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Mineral admixtures in mortars Quantification of the physical effects of inert materials on short-term hydration

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Abstract

This work is the second 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. The first part presented the separation of the different physical effects responsible for changes in cement hydration when chemically inert quartz powders are used in mortars. This second part describes the development of an empirical model, based on semiadiabatic calorimetry measurements, which leads to the quantification of the enhancement of cement hydration due to the heterogeneous nucleation effect at short hydration times. Experimental results show that not all the admixture particles participate in the heterogeneous nucleation process. Consequently, the concept of efficient surface S_{eff} is introduced in the model. S_{eff} is the total admixture surface S (m^2 of mineral admixture/kg of cement) weighted by a function $\xi(p)$. The efficiency function $\xi(p)$ depends only on the replacement rate p and is independent of time, fineness and type of mineral admixture used. It decreases from 1 to 0: Low replacement rates give an efficiency value near 1, which means that all admixture particles enhance the hydration process. An efficiency value near 0 is obtained for high replacement rates, which indicates that, from the hydration point of view, an excess of inert powder does not lead to an increase in the amount of hydrates compared with the reference mortar without mineral admixture. The empirical model, which is mainly related to the specific surface area of the admixtures, quantifies the variation of the degree of hydration induced by the use of inert mineral admixtures. One application of the model, coupled with Powers' law, is the prediction of the short-term compressive strength of mortars.

Keywords: Calorimetry; Degree of hydration; Heterogeneous nucleation; Supplementary cementing materials; Specific surface area

1. Introduction

The work presented here is the second part of an overall project, the aim of which is to develop mix design rules for concrete containing different kinds of mineral admixtures. This purpose is achieved by the application of a global and phenomenological approach, which allows us to propose an empirical model that can be used for the evaluation of physical and chemical effects of mineral admixtures in cementitious materials. The term "global approach" means that physicochemical interpretations of mechanisms and microstructural analysis are intentionally omitted to develop empirical relations between macroscopic properties and the basic characteristics of mineral admixtures.

The different phases of the overall project are recalled in Fig. 1. In the first part [1], it was confirmed that an inert mineral admixture, like quartz powder, enhanced the short-term hydration of cement. This enhancement was due to two opposing 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 proposed for these effects.

This analysis allows us to develop, in this second part, an empirical model to quantify the amount of cement hydrated when inert mineral admixtures are used as cement replacement in mortars. This empirical model can be used to predict the degree of hydration and can be extended, in some cases, to the prediction of short-term compressive strength of mortars. The third and fourth parts will involve the development of the empirical model from compressive strength tests up to 6 months. The final part will take into account the effect of pozzolanic admixtures in compressive strength evolution.

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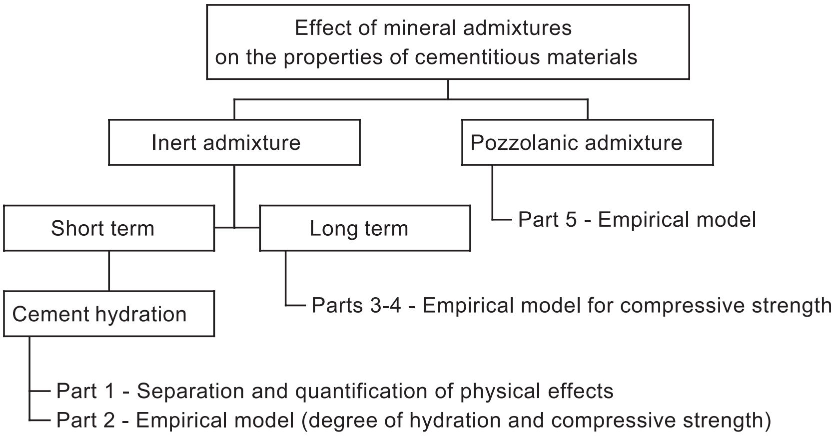


Fig. 1. Phases of the overall project.

This paper presents the second stage of the project. It consists of the quantification, by the means of an empirical model, of the different physical effects responsible for the modification of cement hydration when chemically inert mineral admixtures are used in mortars. The paper includes the following:

- the development of an empirical model that leads to the quantification of the enhancement of hydrated cement due to heterogeneous nucleation effects;
- the presentation of a relationship that predicts the degree of hydration depending on the replacement rate and fineness of the mineral admixture. The prediction is generalized to other mineral admixtures and cement;
- the extension of the empirical model to predict the compressive strength of mortars.

2. Materials and experimental methods

The binder (C1) was a standard OPC (Table 1), CEM I 42,5R, according to French Standard NF P15-301, with a specific surface (Blaine) of 280 m^2/kg (C1).

