Mix design of concrete with high content of mineral additions: Optimisation to improve early age strength

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The concrete industry is an important source of CO_2 gas emissions. The cement used in the design of concrete is the result of a chemical process linked to the decarbonation of limestone conducted at high temperature and results in a significant release of carbon dioxide. Under the project EcoBéton (Green concrete) funded by the French National Research Agency (ANR), concrete mixtures have been designed with a low cement quantity, by replacing cement by mineral additions i.e., blast-furnace slag, fly ash or limestone fillers. Replacement of cement by other materials at high percentages generally lowers the early age strength of the resulting concrete. To cope with this problem, an optimisation method for mix design of concrete using Bolomey's law has been used. Following the encouraging results obtained from mortar, a series of tests on concretes with various substitution percentages were carried out to validate the optimisation method.

Keywords:
CO_2 emissions
Green concrete
Mineral additions
Compressive strength
Optimisation

1. Introduction

Countries that have ratified the Kyoto Protocol are committed to reduce their emissions of carbon dioxide, one of the major greenhouse gases. Carbon dioxide is a naturally occurring greenhouse gas. The reduction of carbon dioxide emitted during the production of cement is an important issue for the construction industry to participate in sustainable development [1]. Cement manufacturing includes decarbonation of limestone at high temperature and requires great energy. Despite the improving energy efficiency of the furnaces, the chemical emissions are virtually irreducible. One of the solutions proposed by engineers and scientists from the construction industry is to replace clinker in cement with secondary raw materials, which can also improve the characteristics of cement and increase the durability of concrete. In this way, reduction of CO_2 emissions is being achieved with some basic benefits of decreasing the consumption of natural raw materials, thermal and electric energy [2]. This replacement would be during the mixing of concrete rather than during the manufacturing of cement as the blended cements have relatively low replacement levels. Several studies were conducted on such types of concrete [3–6], but results do not always conform to standards. Current European Standards (EN 206-1) restrict the use of mineral additions to low proportions during the manufacture of concrete [7]. The standards provide the possibility for the engineer to design a concrete mixture to prove its equivalence in performance compared to a concrete meeting the requirements of the standards [8].

Use of these mineral additions in high percentages as a replacement for cement can result in a concrete with lower compressive strength. But if these mineral additives are used in combination with superplasticizers, then economical concretes can be obtained with enhanced durability and CO_2 emissions reductions [9]. These mineral additions are added in concrete as supplementary cementitious materials and the benefits of using these materials in terms of workability are well established [9–12]. Several studies have been carried out to determine mechanical properties, thermal properties, transport mechanisms and the influence of mineral additions on the durability of blended concrete [13–18].

The suitability of using these mineral additions is well established in the world of concrete, and at the same time if some optimisation of the concrete mixes with mineral additions can be done using some empirical relations, then enhanced performance of the resulting concrete can be achieved. From an economic point of view, use of industrial by-products at large scale is beneficial for sustainable development [19].

Early age strength is a major factor to be addressed while using the mineral additions, as the formwork removal requires a specific strength of concrete to be achieved. Low early age strength has been observed using slag and fly ash additions. In this article, we have suggested a method to optimise the composition of concrete mixtures when using mineral additions keeping in mind these strength requirements and based upon the activation of mineral additions. The main purpose of our approach is to optimise the

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concrete mixture composition with a large substitution of cement by mineral addition and then optimisation of the quantity of water in the mixture to produce the desired early age strength. During this study, first mortar samples were examined in a preliminary study to assess the coefficient of activity for different types of mineral additions and then tests were carried out for concretes as well, to validate the approach. Results of this study should make it possible to promote the use of mineral additions in large quantities, directly in the manufacturing of concrete.

2. Experimental program

2.1. Materials

ordinary Portland cement (CEM I 52.5N CE CP2 NF) was used for both mortar and concrete mixes. The ground granulated blast-furnace slag (GGBS) came from a single batch. Fly ash came from a single batch. Chemical and physical properties of the constituents are detailed in Table 1. The fine aggregate for the mortars was a natural sand of granular class 0–2. Moist sand was used and corrections were made to adjust the exact water quantity. The coarse aggregate of sizes 10/14 and 6/10 mm came from a local gravel provider. The fine aggregate used in concrete was sea sand of granular class 0/4 (Table 2). In optimised mixtures, a polycarboxylate-based superplasticising admixture (Sp1) was used (Table 3).

2.2. Mixture proportioning method

The task of concrete mixture optimisation is to optimise the concrete constituents to get the best possible output in terms of performance. This is done by optimising the mixture compositions by estimating different concrete compositions with different combinations of constituents and then to choose the best variants of these mixtures by comparing their mechanical properties, as well as their durability. Different methods exist for the optimisation of concrete compositions which are based upon equations and models [15,20,21] taking into account the characteristics of constituents and the desired properties of the concrete. The characteristics of the constituents are either measured or calculated by empirical formulas. The method of optimisation proposed in this paper is based upon Bolomey's equation and the data determined by the various tests carried out at the preliminary stage.

In its simplest form, concrete is a mixture of paste and aggregates. The paste, composed of Portland cement and water, coats the surface of the fine and coarse aggregates. Through the chemical reactions of hydration, the paste hardens and gains strength to form the rock-like mass known as concrete. If the concrete has some additional materials in it, then it requires some special consideration which depends upon strength development along with the rheological properties. Rational methods of incorporating additions in concrete have been proposed, considering the fact that the two concretes (with or without mineral additives) can be used to reach the same strength at a given age by adjusting their individual water-to-binder ratios (w/b) [22] (where binder is composed of cement and mineral additions).

