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Mineral admixtures in mortars effect of type, amount and fineness of fine constituents on compressive strength

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Abstract

This work is the third part of an overall project the aim of which is the development of general mix design rules for concrete containing different kinds of mineral admixtures (also named mineral additions or mineral constituents). It deals with the compressive strength of mortars made with up to 75% of crushed quartz, limestone filler or fly ash of different fineness. The paper presents all the experimental results as a sort of database and emphasizes the effects on strength of the nature, amount and fineness of mineral admixtures. For short hydration times (1 to 2 days), the nature of mineral admixture is not a significant parameter, as mortars containing the same amount of different kinds of admixtures having equivalent fineness present similar strengths. For long hydration times (up to 6 months), the excess strength due to fly ash pozzolanic activity is quantified by the difference between the strengths of mortars containing the same proportions of inert and pozzolanic admixtures with the same fineness. In the case of inert mineral admixtures, the increase in strength with the fineness of mineral admixtures cannot be explained by the filler effect, but can be attributed to the physical effect of heterogeneous nucleation. In the next part of this work, these results will be used for the elaboration of an empirical model leading to the quantification of both physical and chemical effects. This model presents strong similarities with the previous model based on calorimetric results.

Keywords: Fineness; Mineral admixtures; Supplementary cementing materials; Mortar; Specific surface area; Compressive strength; Fly ash; Limestone filler; Crushed quartz

1. Introduction

This paper presents the third part of an overall project the aim of which is to develop mix design rules for concrete containing different kinds of mineral admixtures. This objective is achieved by the application of a global and phenomenological approach leading to an empirical model that can be used for the evaluation of the physical and chemical effects of mineral admixtures in cementitious materials. The term “global approach” means that physicochemical interpretations of mechanisms and microstructural analyses are intentionally omitted to highlight the empirical relationships between macroscopic properties and the basic characteristics of mineral admixtures.

The different stages of the overall project are recalled in Fig. 1. In the first two parts [1,2], the enhancement effect of inert mineral admixtures on short-term hydration was studied by means of semi-adiabatic calorimetry. In summary, it was shown that this enhancement was due to two antagonistic physical effects: a dilution effect reducing the amount of hydrated cement and a surface effect, related to heterogeneous nucleation, producing an excess of hydrated cement. A decoupling process was suggested for these effects as well as an empirical model, mainly related to the specific surface area of the admixtures, was developed in order to quantify the variation of the degree of hydration induced by the use of inert mineral admixtures. One application of the model coupled with Powers’ law consists of predicting the short-term compressive strength of mortars. The objective of the subsequent parts of this work is to extend the analysis of the effect of inert and pozzolanic

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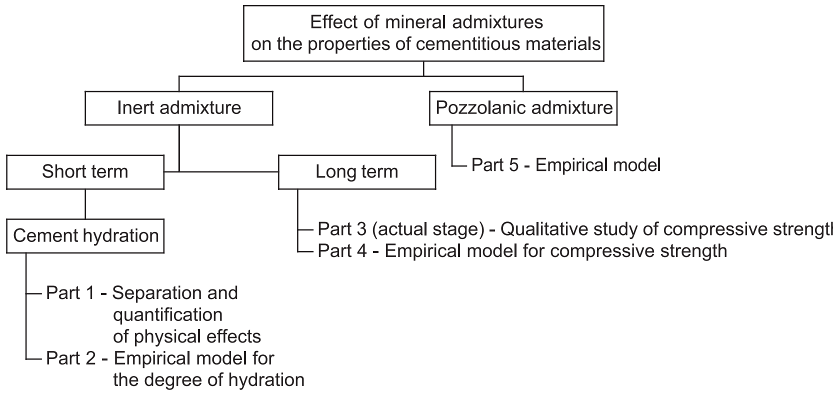


Fig. 1. Phases of the overall project.

mineral admixtures to the short and long-term compressive strength of mortars.

As indicated, this paper presents the third stage of the project, which consists of an experimental study of the influence of type, amount and fineness of inert and pozzolanic mineral admixtures on the compressive strength of mortars up to 6 months. These results will then be used, in the last two parts, in empirical models to quantify the modification of compressive strength of mortars due to physical and pozzolanic effects of mineral powders.

The paper includes:

– the presentation of the results of a large experimental program studying the compressive strength of mortars containing different types, amounts and fineness of mineral admixtures. The results are presented as a database, so as to allow researchers to use them for further investigations and modeling;
– the first-order analysis of the results, including decoupling pozzolanic activity from the overall effect of the mineral admixture.

2. Materials and experimental methods

The binders were standard OPC (Tables 1 and 2), CEM I 42,5R (C1) and CEM I 52,5 (C2) according to French Standard NF P15-301, with specific surfaces (Blaine) of 280 m^2/kg (C1) and 400 m^2/kg (C2). Each cement was received in one batch, mixed and stored in plastic bags until its use in the test program.

Three kinds of mineral admixtures were chosen (Table 2) in order to study a large range of fineness and reactivity (inert to pozzolanic materials):

– Seven finenesses of crushed quartz, identified by their mean diameter in micrometers (μm): Q61, Q35, Q24, Q14, Q11, Q4 and Q2 (Table 2). An angular shape, a density of 2.65 and a crystallized silica content above 99% were a set of common characteristics for all these admixtures. The high crystallized silica content implied that this material was chemically inert, that is, it did not react with hydrated phases of cement at room temperature.
– Three limestone fillers, characterized by an angular shape and a density of 2.70, and also identified by their mean diameter in micrometers (μm): L19, L8 and L3. Limestone is not chemically inert, since it reacts with C_3A and C_4AF to form carboaluminates [3,4]. However, not all researchers agree on the consequences of this reaction on the hydration and compressive strength of cementitious materials [5].
– Two types of raw fly ash (Tables 1 and 2), which can be compared to ASTM Class F fly ash, were identified

Table 1
Chemical and mineralogical compositions of cements (C1 and C2) and fly ash (FAC and FAA)

Oxides	Cement C1 (%)	Cement C2 (%)	Fly ash FAC (%)	Fly ash FAA (%)	Minerals (Bogue)	Cement C1 (%)	Cement C2 (%)
SiO_2	19.8	18.7	52.5	57.3	C_2S	10	10
CaO	63.9	63.0	2.2	1.0	C_3S	61	58
Al_2O_3	4.5	5.5	27.9	24.6	C_3A	7	11
Fe_2O_3	3.2	2.4	5.6	5.0	C_4AF	10	7
MgO	1.1	3.2	1.0	0.6	Gypsum	7	7
Na_2O eq	1.2	0.6	3.7	7.8	Other	5	7
SO_3	3.1	3.0	0.6	0.2			
L.O.I.	0.9	1.4	3.3	5.7			

by their French origin: Cordemais (FAC) and Albi (FAA). They differed in their finenesses (specific surface: 384 m^2/kg for FAC and 312 m^2/kg for FAA) and chemical composition (e.g. loss on ignition [LOI] 3.3% for FAC and 5.7% for FAA). FAA contained more coarse particles (>100 μm), mostly composed of unburned coal [6]. In order to study the effect of the fineness of fly ash on cement hydration, fly ash FAC was ground with a rod mill to three levels of fineness (Table 2): 547 m^2/kg (FAC11), 756 m^2/kg (FAC7) and 909 m^2/kg (FAC5).

The aggregate was a normalized quartz sand (NF EN 196-1), with particle sizes ranging between 0.08 and 2 mm.

The tests were performed on mortars, which are more representative of concrete than cement pastes and more suitable than concrete given the extensive experimental program. The reference admixture-free mix, designed in accordance with French standard NF EN 196-1, was composed of three parts of sand (1.35 kg), one part of cement (0.45 kg) and a half part of water (0.225 kg). All mixes with mineral admixtures involved the same proportions in mass of sand, powder (cement+mineral admixture) and water. The cement replacement by mineral admixture was expressed as the mass fraction (p) of cement in the reference mix (C_o). Replacement rates were 5%, 10%, 17.5%, 25%, 35%, 50%, and 75%.