Three kinds of mineral admixtures were used: crushed quartz, limestone fillers and fly ashes (Table 2). Eight crushed quartz were chosen to study a large range of fineness. They were characterized independently of their fineness by angular shape, a relative density of 2.65 and a crystallized silica content above 99%. This last property allowed us to assume that this material was chemically inert; i.e. it did not react the with the hydrated phases of cement. The finest powders were named by their mean diameter, expressed in μm: Q61, Q35, Q24, Q14, Q11, Q4 and Q2. The coarsest quartz powder, denoted as the reference admixture (Q_{Ref}), had a mean diameter of 215 μm, a specific surface S_S (Blaine) of 23 m^2/kg and a narrow particle size distribution. These characteristics gave this powder a very weak influence on cement hydration, whatever the replacement rate of cement used [1].

Three finenesses of limestone fillers were used (Table 2): 346 (LF19), 497 (LF8) and 782 m^2/kg (LF3). Limestone is not chemically inert because it reacts with C_3A and C_4AF to form carbo-aluminates [2,3]. However, not all researchers agree about the consequences of this reaction on the hydration and compressive strength of cementitious materials [4].

Table 1
Chemical and mineralogical composition of cement C1 and fly ashes (FAC and FAA)

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

Table 2
Physical properties of mineral admixtures

Name	Mean diameter (μm)	Specific surface, S_S (m^2/kg)	Density	Name	Mean diameter (μm)	Specific surface S_S (m^2/kg)	Density
Quartz				*Fly ashes*			
Q_{Ref}	215	23	2.65	FAA	37	312	2.10
Q61	61	187		FAC	24	384	2.20
Q35	35	257		FAC11	11	547	2.40
Q24	24	315		FAC7	7	756	2.54
Q14	14	474		FAC5	5	909	2.60
Q11	11	565					
Q4	4	1070					
Q2	2	2000					
Limestone filler							
LF19	19	346	2.70				
LF8	8	497					
LF3	3	782					

Two F-class fly ashes were also studied (Table 2). They differed by their fineness (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 [5]. To study the effect of the fineness of fly ash on cement hydration, fly ash FAC was ground with a rod grinder to three levels of fineness: 547 (FAC11), 756 (FAC7) and 909 m^2/kg (FAC5).

In all cases, 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, but easier to handle than concrete regarding the large experimental program. The reference mix without admixture, designed according to French standard NF EN 196-1, was composed of three parts by mass 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 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_0). Replacement rates were 10%, 25%, 50% and 75%.

The mix design parameters conformed to the relationship in Eq. (1):

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

where C_0 and C are the mass of cement in the reference and other mixes, respectively, A is the mass of mineral admixture, W is the mass of water and p is the replacement rate of cement by a mineral admixture. Organic admixtures were not used in this study.

Two indicators were chosen to quantify the progress of hydration reactions: the "global degree of hydration," α (Eq. 2), and the relative amount of hydrated cement $C_{\mathrm{h}\%}$, which is related to the mass of hydrated cement C_{h} (Eq. 3).

$$\alpha = \frac{C_{\mathrm{h}}}{C} = \frac{C_{\mathrm{h}}}{C_0\cdot(1-p)} \qquad (2)$$

$$C_{\mathrm{h}\%} = \frac{C_{\mathrm{h}}}{C_0} = \frac{C_{\mathrm{h}}}{C+A} = \alpha\cdot(1-p) \qquad (3)$$

The degree of hydration was measured by semiadiabatic calorimetry using a Langavant calorimeter (NF P 15-436). Then, it was defined as the ratio of heat evolved $Q(t)$ at time t to the total (and theoretical) heat of hydration of the cement Q_∞ (450 J/g for cement C1; [1]). Tests were limited to 48 h to minimize the uncertainties on heat evolved when long-term heating decreased. To compare the progress of reaction between mortars having similar degrees of maturity, the experimental results were corrected using the Arrhenius law to take into account the thermoactivation of the hydration of cement [1,6,7].

3. Previous results

Fig. 2 summarizes the variation of the degree of hydration α at 1 and 2 days, when cement is replaced by increasing proportions of mineral admixtures Q2, Q4, Q24 and Q61. It can be seen that the degree of hydration increases with the quartz powder fineness and replacement rate, which highlights the enhancement effect of mineral admixtures on the hydration of cement [1].

It has been previously shown [1] that the enhancement of hydration (degree of hydration and amount of hydrated cement) is the consequence of two opposing 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.

Assuming that these effects are additive, the amount of hydrated cement in a mortar containing p% of inert powder ($C_{\mathrm{h}p\%}$) is given by Eq. (4).

$$C_{\mathrm{h}p\%(\mathrm{admixture})} = C_{\mathrm{h\ ref}\%(\mathrm{dilution})} + \Delta C_{\mathrm{h}\varphi\%(\mathrm{nucleation})} \qquad (4)$$

Where $C_{\mathrm{href}\%}$ is the amount of hydrated cement considering the dilution effect and $\Delta C_{\mathrm{h}\varphi\%}$ is the excess of hydrated cement coming from the heterogeneous nucleation effect. The dilution effect of cement is deduced from Eq. (3), considering α to be independent of p. It can also be obtained by using the coarse mineral admixture Q_{ref} [1]. The heterogeneous nucleation effect is calculated from Eq. (4) by the difference between $C_{\mathrm{h}p\%}$ and $C_{\mathrm{href}\%}$, both values measured by calorimetry (Fig. 3). The excess of