To improve the performance of a concrete mixture containing mineral additions, an optimisation method was introduced. This empirical method consists of certain equations to be solved for the determination of different parameters (e.g. quantities of water, cement, substitution percentage, the water-to-cement ratio (w/c)) for several different compositions. Because in this study, the mineral addition replacement level is very high, a low compressive strength is produced at early ages. To increase the early age strength, w/b was reduced. Based on this optimisation method, by estimating the quantities of materials required for 1 m^3 of concrete, a trial batch based on these quantities can be made. If adjustments are necessary, further batches should be adjusted by keeping the volume of paste constant and adjusting the superplasticizer dose to produce the desired slump.

For all types of mix design problems, mathematically there is always a system of equations. The mix design task can be formulated with five equations for the five unknowns i.e. V_G, V_S, V_C, V_A and V_W (volume of aggregate, sand, cement, addition and water respectively, for a volume of 1 m^3 of concrete) neglecting the volume of superplasticizer.

$$1\ m^3 = V_G + V_S + V_C + V_A + V_W \quad (1)$$

$$V_G/V_S = x \quad (2)$$

$$V_P = V_C + V_A + V_W \quad (3)$$

$$V_A/(V_A + V_C) = y \quad (4)$$

where x, y and V_P (volume of paste) are the granular proportions, the substitution level of cement by addition and the volume of paste respectively, and x and V_P may be deduced from a reference mixture. The substitution levels were fixed at 25%, 50% and 75%, respectively.

The last equation should link the compressive strength and the proportions of the paste. In the literature, one can find many relations linking proportions and strength, for example, a modified

Table 1
Chemical and physical analysis of cementitious materials.

Chemical/physical composition	Portland cement	Ground granulated blast-furnace slag	Fly ash	Micro-filler
SiO_2	20.6	34.49	55.33	0.3
Al_2O_3	4.4	13.19	25.21	–
Fe_2O_3	2.6	0.4	6.4	–
CaO	64.7	41.03	5.83	–
K_2O	0.85	0.54	1.14	–
Na_2O	0.12	0.43	1.34	–
SO_3	3.3	0.1	0.64	0.01
Cl^-	0.01	0.04	0.012	0.01
MgO	1.5	8.21	–	–
MnO	0.04	0.4	–	–
TiO_2	0.3	0.88	–	–
S^-	<0.01	1.17	–	–
$CaCO_3$	–	–	–	98
Loss of ignition (%)	1.0	–	2–7	–
Blaine (m^2/kg)	330	462	–	2200
Density (kg/m^3)	3110	2890	2210	2700
Passing 45 μm (%)	–	–	70	–
Mean diameter (μm)	–	–	–	3.7

Table 2
Aggregate properties.

Aggregate type	Density kg/m^3	Absorption (%)
Sand 0/2 mm (crushed quartz)	2610	0.4
Sand 0/4 mm (marine)	2650	0.6
Gravel 6/10 mm	2900	0.3
Gravel 10/14 mm	2900	0.3

Table 3
Properties of superplasticizers.

Superplasticizer type	Density (kg/m^3)	Na_2O equivalent (%)	Dry extract (EN 480-8) (%)
Sp1	1050	<1.0	20.3 + 1
Sp2	1050	<1.5	24.3 + 1.2
Sp3	1100	<4.0	39.0

Feret relation [23]. In our study, it was decided to apply Bolomey's equation [24]:

$$f_c = K_B\left(\frac{C+\chi_B A}{W+V} - 0.5\right) \quad (5)$$

where f_c is the compressive strength, χ_B is the coefficient of activity, K_B the constant of Bolomey, C the mass of cement, A the mass of mineral addition, W is the actual mass of water used and V the mass of water equivalent to the volume occupied by the air entrained in the mortar or concrete. χ_B and K_B were deduced from compressive strength tests on mortars. K_B is assumed to have a constant value for a given type of aggregate but varies with age, while χ_B varies with age, addition type, and substitution rate.

2.3. Mixture proportions and experimental procedures

2.3.1. Mortars

Two series of mortar mixtures were studied. The first series (Table 4) were designed with constant volume of paste and a constant water content. The second series (Table 5) were designed resolving the system of Eqs. (1)–(5) for a desired compressive strength f_c to be achieved at 48 h, from the values of K_B and χ_B deduced from the first series.

The principle of the first series of mortar compositions was to maintain the volume of paste constant, as well as the volume of water. Cement was replaced by mineral additions i.e. GGBS and fly ash by simple volume replacement. Eight different mortar mixtures proportions were tested, including a reference mortar with ordinary Portland cement (OPC), four mixtures using GGBS with 25%, 50%, 75% and 85% replacement ratios and three mixture using fly ash with 25%, 50% and 75% replacement ratios. Table 4 provides the mixture compositions of the mortars that were tested. Materials were added in the order: cement/GGBS or fly ash, sand and water. The mortar was mixed for 2.5 min and then cast into $40 \times 40 \times 160\ mm^3$ moulds. Slump values were measured using the mini cone of Abrams (h = 150 mm, D = 100 mm, d = 50 mm). The slump values of fresh mortar prepared using GGBS and fly ash are given in Table 4. Use of GGBS has improved the workability of the mortar with respect to the mortar containing only Portland cement. Mixtures with 50% and 75% additions gave maximum slump values which can be taken as threshold values of GGBS concerning the rheological properties. While in the case of fly ash, the slump value decreased with increasing proportion of fly ash level. Generally it is indicated that use of fly ash improves workability, but according to Kobuku [25] it is not possible to ascertain the reduction in unit water content to fly ash ratios of various countries. Li concluded that the mean particle size of fly ash significantly influences the flow of mortars with incorporation of fly ash [26].

Table 5
Composition and properties of optimised mixtures of mortar.

