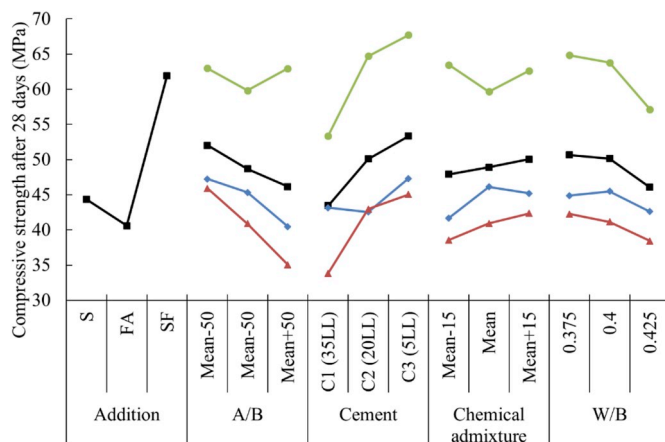


Fig. 7. Median effects of factors and their interactions on the 28-day compressive strength of concrete.

reactions so the hydration heat produced increased with W/B ratio.

4.3. Influence of the factors on compressive strength

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

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

4.4. Concrete mix design tool

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

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

		\bar{X}_A	Addition (%)	Ratio $\frac{W}{B}$	\bar{X}_{C1}	\bar{X}_{C2}	\bar{X}_{C3}
T_{\max_QAC} (°C)	S	34.3	- 0.19. %A + 9.39	$0.67. \frac{W}{B} + 3.32$	31.8	34.4	36.8
	FA	37.0	- 0.26. %A + 6.39	$- 32.00. \frac{W}{B} + 9.02$	34.8	37.5	41.5
	SF	41.6	- 0.16. %A + 1.31	$51.33. \frac{W}{B} - 20.54$	38.6	41.4	44.7
$T_{\text{adia_max}}$ (°C)	S	57.9	- 0.37. %A + 17.98	$- 74.02. \frac{W}{B} + 29.61$	53.2	59.0	61.5
	FA	65.2	- 0.46. %A + 11.50	$- 1.95. \frac{W}{B} + 0.79$	51.5	58.5	63.9
	SF	66.0	- 0.42. %A + 3.47	$92.23. \frac{W}{B} - 36.89$	61.0	67.3	69.7
R_c 2 days (MPa)	S	14.3	- 0.31. %A + 15.417	$- 79.50. \frac{W}{B} + 31.83$	11.4	13.3	18.4
	FA	20.8	- 0.44. %A + 10.86	$98.00. \frac{W}{B} + 39.20$	15.7	20.8	25.8
	SF	31.3	- 0.35. %A + 2.92	$- 66.00. \frac{W}{B} + 26.06$	25.4	31.2	37.1
R_c 28 days (MPa)	S	44.4	- 0.14. %A + 6.64	$- 45.33. \frac{W}{B} + 18.04$	44.3	42.6	47.3
	FA	40.6	- 0.43. %A + 10.74	$- 76.67. \frac{W}{B} + 30.45$	33.9	43.0	45.0
	SF	61.9	- 0.004. %A + 0.03	$- 154.33. \frac{W}{B} + 61.18$	53.4	64.7	67.7

Table 7
Specific requirements.

Addition percentage according to standard EN 206/CN NAF	$0 < S < 0.4$
1	$0 < FA < 0.3$
	$0 < SF < 0.1$
W/B	$0.3 < W/B < 0.6$
B_{eq} (kg)	$280 < B_{\text{eq}} < 400$
Volume of paste (L)	$V_{\text{paste}} \geq 250$
T_{\max_QAC} (°C)	minimal
R_c 28 days for C30 (MPa)	38 MPa

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

Equations (8)–(10) correspond respectively to the variations resulting from the cement type, the W/B ratio and the percentage of additions. These variations correspond to the difference between the median value of the answer X for addition A \bar{X}_A and cement C \bar{X}_C , see equation (4), and the function $f_x(\%A)$ and $f_x(\frac{W}{B})$ – obtained from the effect and interaction analyze for the answer X – and the median value of the answer X for addition A, see equations (5) and (6).

$$\Delta X_C = \bar{X}_C - \bar{X}_A \tag{4}$$

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

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

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

4.5. Application

In this section, the application of this mix design tool to meet specified requirements (Table 7) and to minimize the maximum

Table 8
Tested concrete mix designs.

Addition type	S			FA			SF		
	C1	C2	C3	C1	C2	C3	C1	C2	C3
Cement type	C1	C2	C3	C1	C2	C3	C1	C2	C3
Mix design number	1	2	3	4	5	6	7	8	9
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

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

Addition type	S			FA			SF		
	C1	C2	C3	C1	C2	C3	C1	C2	C3
Cement type	C1	C2	C3	C1	C2	C3	C1	C2	C3
Mix design number	1	2	3	4	5	6	7	8	9
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

temperature in a structure with a notional size of 40 cm is presented.

Equation (7) is used to calculate the volume of paste V_{paste} considering the water to binder ratio $\frac{W}{B}$, the total binder B_{tot} , the addition mass m_{add} and density ρ_{add} and the cement density ρ_c .

$$V_{paste} = \frac{W}{B} \cdot B + \frac{m_{add}}{\rho_{add}} + \frac{B - m_{add}}{\rho_c} \tag{7}$$

The parameters in this mix design tool are the type and quantity of cement, of addition and the quantity of water. The working limits were defined on the basis of the standard EN 206 NAF 1 [7] for an XC4 exposure grade (corrosion by carbonation and variable presence of water) and presented in Table 7. Note that, like the experimental design, the mix design tool has been created for concrete with a fixed granular skeleton. The equivalent binder B_{eq} corresponds to the sum of the quantity of cement C and the activity coefficient k of the addition multiplied by the addition quantity A as defined in equation (8).

$$B_{eq} = C + k \cdot A \tag{8}$$

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

A further condition was then added to the specified requirements, namely a minimum 2-day compressive strength of 20 MPa. The mix designs are presented in Table 9. Concretes 1 to 3 and 7 to 9 already

met the two compressive strength conditions and have therefore not been modified.

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

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

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

5. Conclusion

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

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

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

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

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