The mix design parameters followed Eq. (1)

$$\frac{W}{C+A} = \frac{W}{(1-p)C_0 + pC_0} = \frac{W}{C_0} = 0.5 \quad (1)$$

where C_o and C are the masses of cement in the reference and other mixes, respectively, A is the mass of mineral admixture, W the mass of water and p the replacement rate of cement by a mineral admixture. Organic admixtures were not used in this study.

The mixture was cast in 4×4×16 cm^3 molds and stored in 20 °C water. Strength tests were strictly performed in accordance with French Standard NF EN 196-1. Air content [7] and density measurements of fresh mortars were carried out for some compositions. The strength tests were carried out at seven hydration times (1, 2, 7, 14, 28, 90 and 180 days) and were divided into two parts: for each prism, a flexural test (not presented in this study) followed by two compression tests on the remaining parts (4×4×8 cm^3). The number of tested prisms for each composition varied between 1 and 27.

3. Results and statistical information

In this study, the compressive strength is used as the indicator of the activity of mineral admixtures in mortars and each result is the mean value of several tests. Tables 3–5 present the compressive strength results (mean values and intervals of confidence) of mortars made with cement C1 and containing the different types, amounts and fineness of mineral admixtures.

For the 54 types of mortars studied at different hydration times and representing 332 values in these tables (Ref: 7, Q: 169, L: 49, FA: 107), more than 1000 prisms (1 prism, 4×4×16 cm=2 pieces) were tested. The distribution of the number of tested pieces for the whole experimental program is given in Fig. 2.

The results of the compressive strength of mortars containing cement C2 are found in Table 6. Their qualitative analysis leads essentially to similar conclusions concerning the analysis completed from the results using cement C1. The results with cement C2 will be exploited in greater a future paper.

3.1. Strength as a random variable

The strength measurements of a cement-based material are generally regarded as a population sample of a random variable. Using this sample, i.e. a finite number of experimental data X_i, estimated values of mean M (Eq. (2a)) and standard deviation S.D. (Eq. (2b)) of this random

Table 2
Physical properties of mineral admixtures and binders

Name	Mean diameter (μm)	Specific surface Blaine S_s (m^2/kg)	Density	Name	Mean diameter (μm)	Specific surface Blaine S_s (m^2/kg)	Density
Quartz				*Fly ash*			
Q61	61	187		FAA	37	312	2.10
Q35	35	257					
Q24	24	315		FAC	24	384	2.20
Q14	14	474	2.65				
Q11	11	565		FAC11	11	547	2.40
Q4	4	1070		FAC7	7	756	2.54
Q2	2	2000		FAC5	5	909	2.60
Limestone filler				*Binders*			
L19	19	346		C1	21	280	3.14
L8	8	497	2.70	C2	15	400	3.14
L3	3	782					

Table 3
Compressive strength (MPa) of mortars containing crushed quartz compared to reference mortar (cement C1)

	Replacement rate p (%)	Hydration time (days)						
		1	2	7	14	28	90	180
Reference	0	15.4±0.3	26.4±0.4	37.9±0.8	42.7±0.7	47.3±0.4	52.5±1.3	55.5±0.7
Quartz								
Q61	5	14.7±0.4	22.9±0.6	35.0±0.4		43.9±1.0	50.2±1.5	51.5±0.4
	10	11.9±0.4	20.9±0.5	29.2±0.4		40.9±1.1	47.1±0.3	48.0±2.7
	17.5	10.6±0.4	18.4±0.5	27.6±1.1		38.9±0.7		
	25	9.0±0.4	16.2±0.5	24.5±0.7	29.3±0.9	33.5±0.9	36.6±0.6	40.4±0.7
	35	6.9±0.3	12.7±0.5	18.2±0.4		28.9±3.2	35.8±0.8	
	50	5.3±0.1	8.9±0.2	13.0±0.3		18.6±0.3	24.7±0.4	
Q35	10	12.5±0.6	21.1±0.6	30.2±2.0		42.4±0.4		
	25	10.1±0.4	16.9±0.3	25.3±0.5	30.4±0.2	34.3±1.1		40.4±1.2
Q24	10	13.3±0.3	22.3±0.5	33.1±0.9	36.6±1.5	42.2±1.1	48.2±0.5	48.9±0.8
	17.5	12.4±0.1	20.3±0.4	29.1±0.8	34.3±1.1	39.7±1.0	44.5±1.4	44.7±1.7
	25	10.9±0.1	17.7±0.2	26.6±0.3	31.0±0.5	36.4±0.4	40.7±0.7	42.8±0.6
	35	9.1±0.4	14.6±0.6	21.3±0.5	27.5±0.8	30.9±0.8	36.7±0.6	36.7±0.7
	50	6.0±0.2	10.0±0.2	14.6±0.5	17.9±0.2	20.9±0.8	24.9±0.4	24.4±0.4
	75	1.3±0.1	3.2±0.1	4.9±0.1	5.0±0.1	6.8±0.3	8.1±0.1	7.9±0.2
Q14	10	13.4±0.7	23.0±0.7	32.8±1.6		43.4±0.8		
	25	11.7±0.5	19.0±0.2	28.1±0.8	34.3±0.9	38.7±0.9		43.2±0.9
Q11	10	14.1±0.6	23.6±0.5	33.6±0.6			43.7±0.3	
	25	11.9±0.4	20.1±0.3	29.2±0.3	35.1±0.8	39.6±0.8		46.4±0.9
Q4	10	15.2±0.5	24.7±0.9	36.3±0.9		47.6±0.5	54.9±0.2	
	17.5	14.3±0.2	23.7±0.7	34.4±0.8		46.0±0.6		
	25	13.8±0.3	22.4±0.2	31.6±0.4	37.7±1.7	43.8±1.0	46.3±0.3	50.5±1.2
	35	11.5±0.3	19.6±0.5	28.3±0.3		38.2±1.0		
	50	7.6±0.4	12.7±0.2	18.0±1.0		26.2±0.6	31.3±1.0	
Q2	5	17.5±0.3	26.9±0.1	39.1±0.1		49.0±1.3		57.0±0.6
	10	17.4±0.3	27.7±0.6	38.4±0.7		50.8±1.4	55.9±1.5	57.5±1.6
	17.5	17.3±0.4	26.6±0.6	37.4±0.8		49.1±1.2	54.3±4.0	55.8±1.6
	25	15.1±0.2	24.2±0.4	34.4±0.7	40.2±0.7	45.5±1.3	51.5±0.2	52.4±1.1
	35	13.0±0.4	20.0±0.2	29.0±0.5		41.1±1.0		
	50	9.2±0.2	14.1±0.3	20.7±0.5		30.7±1.1	37.8±1.0	
	75	3.7±0.1	4.9±0.1	8.1±0.2		12.4±0.1	16.9±0.6	22.0±1.1

variable can be calculated. The accuracy on these values is proportionally improved the greater the number (n) of tests.

$$M = \frac{\sum_l^n X_i}{n} \tag{2a}$$

$$S.D. = \sqrt{\frac{\sum_l^n (X_i - M)^2}{n-1}} \tag{2b}$$

The reference mortar was tested at 1 and 28 days on four different occasions (total of 54 and 50 experimental results) in the course of the entire program test lasting almost 2 years, so as to:

– monitor any deviation of the results due to the possible variation of the experimental conditions and ageing of the cement;
– evaluate the law of strength distribution.