	OPC	GGBS		Fly ash	
		Optimised	Optimised	Optimised	Optimised
Addition level (vol.%)	0	50	75	50	50
Addition level (mass%)	0	48	73	41	41
Sand 0/2 (kg/m^3)	1409	1409	1409	1409	1409
Water (kg/m^3)	301	284	253	272	249
Cement (kg/m^3)	501	275	163	295	333
Addition (kg/m^3)	0	256	450	207	234
V_p (l/m^3)	460	460	460	460	460
w/c	0.60	1.03	1.55	0.92	0.75
w/b	0.60	0.53	0.41	0.54	0.44
Sp1 (kg/m^3)	–	0.75	3.75	1.10	4.40
Slump (mm)	80	77	81	80	74
Design data					
f_c 48 h (MPa)	–	15	15	15	15
K_B	21.3	21.3	21.3	21.3	21.3
χ_B	–	0.35	0.38	0.30	0
Experimental validation					
f_c 48 h (MPa) measured	22.7	14.7	17.7	11.1	17.7
K_B	21.3	21.3	21.3	21.3	21.3
χ_B	–	0.34	0.44	0.02	0.10

The specimens were consolidated on a vibrating table, covered by a polyethylene film, and stored at 20 °C and 95% relative humidity. The specimens were demoulded after 23 h and put into a curing tank until the time of test.

The proportions of the second series of mortar mixtures were optimised to improve early age strength. The proportions of the paste were calculated using Bolomey's equation for f_c = 15 MPa at 2 days. The volume of paste was kept constant. Superplasticizer content was adjusted based on slump tests. Mortar mixtures with a higher level of GGBS (50% and 75%) and fly ash (50%) were optimised by reducing w/b, details of which are provided in Table 5.

2.3.2. Concrete

Two series of concrete mixtures were designed. Table 6 gives the proportions of the first series of concrete mixtures. Optimisation was done to reach a compressive strength of 10 MPa at 48 h, using the coefficient of activity χ_B deduced from mortars. The second series (Table 7) was designed using coefficients K_B and χ_B deduced from the first series of concrete results and optimising the use of chemical admixtures to improve the early age strength of fly ash concrete.

Table 4
Composition and properties of mortar.

	OPC	GGBS				Fly ash		
Addition level (vol.%)	0	25	50	75	85	25	50	75
Addition level (mass%)	0	23	48	73	84	19	41	68
Sand 0/2 (kg/m^3)	1409	1409	1409	1409	1409	1409	1409	1409
Water (kg/m^3)	301	301	301	301	301	301	301	301
Cement (kg/m^3)	501	376	251	125	75	376	251	125
Addition (kg/m^3)	0	115	230	345	391	88	176	264
V_p (l/m^3)	460	460	460	460	460	460	460	460
w/c	0.60	0.80	1.20	2.41	4.01	0.80	1.20	2.41
w/b	0.60	0.61	0.63	0.64	0.65	0.65	0.70	0.77
Slump (mm)	80	90	98	98	85	75	55	43
f_c 2 days (MPa)	22.7	19.0	11.4	7.0	4.5	16.0	9.5	3.0
f_c 7 days (MPa)	31.1	28.4	22.0	19.3	19.2	24.9	15.6	5.4
f_c 28 days (MPa)	44.0	44.4	39.6	38.6	36.5	37.5	21.9	7.8
f_c 90 days (MPa)	45.6	46.8	47.4	46.6	43.5	39.5	26.6	9.9

Table 6
Composition and properties of concrete mixtures (kg/m^3).

	OPC	GGBS				Fly ash				
	Réf.	A	B	C Optimised $\chi_B = 0.4$	E Optimised $\chi_B = 0.4$	F	G Optimised $\chi_B = 0.3$	H Optimised $\chi_B = 0$	I Optimised $\chi_B = 0.3$	J Optimised $\chi_B = 0$
Addition level (vol.%)	0	25	50	50	75	25	50	50	59	59
Addition level (mass%)	0	24	48	48	73	19	41	41	50	50
Gravel 10/14	860	860	860	860	860	860	860	860	860	860
Gravel 6/10	210	210	210	210	210	210	210	210	210	210
Sand 0/4	843	843	843	843	843	843	843	843	843	843
Cement	350	263	175	187	109	263	201	224	178	204
Addition	–	81	161	172	301	61	141	157	178	204
w_{net}[a]	199	199	199	192	172	199	182	168	173	153
w added	184.9	181.3	181.3	174.3	154.3	185.3	164.4	162	167.0	147
Vp (/m^{-3})	310	310	310	310	310	310	310	310	310	310
w/c	0.57	0.76	1.14	1.03	1.58	0.76	0.91	0.75	0.97	0.75
w/b	0.57	0.58	0.59	0.53	0.42	0.61	0.53	0.44	0.49	0.38
Sp1 (kg/m^3)	–	–	–	–	3.3	–	2	2	3.3	8
A/A + C	–	0.23	0.48	0.48	0.73	0.19	0.41	0.41	0.5	0.5
A	0.00	80.5	75.2	80.2	46.8	61.3	86.4	96.0	76.3	87.7
Eq. Binder (C + kA)	350.0	335.0	242.7	258.9	151.0	299.3	252.8	281.7	223.4	256.6
w/Eq. Binder	0.57	0.59	0.82	0.74	1.14	0.66	0.54	0.6	0.78	0.6
Slump (mm)	105	137	147	93	237	147	73	30	230	215
f_c 24 h (MPa)	11.9	7.5	3.9	5.2	4.2	5.8	4.5	7.2	4.9	4.4
f_c 48 h (MPa)	21.3	14.2	8.5	10.5	12.2	12.3	10.9	15.0	11.4	14.4

[a] $w_{net} = w$ added + w aggregate − w absorption.

Table 7
Composition and properties of concrete mixtures incorporating 58% fly ash.