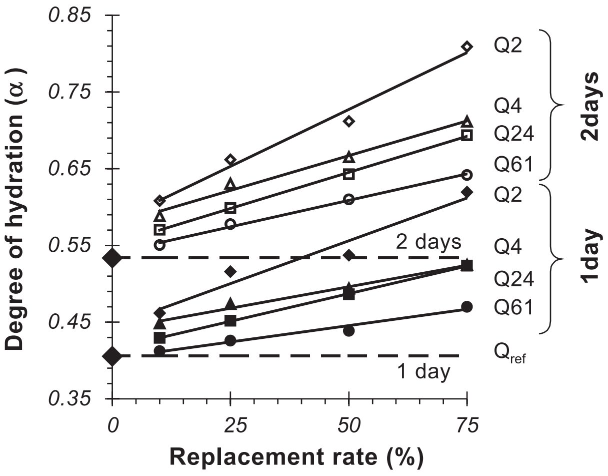


Fig. 2. Degree of hydration of mortars at 1 and 2 days vs. replacement rate of cement by mineral admixture Q2, Q4, Q24, Q61 and Q_{Ref} [1].

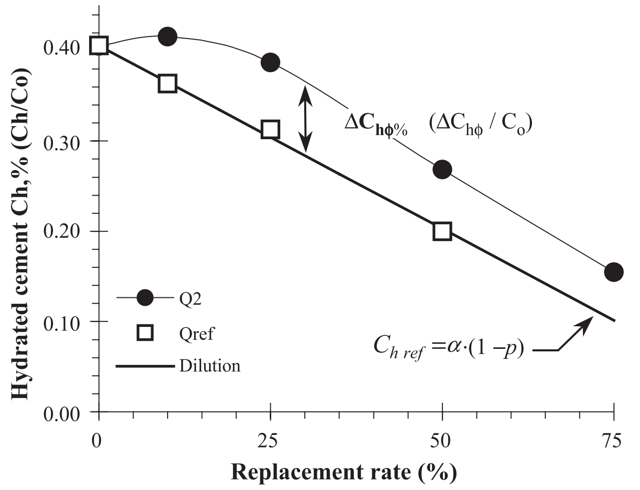


Fig. 3. Amount of hydrated cement ($C_{h\%}$) in mortars containing mineral admixtures Q_{ref} and Q2. Comparison with the theoretical curve (Eq. (3)) considering the dilution effect. Highlight of the excess of hydrated cement $\Delta C_{h\varphi\%}$.

hydrated cement due to fine mineral admixtures is quantified in Fig. 4.

4. Development of an empirical relation

It has been shown that the excess of hydrated cement due to heterogeneous nucleation depends on the fineness of the mineral admixtures and their content in mortar mixes [1].

The aim of this section is to develop a relation leading to a generalization of the effect of fine inert materials on the increase of the amount of hydrated cement due to heterogeneous nucleation. The empirical model developed will then be used to predict the effect of other mineral admixtures on the degree of hydration and compressive strength of mortars.

4.1. Surface of mineral admixture in mortars

The initial approach consisted in combining the two main parameters S_S and p to define the total surface S (per unit mass of cement) of the mineral admixture in the mortar (Eq. 5):

$$S = \frac{S_S \cdot A}{C} = \frac{S_S \cdot pC_0}{(1-p)C_0} = S_S \frac{p}{1-p}\ [\text{m}^2 \text{ of mineral admixture/kg of cement}] \tag{5}$$

Where A, C and C_0 are the mass of mineral admixture, cement and cement in reference mix, respectively, S_s is the specific surface (m^2/kg) of the mineral admixture and p is the replacement rate.

Fig. 5 presents the excess of hydrated cement $\Delta C_{h\varphi\%}$ for different admixture surface S in mortars, at 24 and 48 h, for all replacement rates (10%, 25%, 50% and 75%) and for quartz Q2, Q4, Q24 and Q61. It can be seen that the experimental points $\{S, \Delta C_{h\varphi\%}\}$ do not lie on one single curve but are disposed on individual curves characterized by the replacement rate p. Hence, the effect of mineral admixtures on heterogeneous nucleation does not only depend on the total admixture surface S. This parameter does not meet the stated objective of developing a single generalized relation for the effect of inert powders on the increase of hydration.

4.2. Efficiency of mineral admixtures

For a given mineral admixture, the excess of hydrated cement depends on the amount of admixture: The greater the quantity of admixture used, the smaller the increase in the amount of hydrates due to heterogeneous nucleation.