Fig. 3, which gives the evolution of compressive strength at 28 days of reference mortars, shows that no significant

Table 4
Compressive strength (MPa) of mortars containing limestone fillers compared to reference mortar (cement C1)

	Replacement rate p (%)	Hydration time (days)						
		1	2	7	14	28	90	180
Reference	0	15.4±0.3	26.4±0.4	37.9±0.8	42.7±0.7	47.3±0.4	52.5±1.3	55.5±0.7
Limestone								
L19	10	13.5±0.3	22.7±0.3	35.3±1.1	40.6±0.4	44.2±0.8	49.9±1.8	50.5±2.1
	17.5	11.4±0.3	20.3±0.6	32.4±0.4	36.7±0.6	40.7±0.5	46.4±0.9	48.9±0.8
	25	10.8±0.5	19.0±0.4	29.7±0.9	33.6±0.6	37.8±0.5	42.3±1.0	43.8±1.0
	35	8.5±0.4	15.3±0.4	24.3±1.0	28.4±0.4	32.5±0.9	36.4±1.4	37.2±1.1
	50	5.4±0.3	9.6±0.4	16.4±0.3	19.0±0.4	21.8±0.4	24.7±0.7	24.8±1.2
L8	25	13.0±0.5	21.6±0.5	34.0±0.2	39.1±0.6	43.0±0.4	46.1±1.6	48.7±1.9
L3	25	11.9±0.3	20.3±0.2	31.6±0.8	37.4±0.7	41.1±0.3	45.7±0.7	47.1±1.4

Table 5
Compressive strength (MPa) of mortars containing fly ash compared to reference mortar (cement C1)

	Replacement rate p (%)	Hydration time (days)						
		1	2	7	14	28	90	180
Reference	0	15.4±0.3	26.4±0.4	37.9±0.8	42.7±0.7	47.3±0.4	52.5±1.3	55.5±0.7
Fly ashes								
FAA	10	13.7±0.5	23.3±0.5	33.3±1.4	38.8±0.5	44.4±0.7	51.4±1.6	58.0±1.3
	17.5	12.1±0.5	20.8±0.4	30.9±0.8	35.6±0.6	40.1±0.6	50.7±0.9	59.6±2.2
	25	10.2±0.6	18.1±0.3	27.2±0.6	31.3±0.3	37.9±0.8	49.9±1.2	57.4±2.2
	35	8.3±0.2	14.2±0.2	21.9±0.3	25.9±0.4	32.0±1.0	45.1±0.6	53.5±1.2
	50	4.5±0.3	8.7±0.1	14.2±0.4	17.1±0.7	20.5±0.5	31.9±0.9	42.0±2.0
FAC	10	15.0±0.2	23.5±0.7	33.7±0.8	39.9±0.5	44.8±1.4	55.1±1.0	58.5±1.2
	17.5	11.5±1.0	20.4±1.1	31.0±0.5	36.3±1.9	44.1±0.9	55.2±2.5	62.3±2.1
	25	10.0±0.6	17.9±0.7	27.8±0.4	33.2±1.3	40.0±0.9	56.6±1.7	60.4±1.8
	35	8.4±0.5	15.4±0.8	23.3±0.8	29.2±1.6	36.2±1.6	53.2±1.4	59.6±1.8
	50	4.1±0.4	9.6±0.4	16.1±0.3	19.0±0.3	23.3±0.5	37.9±0.8	47.4±1.2
	75	0.8±0.1	2.5±0.1	5.4±0.2	5.9±0.4	6.7±0.7	9.3±0.5	18.0±0.7
FAC11	25	13.1±0.3	21.7±0.4	32.2±0.4		45.9±1.1	60.3±1.6	68.2±2.3
FAC7	25	14.2±0.4	23.2±0.3	33.7±0.5		50.1±2.0	65.1±2.2	72.1±2.1
FAC5	25	14.4±0.2	23.4±0.3	36.0±0.6		54.4±1.0	71.6±1.3	73.9±4.2
FAC<80 μm	25	10.9±0.3	18.8±0.5	28.9±0.8	34.5±0.9	42.0±0.4		61.8±3.1
FAC>80 μm	25	8.2±0.3	14.2±0.2	21.9±0.3	22.3±1.0	27.4±0.4		37.8±2.0

decrease in strength affected the mortars over the test program period. It can thus be concluded that there was no alteration of the cement for up to nearly 2 years. Since all the other mortars were prepared within this period, their strength variations should be attributed neither to the evolution of the cement nor to the modification of the experimental conditions.

In most statistical analysis of experimental results, it is assumed that the data follows a Laplace–Gauss law, which is characterized by a mean value M and a standard deviation S.D. It is generally admitted that this law can be applied to compressive strength measurements and in the case of concrete, a few analyses can be found in the literature [8].

The verification of this assumption for mortars from the data of this study was made using the Henry test on the 50 experimental points of the strength at 28 days. As can be seen in Fig. 4, the curve obtained is almost a straight line (with a coefficient R^2=0.98), indicating that the data actually follows a Laplace–Gauss law.

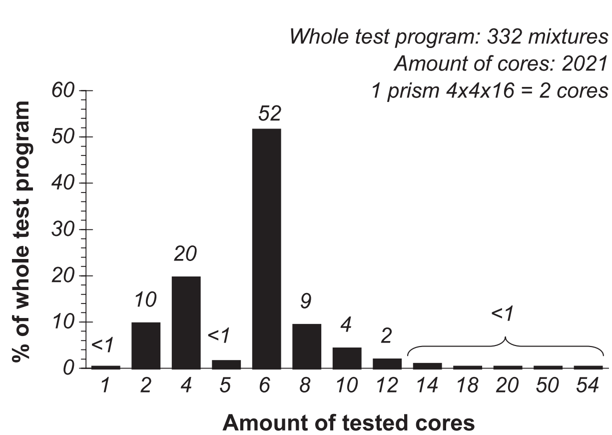


Fig. 2. Distribution of tested pieces for the whole experimental program.

3.2. Accuracy of the measurements

3.2.1. Interval of confidence

As in every measurement, the strength is obtained from a limited amount of tests and is consequently affected by errors due to uncertainties in the measurement itself. Thus, mean value M calculated from n experiments is only an estimate of real mean value M^* of the random variable “strength.” The error committed in M can be quantified from a probabilistic point of view by means of interval of confidence I_β where I_β is defined as the range in which real mean value M^* can be with a probability of confidence β (Eq. (3)). In practice, I_β is centered on the mean value M of a measurement and its magnitude is twice error ε_β where ε_β is calculated from Eq. (4), using standard deviation S.D., number of tests n and a Student coefficient t_β depending on n and β (Fig. 5); assuming a probability of confidence of 95% as is usual in material science. For a required precision, it is possible to calculate the minimum number of tests that has to be made from Fig. 5.

$$P\left(|M - M^*| \le \varepsilon_\beta\right) = \beta \text{ and } I_\beta = \lfloor M - \varepsilon_\beta;\, M + \varepsilon_\beta \rfloor \tag{3}$$

$$\varepsilon_\beta = \frac{S.D.t_\beta}{\sqrt{n}} \tag{4}$$

3.2.2. Experimental dispersion versus compressive strength

Fig. 6 shows the standard deviation versus the compressive strength for the whole test program (all mortars mixtures and hydration times). A general tendency is observed, in spite of the high dispersion of the data. Globally, S.D. increases with compressive strength (M), meaning that the absolute error in MPa is greater for mortars having high strengths. It can be noted that there is no

Table 6
Compressive strength (MPa) of mortars containing crushed quartz compared to reference mortar (cement C2)

	Replacement rate p (%)	Hydration time (days)				Replacement rate p (%)	Hydration time (days)		
		1	2	28			1	2	28
Reference		17.9±0.3	28.9±0.7	58.8±2.1					
Quartz									
Q61	10	15.5±0.7	25.2±1.0	52.5±1.5	Q2	10	22.4±0.6	35.2±1.0	57.6±0.9
	25	11.3±0.3	18.2±0.6	41.2±1.9		25	19.7±0.6	29.0±1.3	47.3±1.1
	50	6.2±0.2	9.7±0.4	21.7±0.7		50	12.0±0.4	17.2±0.7	31.0±1.2
	75	1.7±0.1	3.4±0.2	6.3±0.5		75	4.6±0.2	6.0±0.1	13.3±0.5
Q24	10	15.6±0.3	25.3±0.5	50.7±1.3	Q4	10	20.0±0.4	31.3±0.9	55.2±1.5
	25	12.9±0.3	21.2±0.4	42.2±1.4		25	17.9±0.4	26.0±0.9	44.6±1.7
	50	7.5±0.3	11.4±0.2	23.5±0.4		50	10.4±0.3	15.0±0.4	26.7±0.6

particular effect of the type of mineral admixture on this tendency.