Concrete mixture (kg/m^3)	C1	C2	C3	C4	C5
Addition level (vol.%)	58	58	58	58	58
Addition level (mass%)	50	50	50	50	50
Gravel 10/14	843	843	843	843	843
Gravel 6/10	205	205	205	205	205
Sand 0/4	762	762	762	762	762
Cement	186	186	186	186	186
Fly ash	181	181	181	181	148
Micro-filler	–	–	–	–	40
w_{net}	156	155	156	154	154
Vp (l/m^3)	302	300	302	298	297
w/c	0.84	0.83	0.84	0.83	0.83
w/b	0.42	0.42	0.42	0.42	0.41
Water temperature (°C)	20	20	64	20	20
Sp (kg/m^3)	4.3	3.3	4.3	1.9	1.6
Superplasticizer Type	Sp1	Sp2	Sp1	Sp3	Sp1
Sp (% of cement)	2.3	1.8	2.3	1.0	0.87
Air entraining admixture (kg/m^3)	0.37	0.37	0.37	0.37	0.37
A/A + C	0.49	0.49	0.49	0.49	0.49
A	80	80	80	80	80
Eq. Binder (*C* + kA)	234	234	234	234	234
w/Eq. Binder	0.66	0.66	0.66	0.66	0.66
Slump (mm)	180	210	220	240	190
f_c 24 h (MPa)	7.5	9.0	6.0	9.9	9.8
f_c 48 h (MPa)	12.0	12.4	9.8	17.0	17.1
Design data					
f_c 48 h (MPa)	12	12	12	12	12
K_B	13.4	13.4	13.4	13.4	13.4
χ_B	0.18	0.18	0.18	0.18	0.18
Experimental validation					
f_c 48 h (MPa) measured	12.0	12.4	9.8	17.0	17.1
K_B	13.4	13.4	13.4	13.4	13.4
χ_B	0.18	0.19	0.03	0.48	0.47

The concrete mixtures of the first series (Table 6) were designed from a mixture incorporating 350 kg/m^3 of ordinary Portland cement. The principle of the concrete compositions was to maintain a constant volume of paste and constant quantities of coarse and fine aggregates. Concrete compositions were optimised from the coefficient of activity calculated from mortar tests and without any preliminary tests on concrete. The K_B value depends upon the strength of the cement and granular material so that the value for concrete is different from the value for mortars. It was assessed from the following relation: $K_B = G \cdot \sigma_c$, where G is the coefficient related to aggregates and σ_c is strength of cement after 2 days (in the design of optimised concrete compositions $G = 0.5$ and $\sigma_c = 24$ MPa for the cement CEM I 52.5).

The concrete mixtures of the second series (incorporating 58% of fly ash, Table 7) were designed from a mixture using the same mixing conditions and superplasticizer Sp1 of the first series. The coefficient of activity χ_B was assumed to be equal to 0.18 and K_B equal to 13.4, from tests on the first series of concrete (Section 4). The optimisation was done to reach a strength of 14 MPa at 48 h. Concrete mixtures (Table 7) were tested under five different mixing conditions including the use of different superplasticizers (three types; Sp1, Sp2 and Sp3 – described in Table 3), the use of hot water (Table 7) during fabrication of the concrete and use of a micro-filler replacing a part of the fly ash. An air entraining admixture designated as AER5 was also used. Sp1 is a polycarboxylate-based superplasticising admixture, Sp2 is also polycarboxylate-based but is used by the precast concrete industry and Sp3 is designed so that the orientation of the molecules on the cement grains doesn't delay hydration. The main ingredients of the concrete i.e. cement, sand, gravel and fly ash, were of the same type as in the previous concrete mixtures containing fly ash.

Materials were added in the order: cement/GGBS or fly ash, sand and gravel. After mixing dry for 30 s, water was added for the next 30 s, then after mixing for 1 min; superplasticizer was added and left to be mixed for the next 90 s. Slump values were measured using the Abrams cone. The concrete was cast into 11 × 22 cm cylinders. The specimens were consolidated using a pneumatic drive vibrator before being stored at 20 °C and 95% relative humidity. The specimens were demoulded after 23 h and were put into the curing tank maintained at 20 °C until the time of test.

3. Experimental results

3.1. Determination of coefficient of activity χ_B from mortar

The method of optimisation is based upon the calculation of the coefficient of activity of a mineral addition (based upon the experimental results). First of all, a test data base from the mortar results was prepared (Table 4) and then the coefficient of activity was calculated for each level of replacement of cement and at different ages using Bolomey's equation. Replacing C in Eq. (5) by $C = (1-p)C_0$ and A by $A = pC_0$, where $p = A/C_0$ is the substitution rate by mass, C is the mass of cement used for the composition with mineral addition, A is the mass of mineral addition used, and C_0 is the mass of cement used in the reference mortar, one obtains the following equation:

$$f_c = K_B\left(\frac{((1-p)+p\chi_B)C_0}{W+V} - 0.5\right)$$

Further, one can deduce the value of χ_B from above equation as given below

$$\chi_B = \left(\left(\frac{f_p}{K_B} + 0.5\right)\left(\frac{W+V}{C_0}\right) - (1-p)\right)\Big/ p$$

where p is the substitution rate of cement by mineral addition on a mass basis and f_P the respective designed strength of the mortar.

Figs. 1 and 2 present the strength development of different mortar mixtures containing GGBS and fly ash, respectively. Concrete mixtures made of cements blended with GGBS show low strength at early age while exhibiting equal or more strength at later stages due to the fact that GGBS has a low degree of hydration at early age with respect to that of Portland cement. But this behaviour also depends upon the GGBS level in the concrete mixture. This difference of strength may remain until later stages for the GGBS levels of 75% or 85% replacement. But a very high improvement in relative strength at 7 days can be noticed with reference to 2 day strength.

Slow development of strength in fly ash concrete can be explained by a lower degree of fly ash reaction, when used in combination with cement. Studies [27–30] have shown that high-volume fly ash paste achieved a lower degree of fly ash reaction; even more than 80% of the fly ash still remained unreacted after 90 days of curing in the pastes with 50% fly ash, which is obviously due to the slow pozzolanic reaction of fly ash.