One possible physical interpretation of these results is to suppose that a particle of admixture influences the hydration kinetics of a cement grain only if the particles are close enough to interact one with another. When the amount of mineral admixture is small, the quartz particles have a higher probability of being near one or many cement grains. Of course, when the amount of mineral admixture increases, this probability decreases because some quartz particles can be isolated from cement grains. In this case, only a small fraction of the mineral admixture is efficient in the hetero-

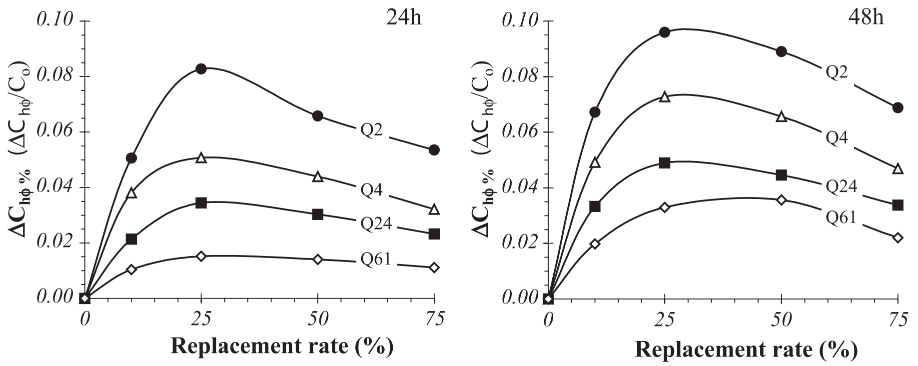


Fig. 4. Excess of hydrated cement $\Delta C_{h\varphi\%}(\Delta C_{h\varphi}/C_o)$ at 24 and 48 h of mortars containing increasing proportions of mineral admixtures Q2, Q4, Q24 and Q61.

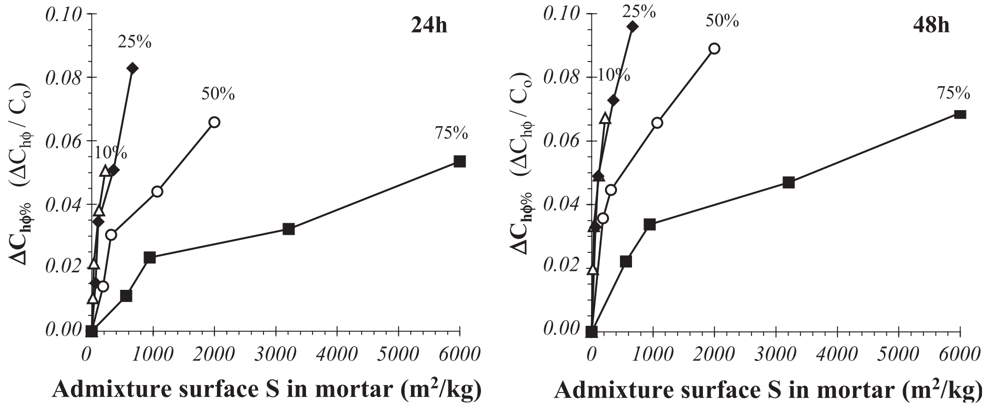


Fig. 5. Excess of hydrated cement $\Delta C_{h\varphi\%}(\Delta C_{h\varphi}/C_o)$ at 24 and 48 h vs. mineral admixture surface area S in mortars.

geneous nucleation process by supplying mineral surfaces on which hydrates can precipitate.

The previous results lead us to expect the existence of an efficiency function, indicating that for a given surface of admixture, a small amount of inert powder has an optimum efficiency and leads to the hydration of a large amount of cement by a germination process, while the use of a large amount of inert powder has a limited effect. Hence, this efficiency function must reach maximum values for low replacement rates and tend to 0 for high replacement rates.

Considering these remarks, the quantification of the efficiency of an inert powder can be obtained by supposing that the efficient surface S_{eff} of a mineral admixture influencing the hydration process is equal to the total admixture surface S weighted by a function $\xi(p)$, only depending on the replacement rate p (Eq. 6):

$$\begin{aligned} S_{\text{eff}} &= S \times \xi(p) \\ &= S_S \frac{p}{1-p} \times \xi(p) \text{ [expressed per unit mass of cement]} \end{aligned} \qquad (6)$$

The values of the efficiency function $\xi(p)$ were calculated in such a way that the overall experimental points $\{S_{\text{eff}}, \Delta C_{h\varphi\%}\}$ fitted on a single curve. The details of the calculations are reported elsewhere [5]. The efficiency function $\xi(p)$, which depends only on the replacement rate p, is given in Fig. 6. It should be noted that the efficiency functions calculated from the results at 24 and 48 h are almost the same. It can be concluded that $\xi(p)$ is independent of time. Moreover, it will be shown that this function is also independent of the nature and fineness of the cement and mineral admixture used.

$\xi(p)$ is near 1 for low replacement rates and tends to 0 for high replacement rates:

- an efficiency near 1 means that all admixture particles enhance the hydration process of cement;
- an efficiency near 0 indicates that, from the hydration point of view, the use of an inert powder does not lead to an increase in the amount of hydrates compared with the reference mortar without mineral admixture. Practically, for very high replacement rates, most inert particles do not influence the hydration reactions of cement, and the overall increase in hydrated cement remains negligible.

According to Eq. (6), the efficient surface of a mineral admixture tends to 0 in three cases: when the replacement rate is near 0 ($p \rightarrow 0$) or near 100% ($\xi(p) \rightarrow 0$), or for coarse powders for which the specific surfaces S_S are very low.