A simple straight line was chosen (Eq. (5)) and its slope a is equal to 0.031 for our experimental data on mortars. Neville [9] also observed a linear relationship for concrete between these parameters, but found a higher slope (0.044), which probably indicates that a higher dispersion affects concrete, especially its compressive strength.

$$S.D. = aM \tag{5}$$

Eqs. (4) and (5) can be combined in order to express the error as a function of compressive strength and number of tested mortar pieces (Eq. (6)).

$$\varepsilon_\beta = \frac{t_\beta}{\sqrt{n}}(aM) = \frac{t_\beta}{\sqrt{n}}(0.031M) \tag{6}$$

Fig. 7 illustrates this relationship for mortars up to 75 MPa when the number of tested pieces is comprised between 3 and 15.

It can be observed that:

– the error reaches more than 5 MPa for high strength mortars when only three pieces are tested. The expected error with two pieces (not shown in Fig. 7) is over 20 MPa for mortars of 75 MPa;
– the strength measurement of six pieces, corresponding to three prisms of mortar in the French standard NF EN 196-1, should lead to errors lower than 2.5 MPa.

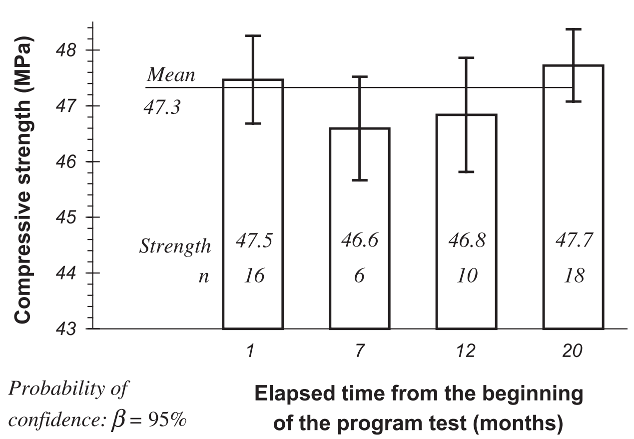


Fig. 3. Evolution of compressive strength at 28 days of the reference mortar (cement of a single batch) between the beginning and the end of the experimental program.

4. Discussion of the results

A global observation of the results shows that strength depends on all measurable parameters: time of tests, nature, amount and fineness of mineral admixtures used. Moreover, it can be noted that in some cases, the strength of mortars with mineral admixtures is greater than the strength of the reference mortar. This phenomenon occurred for fly ash after 28 days, but also for finely ground quartz used at low replacement rates.

The following parts of the paper develop two points of view concerning the qualitative analysis of the results: the first focuses on the amount of mineral admixtures, and the second on their fineness. In each case, the nature of mineral admixtures is taken into account.

4.1. Effect of nature and amount of mineral admixtures on compressive strength

With the aim of analyzing the effect of nature and amount of mineral admixtures on the compressive strength

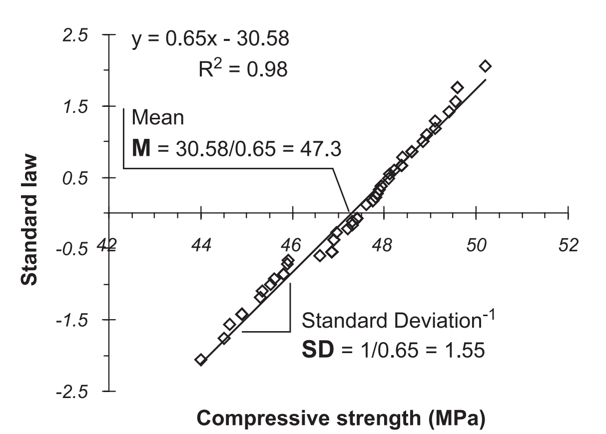
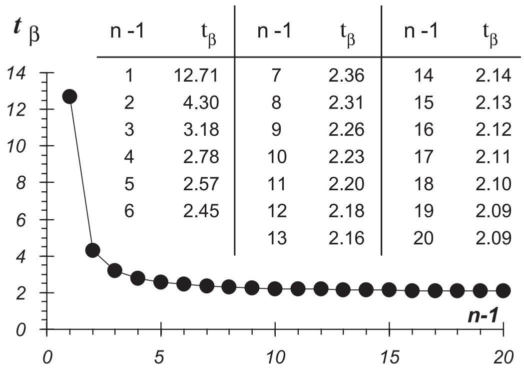


Fig. 4. Statistical representation of the 50 experimental points of the strength at 28 days. Verification of the Laplace–Gauss law using the Henry straight line test.



n -1	t_β	n -1	t_β	n -1	t_β
1	12.71	7	2.36	14	2.14
2	4.30	8	2.31	15	2.13
3	3.18	9	2.26	16	2.12
4	2.78	10	2.23	17	2.11
5	2.57	11	2.20	18	2.10
6	2.45	12	2.18	19	2.09
		13	2.16	20	2.09

Fig. 5. Student coefficient t_β as a function of the degree of freedom ($n-1$), for a probability of confidence β=95%.

of mortars, it was decided to compare only the results of mortars containing powders of equivalent fineness. Consequently, four mineral admixtures having a specific surface close to that of cement C1 (280 m^2/kg) were chosen: Q24 (315 m^2/kg), L19 (346 m^2/kg), FAC (384 m^2/kg) and FAA (312 m^2/kg). Fig. 8 gives the evolution of compressive strengths at 1, 2, 7, 14, 28, 90 and 180 days for mortars containing up to 75% of these mineral admixtures.

For very short terms (1 to 2 days) and for this fineness only, compressive strength decreased linearly with the replacement rate of all four mineral admixtures, recalling Feret's law (which is nearly linear for replacement rates below 75%). A more detailed analysis will be carried out in the next article. For these hydration times, the differences between the four curves were statistically insignificant, as shown by the interval of confidence in the data (Fig. 8). Hence, from a mechanical point of view, the nature of the mineral admixtures cannot be distinguished from inert and pozzolanic powders having similar fineness, since they all had the same effect on mortars. It can be concluded that for short-term compressive strengths, the amount of mineral admixture is the only significant parameter which has to be taken into account.

At 7 and 14 days, mortars containing limestone filler show higher compressive strengths than mortars with crushed quartz. This difference in strength becomes insignificant after 28 days, since, from this hydration time, the mortars containing quartz and limestone present almost the same compressive strengths for a given replacement rate. The particular effect of limestone filler on compressive strength is discussed later.

For 28 days and over, the compressive strength of an inert powder such as Q24, the fineness of which is close to the fineness of the cement, follows, as for short-term behavior, a linearly decreasing function depending on replacement rate p (Fig. 9). The linearity is no longer respected for mortars made from fly ash, since pozzolanic activity is initiated near 28 days. A quantity of around 20% of fly ash leads to a maximum strength. This optimum value has already been seen in the literature [10]. This activity of fly ash, leading to a noticeable increase in compressive strength compared to inert admixtures, was developed earlier in the case of FAC (between 14 and 28 days) compared to FAA (after 28 days). However, at 6 months, the difference in strength was reduced. The similar compressive strength between mortars with FAC and FAA at 180 days apparently shows that the evolution of the pozzolanic reaction of FAA is not reduced, but only retarded. This delay is due to many variables, which influence the strength development of fly ash mortars, the main ones being chemical composition, particle size and reactivity [11].

To sum up, in the case of mineral admixtures having a fineness similar to the fineness of cement, short-term behavior only depended on replacement rate p, the nature of the admixture being a secondary parameter. The nature of the admixture became significant after pozzolanic activity took place. The evolution of strength versus p for inert and pozzolanic admixtures will be used later to isolate the increase in strength uniquely due to pozzolanic reaction.