Figs. 3 and 4 show the coefficient of activity calculated for GGBS and fly ash respectively using Bolomey's equation for different level of substitutions. The results show that the coefficient of activity varies for each mixture at different age and cannot be taken as a constant number for all levels of additions. According to French standard NF EN 206-1, the maximum substitution rate of addition to be taken into account to calculate the equivalent binder value is limited to 30% and the coefficient of activity k has been regarded as a constant value i.e., 0.9 for slag, 0.4–0.6 for fly ash and 0.25 for limestone filler. It is noticeable that the coefficient of activity depends upon both the time, substitution type and substitution rate, while the current standards consider it as a constant when calculating the equivalent binder content. The coefficient of activity for various levels of mineral additions at different ages is quite distinct, as mixtures with higher levels of mineral additions show a lower coefficient of activity at early ages.

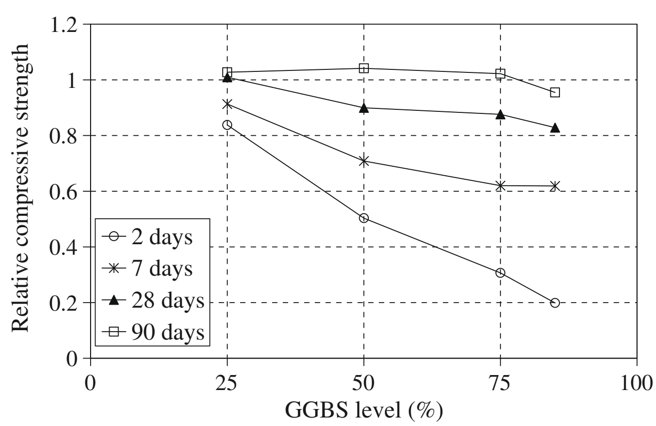

Fig. 1. Effect of GGBS level on relative compressive strength of mortars.

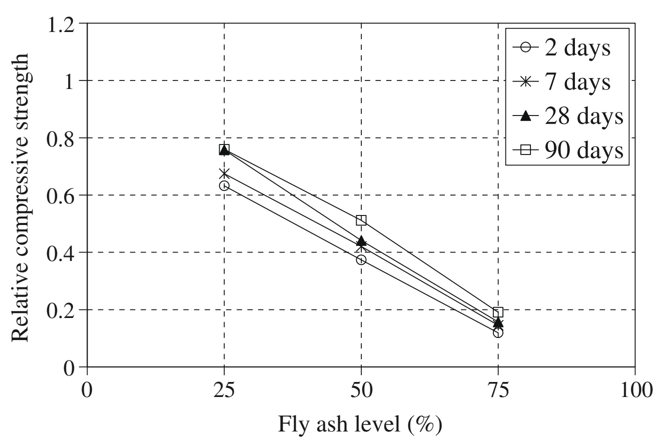

Fig. 2. Effect of fly ash level on relative compressive strength of mortars.

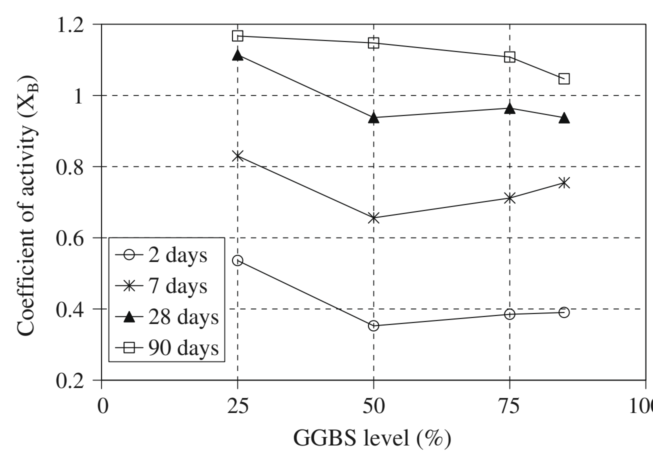

Fig. 3. Coefficient of activity according to Bolomey for different GGBS levels.

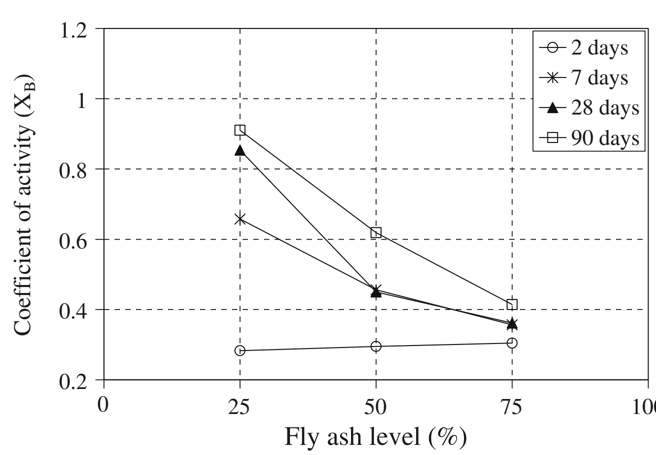

Fig. 4. Coefficient of activity according to Bolomey for different fly ash levels.

3.2. Application of mixture proportioning method on mortar

Relative strength had been defined as the ratio of the strength of the mortar incorporating a mineral addition to the strength of the Portland cement mortar. The results of relative strength for different GGBS and fly ash levels (Fig. 5) show the very slow strength development at early ages. Early age strength appears to be the most important factor to prove the use of mineral additions in large quantities for the construction industry. In order to remove formwork and then continue further construction activity, a minimum strength of structural members is required. This difference of strength with reference to Portland cement induced an effort to optimise the mix design by reducing the water content, while increasing the strength. The proportions of the paste were calculated using Bolomey's equation for $f_c = 15$ MPa at 2 days. Results show that the proposed optimisation has worked quite well under the given conditions, as the decrease in w/b led to a more dense formation and a hardening process that started earlier than normal (Table 5). As a consequence, improved early age strength was achieved, except for the 50% fly ash mixture optimised with a coefficient of activity $\chi_B = 0.3$, whereas the 50% fly ash mortar optimised with a coefficient of activity $\chi_B = 0$ reached 15 MPa. So the coefficient of activity of fly ash at 2 days would be closer to 0 (rather than 0.3). Non-optimised (Table 4) and optimised (Table 5) 50% fly ash mixtures are actually not so different. Some scattering of the results due to mixing conditions could explain the lower improvement of early age strength than predicted.