The application of the efficiency concept to the experimental points is given in Fig. 7. The excess of hydrated cement as a function of the efficient surface is characterized by two single curves and only depends on the age of the mortar. The enhancement of hydration is negligible when the efficient surface is near 0, corresponding to the case for which the hydration of mortars with and without mineral admixtures are the same. It can be seen from Fig. 7 that the most significant excesses of hydration are obtained for efficient surfaces near 500 m^2/kg, corresponding to the finest admixture (Q2) and for the replacement rate of 25%.

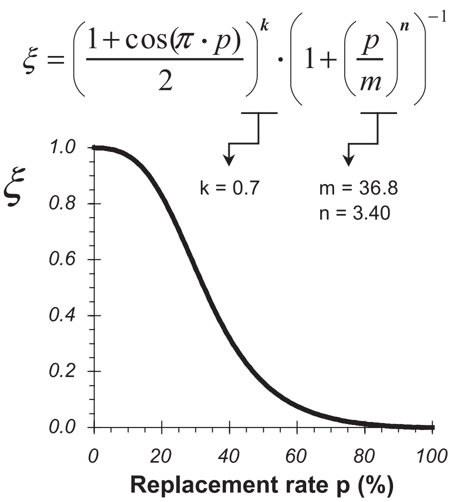


Fig. 6. Efficiency function $\xi(p)$, which is independent of S_S.

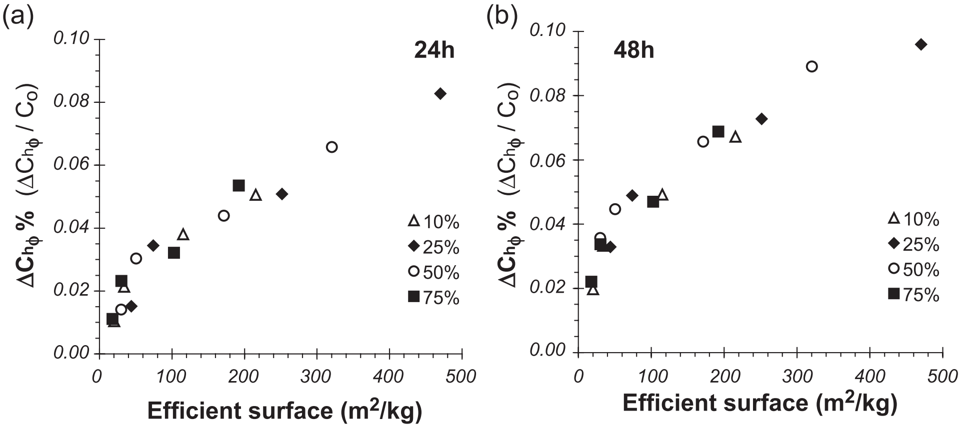


Fig. 7. Excess of hydrated cement $\Delta C_{h\varphi\%}(\Delta C_{h\varphi}/C_o)$ at (a) 24 and (b) 48 h vs. efficient surface area of mineral admixtures.

A mathematical relation between the excess of hydrates $\Delta C_{h\varphi\%}$ and the efficient surface S_{eff} can be proposed (Eq. 7), where a, b and c are empirical parameters.

$$\Delta C_{h\varphi\%}(t) = \frac{a}{1\left(\frac{b}{S_{eff}}\right)^{c}} \tag{7}$$

Fig. 8 summarizes the experimental points and the calculated curves at 24 and 48 h and the parameters of Eq. (7) obtained by least square analysis. For the experimental conditions of this study, no time-dependent values of a and b were obtained, while parameter c depended on the time of hydration of the mortars.

5. Utilization of the empirical model: a prediction tool

The empirical model previously developed allows us to propose predictive relations for the effects of inert mineral admixtures on the degree of hydration and on the compressive strength of mortars. These equations are further discussed with respect to the other mineral admixtures.

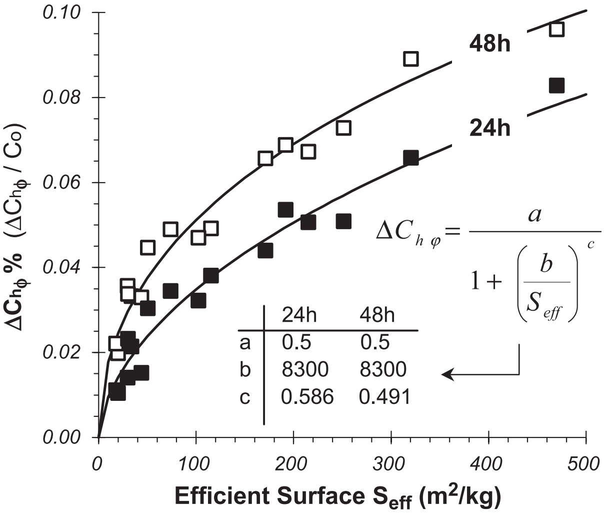


Fig. 8. Excess of hydrated cement $\Delta C_{h\varphi\%}(\Delta C_{h\varphi}/C_o)$ at 24 and 48 h vs. efficient surface area of mineral admixtures. Fitting of the experimental points to a mathematical relation.