4.2. Effect of nature and fineness of mineral admixtures on compressive strength

The effect of nature and fineness of mineral admixtures on the compressive strength of mortars is analyzed here using a constant replacement rate of 25%. The admixtures were coarser or finer than cement (280 m^2/kg): Q61 to Q2 (187–2000 m^2/kg), L19 to L3 (346–782 m^2/kg), FAA to FAC5 (312–909 m^2/kg). Fig. 10 shows compressive strength as a function of the specific surface, up to 180 days, and Fig. 11 summarizes these results on a semi-log scale. For all hydration times tested, it can be seen that compressive strength increased with the fineness of the admixture used, the experimental data following a logarithmic evolution. The increase of strength with fineness cannot be attributed either to a decrease of the air content of mortars or to an increase in the density of fresh mixtures,

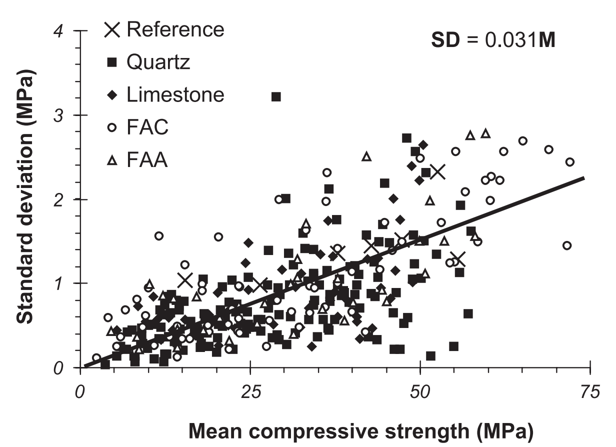


Fig. 6. Standard deviation versus compressive strength for all mortar mixtures and hydration times.

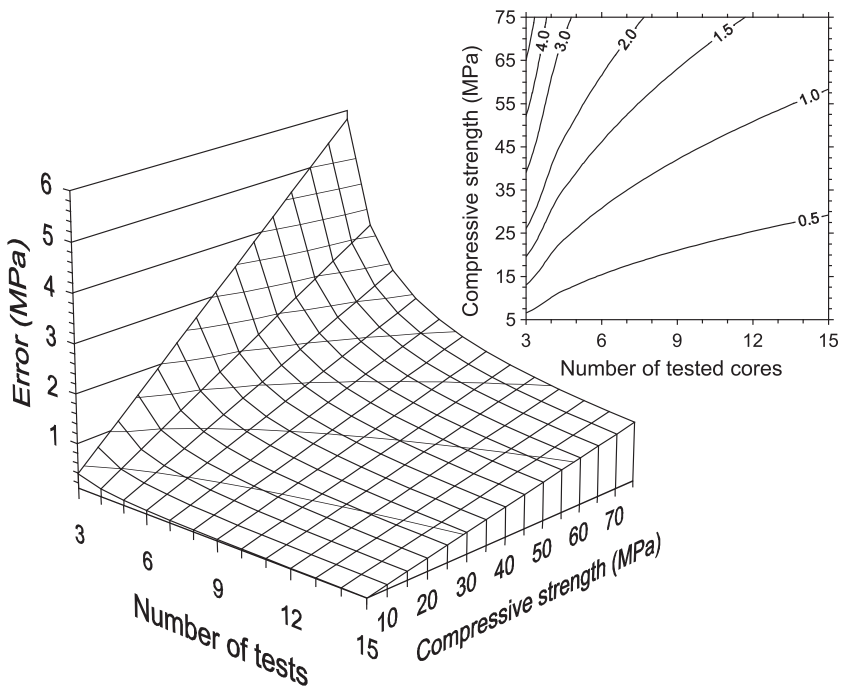


Fig. 7. Expected error ε_β as a function of the mean compressive strength of mortar and number n of measurements ($3<n<15$).

since the variations in these parameters are weak for quartz and limestone (Fig. 12).

For short hydration times (1 to 2 days), almost all experimental points of the different mineral admixtures are on single curves, confirming that compressive strength is independent of the nature (quartz, limestone or fly ash) of the powder used for a large range of fineness. The only exception concerned the three crushed fly ashes (FAC11, FAC7 and FAC5), which show a slight increase in compressive strength (less than 10%) for a given fineness compared to other materials. This increase is attributable to the higher compactness of fresh mortars when these admixtures are used: density and air content of 2.28 and 1.5%, respectively, against 2.24% and 3% for other mixtures (Fig. 12).

Between 7 and 28 days, the experimental points of mortars containing limestone fillers moved away from the inert materials curve, confirming here that the increase in strength observed earlier for all replacement rates when using L19, are also present in the two other finenesses of limestone filler (L8 and L3) (Fig. 13). This increase is not due to a lowering of mortar porosity, as was the case for crushed fly ash, since the density and the air content of quartz and limestone mixtures are almost the same (Fig. 12). Thus, it seems reasonable to believe that there is a particular mechanism which improves the compressive strength of mortars containing limestone filler from 2 days or more onwards. However, it must be noted that the increase in strength became negligible after 28 days. Some authors report that the formation of aluminates and carboaluminates may improve the compressive strength of concrete [5], but the literature in general is not absolutely clear on this subject. Our own investigations (SEM and XRD) have not yet led to elucidating the mechanism responsible for these results.

For long-term behavior (more than 28 days), the results show that in the case of non-pozzolanic admixtures (limestone filler and quartz), the effect of fineness on compressive strength is maintained over time. For mortars containing pozzolanic admixtures (fly ash), the effect of fineness is significant, as can be observed by the increase of the slopes over time in Fig. 11.

4.3. Physical and pozzolanic activities of mineral admixtures

4.3.1. Increase in compressive strength due to physical activity

The increase in strength with specific surface area of non-pozzolanic admixtures (limestone filler and quartz) is the consequence of various physical phenomena, the two main ones being the effect of particle size distribution (filler effect) and the effect due to heterogeneous nucleation [1,2,12].

The filler effect implies a modification of the initial porosity of the mix, which can be related to variations in density and air content of fresh mortar mixtures. Since neither density nor air content varies significantly for quartz and limestone mortars (Fig. 12), the filler effect cannot explain the increase in strength of our mortars.

Heterogeneous nucleation, which has already been observed by several authors [13–16], is probably the main physical effect responsible for the increase in strength associated with the fineness of the mineral admixtures used.