3.3. Application of mixture proportioning method on concrete

Strength evolution with respect to time is different for mortar and concrete, but the strength development in mortar is a good indication of strength development in concrete. So, the coefficient of activity χ_B measured from mortars was used as an input parameter to design the concrete mixtures, without any laborious preliminary tests on concrete.

For this purpose, concrete mixtures with different GGBS and fly ash levels were selected (Table 6). To compare the real benefits of this method, mixtures without any optimisation (simple replacement of cement with respective proportion of mineral additions) were also tested.

3.3.1. Early age compressive strength

Table 6 presents the compressive strengths obtained at early ages (24 and 48 h) for concrete mixtures containing GGBS and fly ash. Strength obtained at 48 h for the optimised concrete mixture is greater than or equal to the design strength of 10 MPa. Although they could not meet the strength possessed by the ordinary Portland cement, among the mixtures with mineral additions, 50% simple replacement had 2 MPa less strength at 2 days compared to 50% optimised. Even 75% of GGBS exceeded the design strength. The optimisation method developed is therefore satisfactory with respect to strength and sufficiently simple and robust for industrial applications.

In the long term, concrete mixtures with GGBS have values very close to the concrete mixture with ordinary Portland cement (Fig. 6). The compositions with fly ash have a significantly lower compressive strength than the reference (Fig. 7), but still greater than required by standards. For example, the minimum characteristic strength required by NF EN 206-1 for XC3–XC4 exposure classes is 25 MPa at 28 days.

3.3.2. Improvement of optimised mixture design for concrete containing fly ash

Experimental work and results showed the need for further investigation on the optimisation of strength of fly ash concrete. It was observed that the reduction in water content and use of superplasticizer were not enough to obtain the design strength for mixtures with the higher percentages of fly ash. The reduction in water content increased the viscosity of the concrete mixture, the volume of entrapped air and consequently the porosity. To improve the lower strength shown by some concretes with additions of fly ash, a series of concrete mixtures were studied to improve

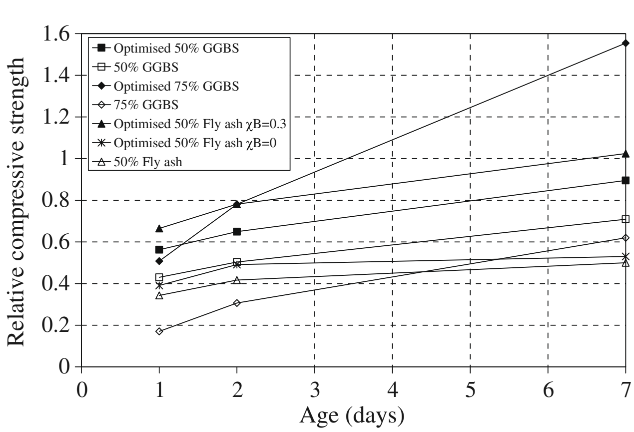

Fig. 5. Effect of optimisation over strength of mortars with mineral additions.

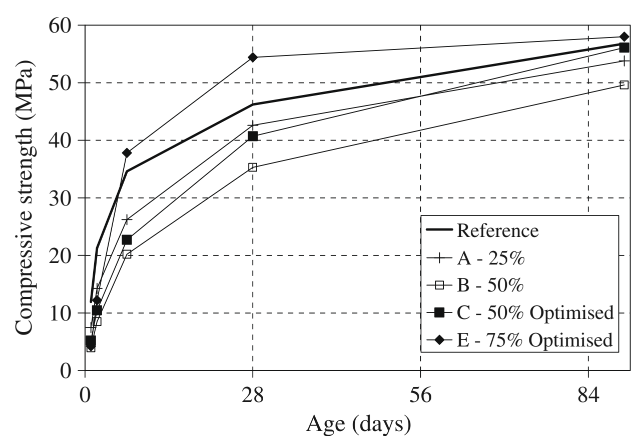

Fig. 6. Strength development of concrete with GGBS.

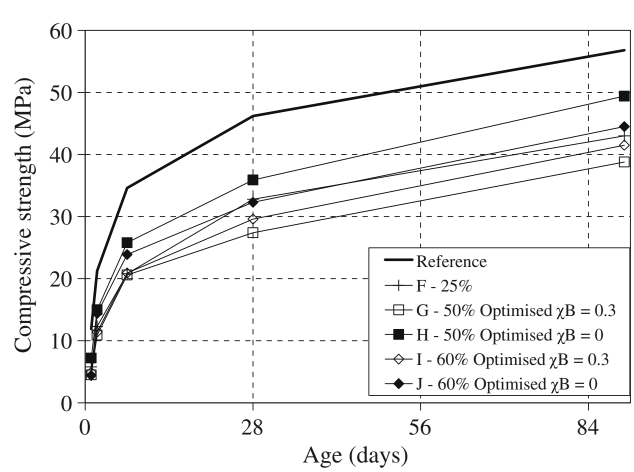

Fig. 7. Strength development of concrete with fly ash.