5.1. Prediction of degree of hydration

5.1.1. Using the empirical model

Fig. 9 summarizes the steps required to predict the short-term degree of hydration of a mortar containing an inert mineral admixture. The degree of hydration (or the amount of hydrated cement) of a mortar containing p% of an inert mineral admixture is obtained from Eqs. (3) and (4) as the sum of the dilution effect and the heterogeneous nucleation effect.

5.1.1.1. Dilution effect. It has been shown previously [1] that dilution does not modify the degree of hydration of the mortar ($\alpha_{ref} = \alpha_o$). Then, the elements needed for the evaluation of this effect are the degree of hydration of the reference mortar without mineral admixture at time t (α_o) and, possibly, the replacement rate p (for the calculation of the amount of hydrated cement).

5.1.1.2. Heterogeneous nucleation effect. This effect is evaluated by calculating the excess of hydrated cement ($\Delta C_{h\varphi\%}$) using Eq. (7), which depends on the efficient surface S_{eff}. S_{eff} is obtained from the specific surface of the mineral admixture, the replacement rate used in the mortar and the efficiency function $\xi(p)$. The parameters a, b and c, which are used to relate the efficient surface to the excess of hydrated cement, depend on the cement used. Our tests seem to show that the fineness of cement has the greatest effect on their values. Only parameter c varies with the age of the mortars.

5.1.2. Application and discussion

Four levels of experimental data (Table 3) have been defined for the prediction of the degree of hydration of other mortars containing mineral admixtures, following the procedure given in Fig. 9.

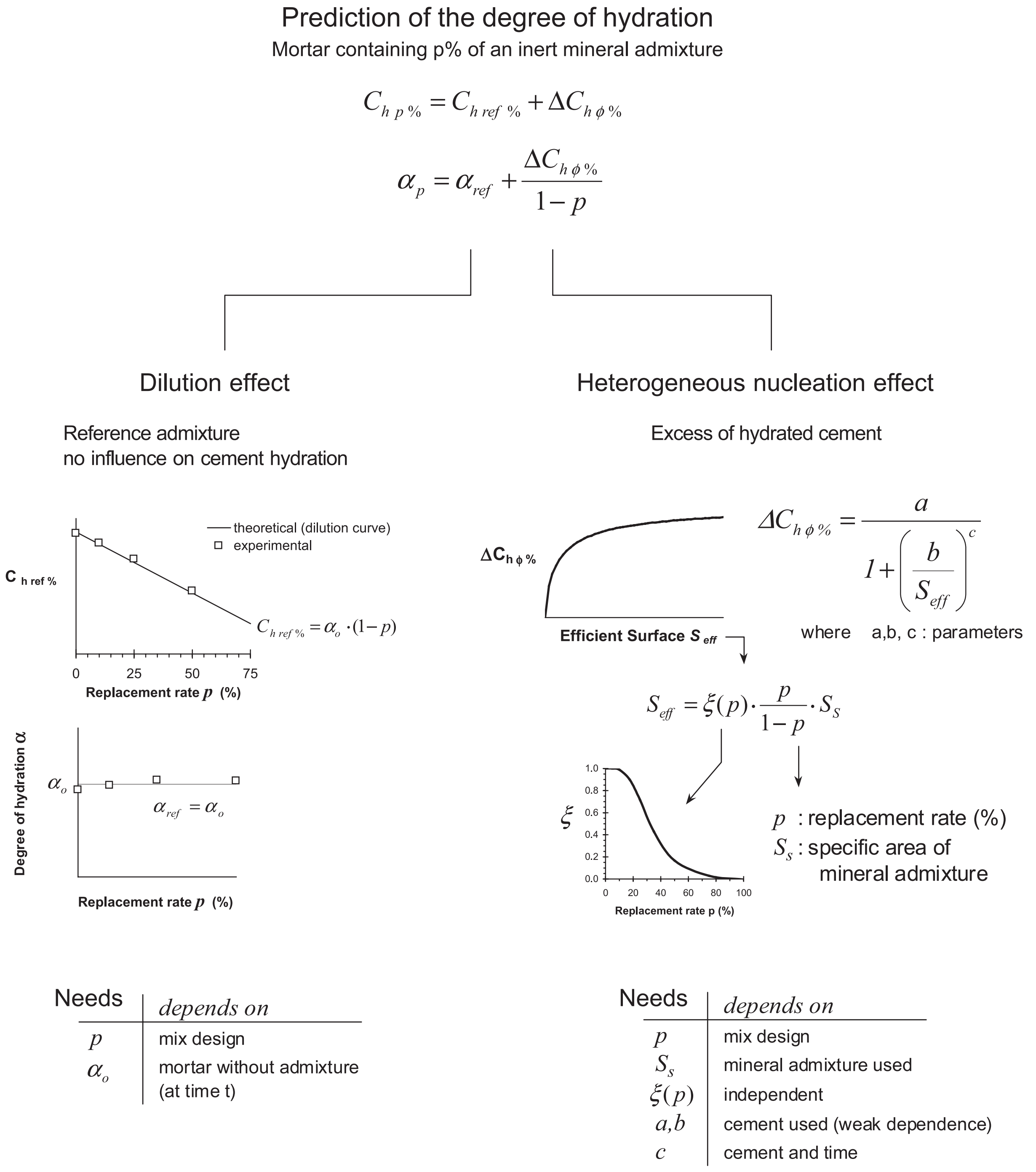


Fig. 9. Schematic representation of the steps to be followed to predict the short-term degree of hydration of a mortar containing an inert mineral admixture.