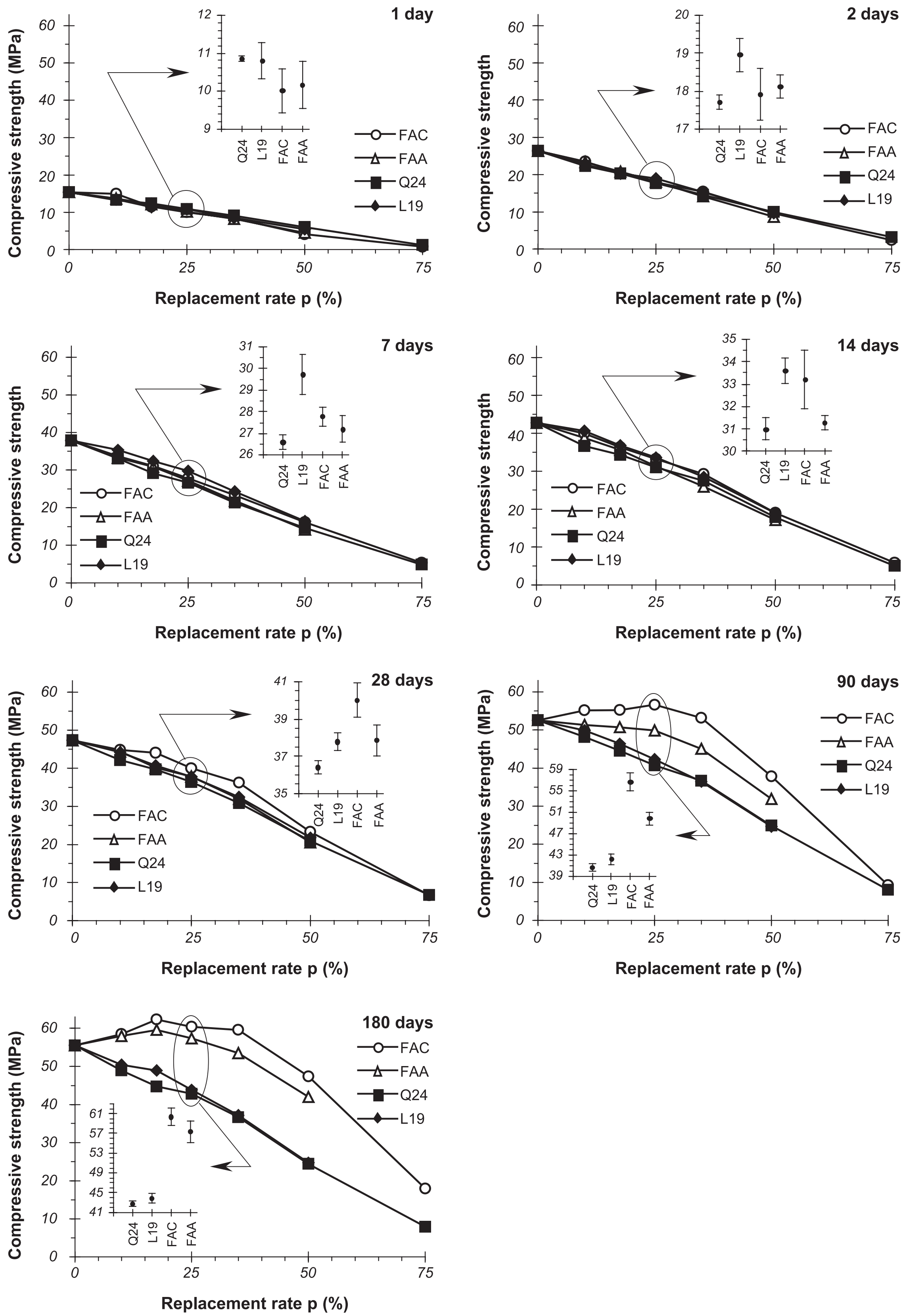


Fig. 8. Evolution of compressive strength at 1, 2, 7, 14, 28, 90 and 180 days for mortars containing up to 75% of admixtures having equivalent fineness (Q24, L19, FAC and FAA) as a cement replacement. Probability of confidence: β=95%.

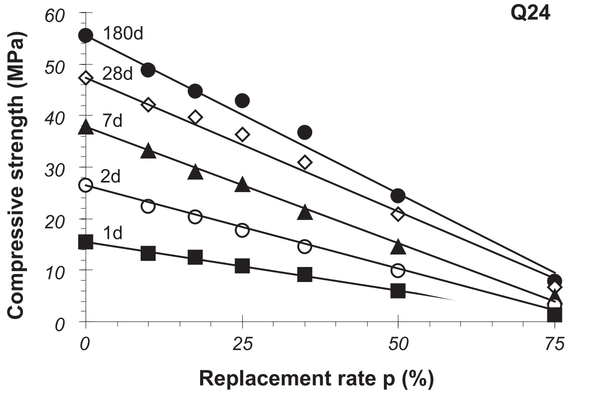


Fig. 9. Linear decrease of compressive strength with p, for mortars containing Q24 (results at 14 and 90 days have been omitted in order to lighten the figure).

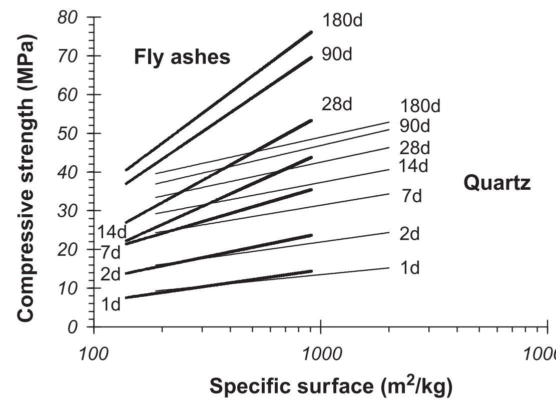


Fig. 11. Effect of admixture fineness on compressive strength of mortars containing 25% of quartz and fly ashes (between 1 and 180 days).

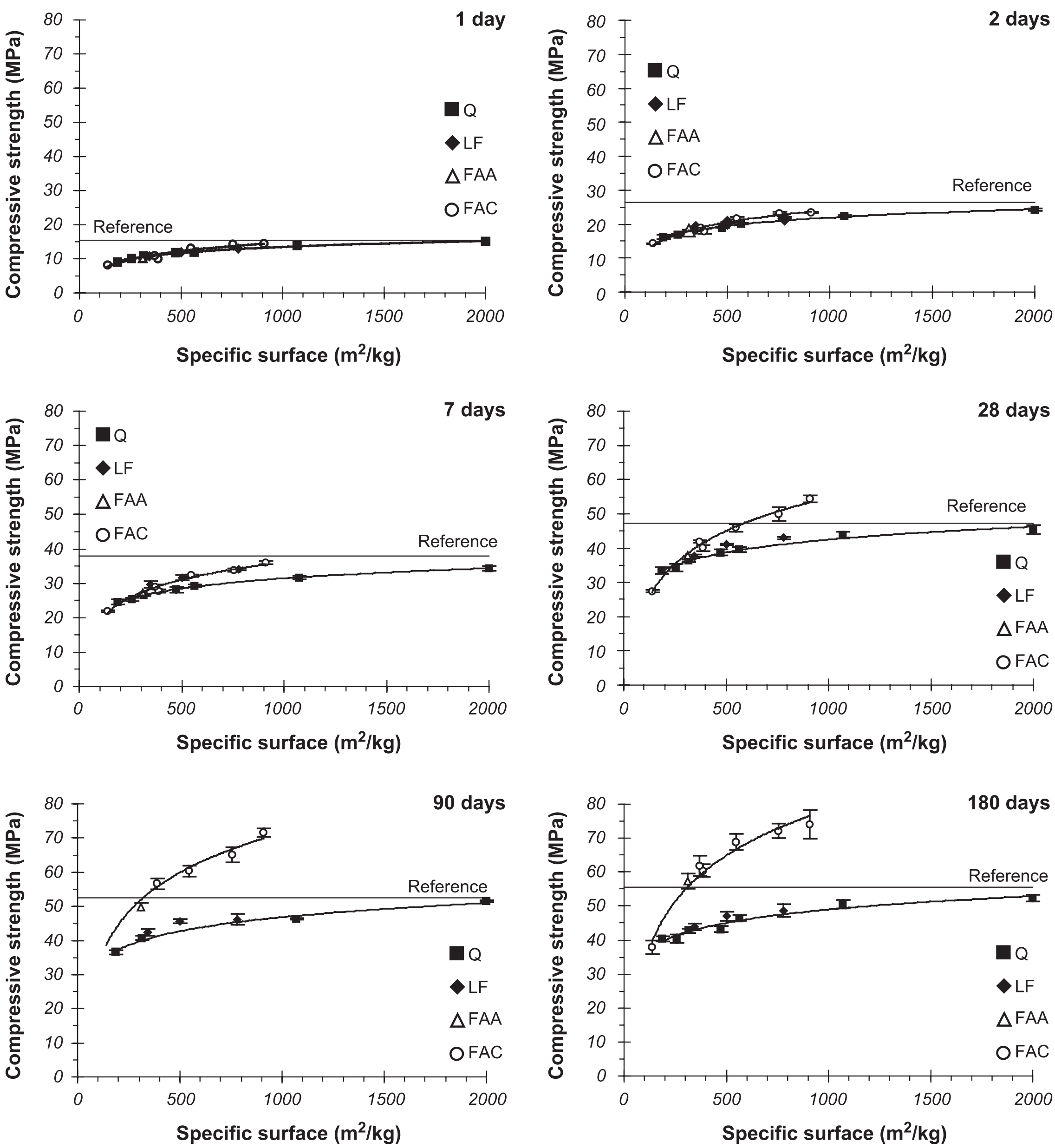


Fig. 10. Effect of admixture fineness on compressive strength of mortars containing 25% of quartz, limestone and fly ash.