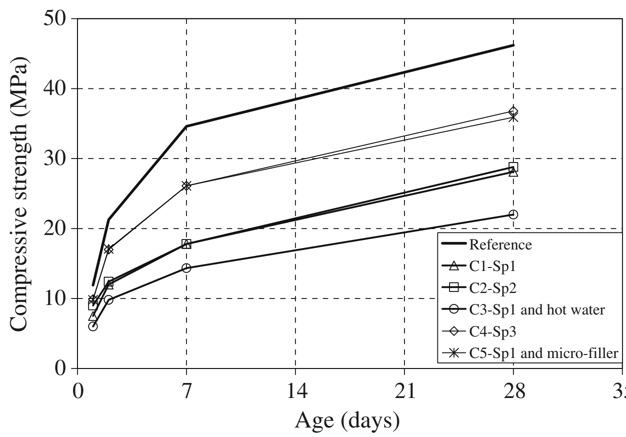

Fig. 8. Strength development of concrete containing fly ash under different mixing conditions and chemical admixtures.

the compressive strength at early ages. Details of these concrete mixtures are shown in Table 7.

Compressive strength development of these concrete mixtures containing fly ash is shown in Fig. 8. Concrete mixture C1 is taken as the reference mixture. Use of superplasticizer type Sp2 did not significantly improve the properties of concrete. Concrete mixture C3 showed an improvement in fluidity of the concrete due to the use of hot water during fabrication, but on the other hand, it reduced the strength of the concrete. Concrete mixtures C4 and C5 showed higher strengths at early ages and also in the long term. But, C5 can be termed as a better option due to the use of a lower quantity of superplasticizer. Addition of micro-filler has improved not only the workability of the concrete, but the strength as well. Micro-fillers do not participate in the chemical reactions, but their better performance can be attributed to their action as an accelerator during early cement hydration, as they will provide nucleation sites for the hydration of the C_3S and C_2S, shortening the dormant stage and accelerating the hydration reactions [31]. However, the use of micro-fillers needs further investigation taking into account its proportional use and durability factors.

4. Discussion

The optimisation method is principally based upon the fact that strength increases with the reduction of w/b above a threshold value. Cement requires a minimum water content to hydrate. The main hydration products are an amorphous hydrated calcium silicate of variable composition, usually given the symbol C–S–H and $Ca(OH)_2$. Theoretically, a w/c of 0.24 should be sufficient to fully hydrate cement based on the chemically bound water [32], but a w/c of about 0.38 is necessary to obtain full hydration as the hydration reaction is expansive and the C–S–H absorbs (gel) water as it grows [32–34]. Water added above this w/c is required to have a more workable concrete. In the concrete mixtures, the water content was reduced, but to improve the workability of concrete, superplasticizers were added. The workability and strength also depends upon the viscosity of the mixture. De Larrard [20] has proposed a model to predict the viscosity of a concrete mixture, which shows the dependence of viscosity on water content. According to his model, viscosity is expressed as $\exp(a \cdot \varphi/\varphi_o + b)$, where φ is the total concentration of solid materials i.e., $(1000 - w)/1000$, and φ_o is the maximum concentration of solid materials. Hence, there should be an intermediate approach between the fact that reducing the water content increases the viscosity and keeping the water content constant requires an augmentation in the cement content to increase the strength, which have direct impacts on economy and ecology. As an intermediate approach, we started with a concrete composition based upon a relatively high volume of paste with a cement content of 350 kg/m^3 (Table 6), compared to the ordinary concrete compositions being used in the national construction industry.

In mortars, K_B used for the optimised mixture composition was the same as that used to calculate the χ_B of the additions, which allows calculating the effective χ_B from the resulting mortar strengths of the optimised compositions (Table 5). Design and calculated coefficients of the activity of mortar compositions with slag are comparable to each other but in the case of fly ash the calculated χ_B is very much lower than the design χ_B = 0.3. So, two values of the coefficient of activity were employed to optimise the fly ash concrete mixtures, namely χ_B = 0 and χ_B = 0.3.

Table 8
Experimental validation of Bolomey's equation.

(kg/m^3)	OPC	GGBS				Fly ash				
	Réf.	A	B	C Optimised	E Optimised	F	G Optimised	H Optimised	I Optimised	J Optimised
Addition level (vol.%)	0	25	50	50	75	25	50	50	59	59
Addition level (mass%)	0	24	48	48	73	19	41	41	50	50
Gravel 10/14	860	860	860	860	860	860	860	860	860	860
Gravel 6/10	210	210	210	210	210	210	210	210	210	210
Sand 0/4	843	843	843	843	843	843	843	843	843	843
w_{net}	199	199	199	192	172	199	182	168	173	153
Cement	350	263	175	187	109	263	201	224	178	204
Addition	–	81	161	172	301	61	141	157	178	204
Design data										
f_c 48 h (MPa)	–	–	–	10	10	–	10	10	10	10
K_B	–	–	–	12	12	–	12	12	12	12
χ_B	–	–	–	0.4	0.4	–	0.3	0	0.3	0
Experimental validation										
f_c 48 h (MPa) measured	21.3	14.2	8.5	10.5	12.2	12.3	10.9	15.0	11.4	14.4

χ_B	–	0.4	0.4	0.4	0.4	0.3	0.3	0	0.3	0.3	0	0.3
$\left(\frac{C+\chi_B A}{W} - 0.5\right)$	1.26	0.98	0.7	0.83	0.83	0.91	0.83	0.83	1.11	0.84	0.83	1.23
K_B	–	13.4	13.4	13.4	13.4	13.4	13.4	17.6	13.4	13.4	17.6	13.4
$K_B \cdot \left(\frac{C+\chi_B A}{W} - 0.5\right)$	–	13.1	9.4	11.2	11.2	12.2	11.2	14.7	14.9	11.2	14.7	16.5