- Level 1, for which the conditions of prediction are near those used for the development of the empirical model: the same cement (C1) and type of mineral admixture (quartz). The modifications concern only the replacement rate (p) or the fineness of the mineral admixtures.
- Level 2: use of the same cement (C1); the main modifications are the nature and fineness of the mineral admixture (limestone).
- Level 3: use of the same cement (C1); the mineral admixtures are coal fly ashes, the pozzolanic reaction of which should be negligible for short-term applications.
- Level 4: use of data from the literature [8]. The compositions of the mortars are very different from those used for the development of the empirical model; different cements (C2 and C3, described in the literature [8]), mineral admixture (limestone), fineness and replacement rates.

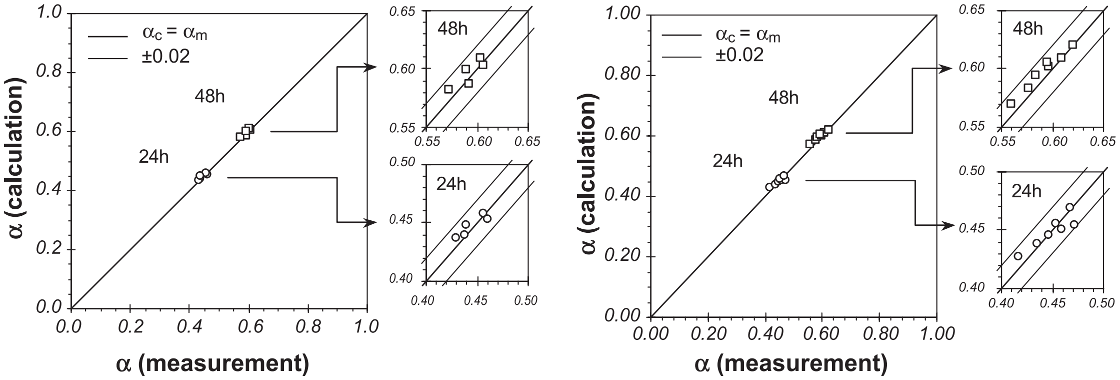
The results of the predicted degrees of hydration, compared with measured values, are shown in Fig. 10a to d.

Table 3
Composition parameters of mortars used to evaluate the ability of the empirical model to predict the short-term degree of hydration of mixtures containing *p*% of a mineral admixture

	Cements	Fineness (m^2/kg)	Types of mineral admixture		Fineness (m^2/kg)	Replacement rates
Level 1	C1	280	Crushed quartz	Q24	315	17.5–35%
				Q11, Q14, Q35	257, 474, 565	25%
Level 2	C1	280	Limestone filler	L19	346	10–17.5–25–35–50%
				L8, L3	497, 782	25%
				FAA	312	25%
Level 3	C1	280	Fly ashes	FAC	384	10–17.5–25–35–50–75%
				FAC11, FAC7, FAC3	547, 756, 909	25%
Level 4	C2	280	Limestone filler	F2	175	10–20%
Ref. [8]	C3	450		F1, F2	550, 175	10–30%

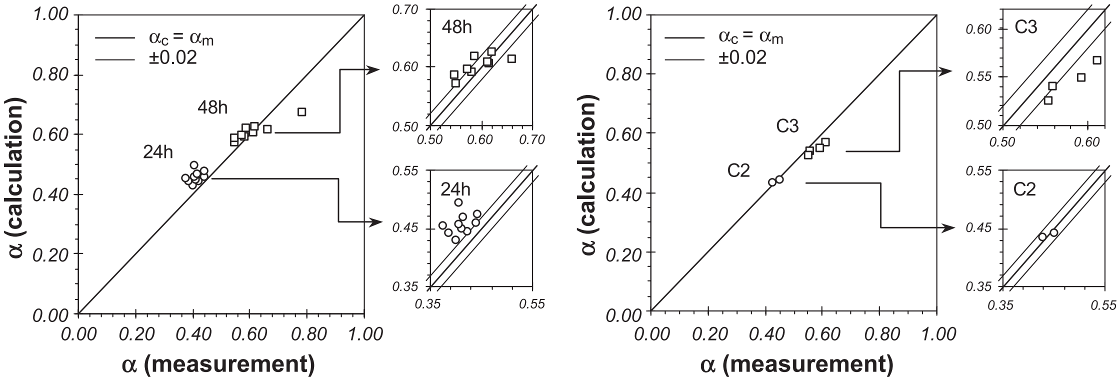
When the cement is the same as the one used for the development of the empirical model, it can be seen that the prediction is within the limits of the 2% error for inert mineral admixtures like quartz powders (Fig. 10a—Level 1) and limestone fillers (Fig. 10b—Level 2).