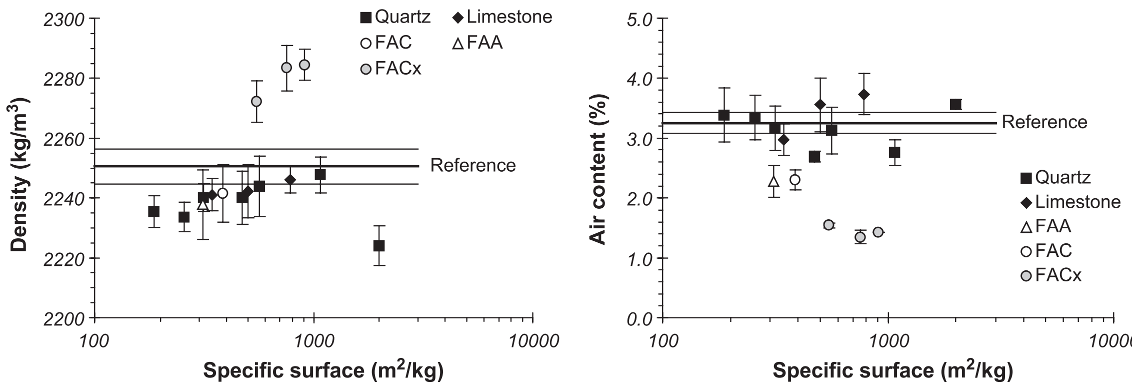


Fig. 12. Density and air content of mortars containing 25% of mineral admixture.

Heterogeneous nucleation is a physical process leading to a chemical activation of the hydration of cement. It is related to the nucleation of hydrates on foreign mineral particles, which catalyzes the nucleation process by reducing the energy barrier. As already exposed [1], it depends on:

- the fineness of mineral admixture particles, since the decrease of particle size favors nucleation;
- the amount of mineral admixture used, since the probability for nucleation sites to be near to cement particles increases with the amount of foreign particles;
- the affinity of the mineral powder to cement hydrates [17], which is related to the nature of the mineral used.

The quantification of the effect of heterogeneous nucleation on strength will be effected in a future paper.

4.3.2. Increase in compressive strength due to pozzolanic activity

The differences in strength of mortars with inert and pozzolanic admixtures are significant after 7 days (Figs. 14 and 15), revealing the pozzolanic activity of fly ash. From these experimental results, it is possible to quantify the increase in strength Δf due to pozzolanic reaction by the difference in strength between fly ash mortars f_{FA} and inert quartz mortars f_{Q} (Eq. (7)).

$$\Delta f(p, S_{\mathrm{s}}, t) = f_{FA}(p, S_{\mathrm{s}}, t) - f_{Q}(p, S_{\mathrm{s}}, t) \quad (7)$$

The excess in compressive strength Δf was calculated at the same hydration time t, at the same replacement rate p and at an equivalent fineness S_{s} of mineral admixture.

Fig. 14 shows the increase in compressive strength due to pozzolanic reaction for FAA and FAC calculated with Q24, which has an equivalent fineness to the two raw fly ashes. Δf is significant after 7 and 28 days for FAC and FAA, respectively, and it increases significantly over time. The curves present maximum values around 35% to 40% of replacement rates. This optimum content of fly ash leads to the highest excess strength due to a pozzolanic effect.

Fig. 15 shows Δf for different finenesses of fly ash (raw and ground admixtures). The strength of mortars containing inert materials (quartz) and having an equivalent fineness to fly ash was calculated using a logarithmic evolution obtained from data in Fig. 10. The pozzolanic activity calculated using this method is also displayed from 7 days and subsequently it increased to 180 days. For all hydration times, pozzolanic activity increased with the fineness of the fly ash, showing the importance of particle size on pozzolanic reaction.

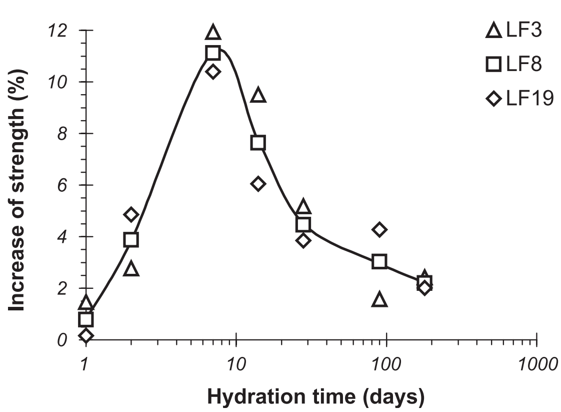


Fig. 13. Temporary increase of strength as a percentage of mortars containing 25% of limestone fillers, compared to mortars with 25% of crushed quartz of equivalent fineness. The values for quartz were calculated from the evolution given in Fig. 10.

4.4. Effect of inert and pozzolanic admixtures in mortars compared to a reference admixture-free mortar

Fig. 16 summarizes the effect of inert and pozzolanic mineral admixtures on compressive strengths of mortars at 1, 28 and 180 days. The results, expressed in terms of fractions of strength of a reference admixture-free mortar, were obtained by interpolation of the data. The only extrapolated results, which should be considered with caution, concern high replacement rates of cement by ground fly ash. Experimental points (white dots) are included in each figure.

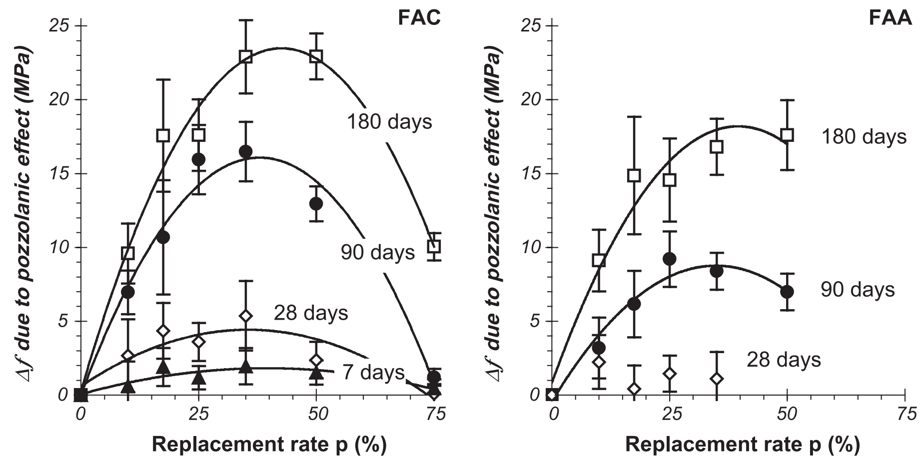


Fig. 14. Increase in strength (Δf) due to pozzolanic effect of mortars containing up to 75% of fly ash (FAC or FAA) in cement replacement.

In the case of inert admixtures (quartz and limestone fillers):

– the isostrength curves have the same shape between 1 and 180 days, confirming that the physical effects of fillers are developed at early ages and then maintained over time. However, their efficiency slightly decreased with time. As an example, 25% of 2000 m^2/kg filler led at 1 day to the same strength as reference mortar without admixture, while the same mix reached around 95% of the reference strength at 180 days;
– fineness has a significant effect for specific surfaces below 500 m^2/kg;
– for high replacement rates, the specific surfaces over 500 m^2/kg (upper right corner) have only a weak influence on compressive strength. Filler grinding does not seem justified for these mixtures since no significant gains in strength were obtained when using high amounts of very fine fillers.