In concrete, K_B used for the optimised mixture composition was not the same as that used to calculate the χ_B of the additions in mortars. So, validation of the method can only be made through the determination of a common coefficient K_B from measured strengths and assumed coefficients of activity (Table 8). According to Bolomey, f_c is a linear function of $\frac{C+\chi_B A}{W+V} - 0.5$ and the coefficient K_B. In Fig. 9, we have presented the strength as a function of $\frac{C+\chi_B A}{W+V} - 0.5$ using the χ_B values from the design data. This enables us to validate this approach (Table 8) as the strength values obtained from the regression curve are close to the actual measured values (except for the 50% and 59% fly ash concretes H and J, designed with $\chi_B = 0$), with a common K_B value of 13.4 MPa, which is higher than the value of $K_{B\ design} = 12.0$ MPa. The 50% and 59% fly ash concretes H and J showed significantly higher strengths (respectively 15 and 14.4 MPa) than the design value (10 MPa) and the other optimised mixtures. This can be explained by either a higher K_B value, which is not consistent with previous results, or a higher χ_B value. Assuming a common value of $K_B = 13.4$ MPa, measured strengths and Bolomey's Eq. (5) lead to experimentally assessed values of χ_B respectively equal to 0.31 and 0.18. This confirms that the value chosen from preliminary tests on mortars $\chi_B = 0.3$ was realistic for a 50% fly ash concrete mixture. In Fig. 10 and 2-day strengths calculated from these parameters and Bolomey's equation are plotted against measured values. The graph shows good correlation, which confirms the relevance of this method based on Bolomey's equation and coefficients of activity χ_B assessed from preliminary tests on mortars.

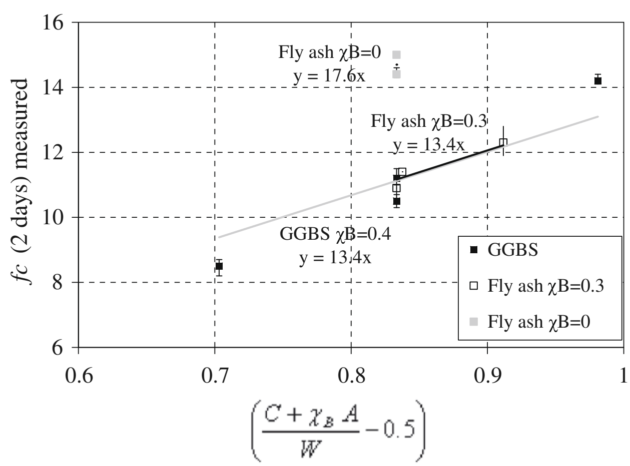

Fig. 9. Experimental validation of Bolomey's equation.

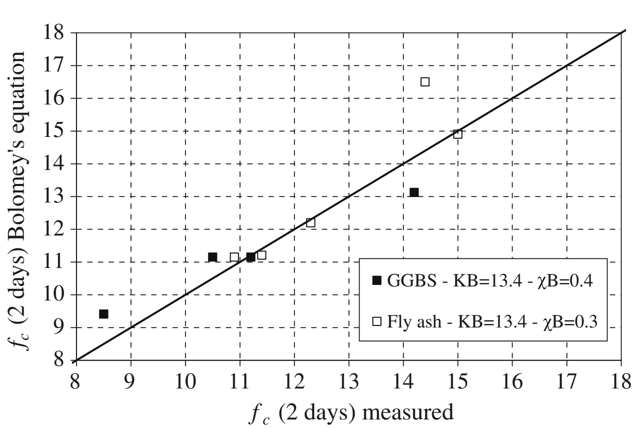

Fig. 10. Comparison between measured strength and strength from Bolomey's equation.

As a consequence, the values of $K_B = 13.4$ MPa and $\chi_B = 0.18$ were chosen to improve early age strength $f_{c\ design} = 12$ MPa of the second series of 58% fly ash concretes (Table 7). Use of hot water caused a decrease in the effective coefficient of activity χ_B. Conversely, the use of superplasticizer Sp3 and micro-filler resulted in an increase in early age strength. Superplasticizer Sp3 has a higher dry extract quantity than Sp1 and Sp2, but its dosage is lower and the addition of the micro-filler leads to a significantly lower Sp1 content. So the strengths measured on the C4 and C5 concretes suggest that the influence of chemical admixtures comes from enhanced workability which leads to a denser microstructure, rather than from a direct increase in the chemical reactivity of the cementitious materials.

5. Conclusions

The preliminary results of this ongoing study show that using mineral additions in large replacements can lead to good compressive strength even at early age. Our optimisation method is sufficiently simple and robust for industrial applications, because the main parameter to determine is the coefficient of activity of the mineral addition used, and it can be obtained easily using mortars.

The French standards on ready-mixed concrete limit the inclusion of minerals additions in concrete to be taken in account for the calculation of equivalent binder content and consider the coefficient of activity of the additions as a constant value. According to the results of this study, it appears that this coefficient depends strongly on the concrete age, type of addition, rate of substitution of cement and w/b.

The method proposed in this paper does not allow the user to take into account the dependency of the coefficient of activity upon w/b. Hence, it resulted in some approximations and overestimations of χ_B for lower w/b.

Mixtures with high replacement levels often have a relatively high proportion of superplasticizers and they are characterized by a viscous concrete in the fresh state. A moderate approach can be followed; instead of considering the volume of paste constant (equal to that of a reference mix-approach applied here), take the water as a constant quantity (same system of equations by taking V_W constant instead of V_P); however it becomes costly due to the increase in binder volume. Improvements can be made by superplasticizers or activators of the latest generation, to be used in smaller proportion, which do not delay the setting.

Although the results have proven this approach to mixture design feasible, a comprehensive optimisation process must take into account the overall performance of a concrete, especially its shrinkage and its tendency to cracking and durability in defined exposure conditions.

Acknowledgements

This study has been performed in the project EcoBéton which is supported by the French National Research Agency (*ANR – Agence Nationale pour la Recherche*) under Grant Number ANR-06-RGCU-006. The assistance of the project partners is gratefully acknowledged.

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