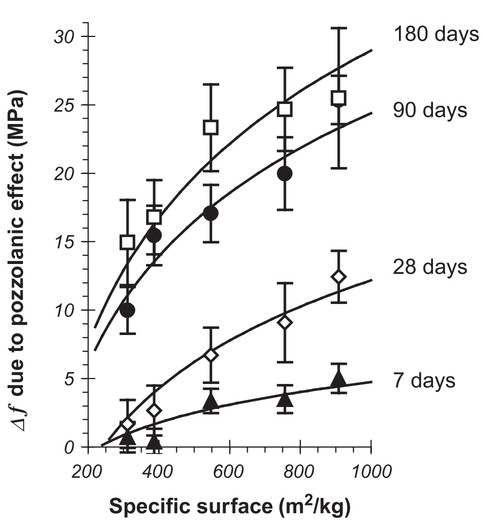


Fig. 15. Increase in strength (Δf) due to pozzolanic effect of mortars containing 25% of fly ashes (FAC, FACx and FAA) in cement replacement.

In the case of pozzolanic admixtures (fly ash):

– the shapes of isostrength curves evolved significantly between 1 and 180 days due to pozzolanic reaction, which was mainly effective after 28 days. As expected, the efficiency of fly ash increased significantly with time, which could be helpful in various ways:
  For a given fineness and replacement rate, strength increased significantly with time: 25% of 900 m^2/kg fly ash led to less than 95% of reference strength at 1 day, while it led to more than 110% and 130% at 28 days and 6 months, respectively.
  For a given replacement rate (e.g. 25%), a high specific surface is necessary (greater than 900 m^2/kg) to preserve the strength of the reference at 1 day. This required fineness decreased over time: for 25% of fly ash, 600 m^2/kg at 28 days and 300 m^2/kg at 6 months.
  For a given fineness, (e.g. 900 m^2/kg), increasing parts (with time) of fly ash can be used in order to maintain the strength of the reference mortar: 20% at 1 day, 35% at 28 days and more than 50% at 6 months.
– between 1 and 180 days, the isostrength curves progressed from oblique to horizontal lines, the latter ones indicating that for a given specific surface, high compressive strength can be obtained for a large range of replacement rates.
– the closeness of isostrength lines revealed a significant effect of fineness on mortar strength. Thus, fly ash grinding could be useful since significant gains in strength are obtained from the use of fine reactive particles.

5. Conclusion

This paper presents the results of more than 2000 compressive strength measurements between 1 day and 6 months on mortars containing up to 75% of inert and

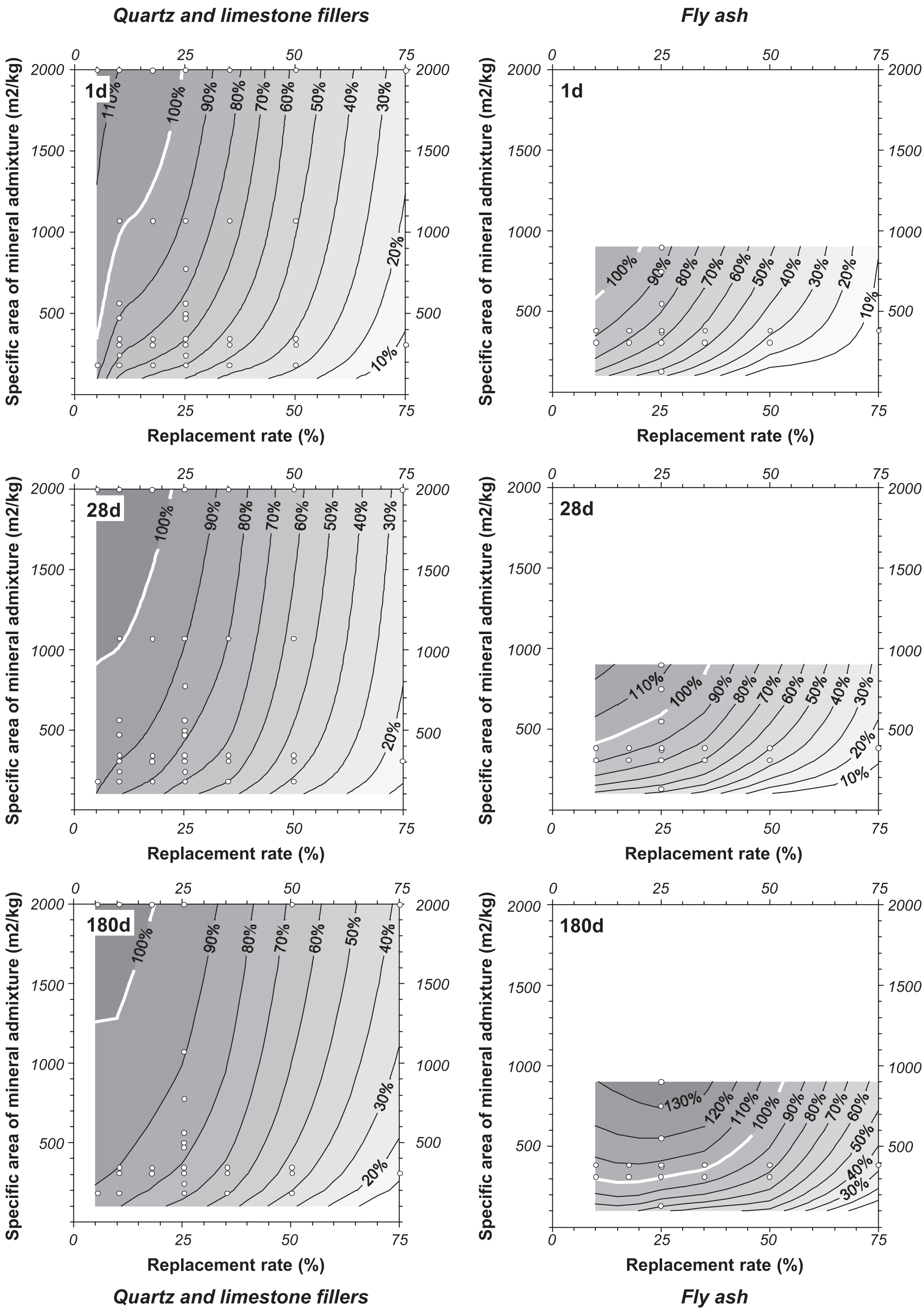


Fig. 16. Isostrength curves of mortars at 1, 28 and 180 days, expressed as fractions of the strengths of a reference admixture-free mortar, obtained when inert and pozzolanic admixtures of different fineness are used at several replacement rates. (white dots=experimental points)

pozzolanic admixtures. One of the authors' objectives was to maintain strict control of the experimental conditions, so as to have comparable compressive strength results of mortars with different kinds of mineral admixtures (i.e. quartz, limestone and fly ash).

The statistical analysis of the data showed that standard deviation increased with compressive strength, meaning that uncertainty was greater for mortars with high strengths.

The analysis of the experimental results highlighted the effect of nature, amount and fineness of mineral admixtures on the compressive strength of mortars:

– It was shown that for short hydration times, the nature of the mineral admixture was not a significant parameter, since mortars containing the same amounts of crushed quartz, limestone filler and fly ash of equivalent fineness presented similar strengths.
– It was confirmed that strength increased with the fineness of mineral admixtures. In the case of inert mineral admixtures, this increase in strength cannot be explained by the filler effect, since neither density nor air content varies significantly for these mortars. Hence, it was concluded that this increase is due to the physical effect of heterogeneous nucleation.
– The excess in strength due to the pozzolanic activity of fly ash was quantified from the difference in strength between mortars containing the same proportions of inert and pozzolanic admixtures with the same fineness. Pozzolanic activity led to a maximum excess of compressive strength when the replacement rate was near 35% to 40%.

The forthcoming part of this work (Fig. 1) will be devoted to quantitative analyses of the experimental results by the separation of the physical effects of mineral admixtures, and by the development of an empirical model comparable to the model developed earlier from calorimetric results [2]. This model will also include the use of an efficiency function depending only on the amount of admixture used.

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