The attempt to extend the use of the empirical model to fly ashes leads to incorrect results at 24 h (Fig. 10c). The overestimation of the degree of hydration is due to the retarding effect of fly ash before this age. This effect induces a delay in the beginning of the hydration reactions, as shown in Fig. 11, which gives the variation in the degree of hydration with age of mortars containing fly ashes. The retarding effect of fly ashes on cement hydration, which has been reported in the literature [9], appears to be complex and may depend on the chemical and physical natures of the fly ash used. In most cases, fly ash seems to retard the very early hydration (before the induction period) of both C_3S and C_3A. This retardation could be due to aluminate ions or organic matter dissolved from the fly ash into the aqueous phase, delaying the nucleation and crystallization of $Ca(OH)_2$ and C-S-H [10,11]. However, after the induction period, this delay is



(a) Level 1 (cement C1, crushed quartz Q11, Q14, Q24 and Q35)

(b) Level 2 (cement C1, limestone fillers L19, L8 and L3)



(c) Level 3 (cement C1, fly ashes FAA and FAC)

(d) Level 4 (cement C2 and C3, limestone filler, at 24h)

Fig. 10. Comparison between the degrees of hydration measured by calorimetry and calculated using the empirical model.

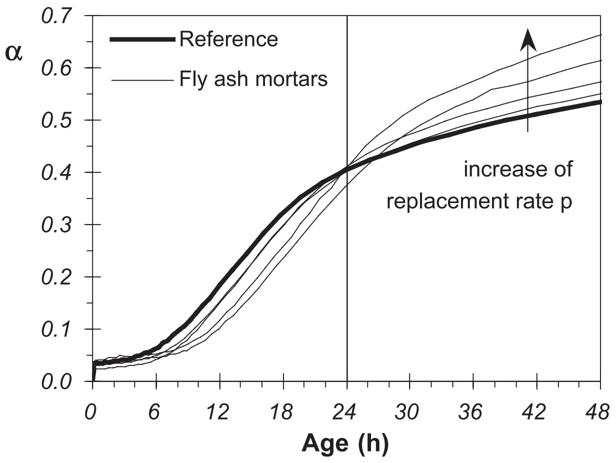


Fig. 11. Variation of the degree of hydration with age of mortars containing fly ashes.

compensated by heterogeneous nucleation [11,12]. Our results confirm this phenomenon between 24 and 48 h (Fig. 11), which explains why the predictions of the degree of hydration are better at 2 days.

Fig. 10d shows the results of the prediction for Level 4 (only available at 24 h) [8]. It can be seen that the prediction of the degree of hydration is within the limits of the 2% error for cement C2, which has the same range of fineness as cement C1 previously used to develop the empirical model.

However, the calculation with cement C3 (450 m^2/kg), which has a greater fineness than cement C1 does, gives incorrect predictions. The underestimation of the degree of hydration means that heterogeneous nucleation has a more significant effect on cement having greater fineness. Hence, the fineness of the cement is an important factor that influences the values of the empirical parameters of Eq. (7). The new parameters, calculated using experimental results with cement C3, are compared with the parameters related to cements C1 and C2 (Table 4).

The empirical model leads to correct predictions of the degree of hydration for:

- Mineral admixtures like quartz and limestone when the cements used have similar properties. More tests using other cements should be performed to assess its effect on the parameters used in the empirical model.
- Fly ash after the 1-day induction period (but before the onset of the pozzolanic reaction).

Table 4
Parameters of Eq. (7), for cements C1, C2 and C3

Cement	Fineness (m^2/kg)	24 h			48 h		
		a	*b*	*c*	*a*	*b*	*c*
C1	290	0.5	8300	0.586	0.5	8300	0.491
C2	280	0.5	8300	0.586	0.5	8300	0.491
C3	450	0.5	8300	0.440	–	–	–

5.2. Prediction of short-term compressive strength

5.2.1. Strength equations at macroscopic level

Several approaches can be used to describe the development of strength during the hydration process at the engineering level. The main concepts are based on the effect of the porosity, the degree of hydration and the volume of the gel (hydrated cement). These three concepts are closely related to one another [13].

The strength–porosity relations are often expressed using the water/cement (W/C) ratio and the air content, as the porosity of concrete is directly related to these parameters. This is the case for the widely used (nonlinear) formulas of Féret [14], Abrams [15], Bolomey [16] and others [17–20], and for more recent relations like those of Atzeni et al. [21], Osbaeck [22], Jambor [23,24], Watson [25] and Popovics [26].

Some authors suggest that the pore shape and the pore size distribution are important factors influencing the compressive strength of cement pastes [27,28], but not all experimental works confirm these views [29–31]. Nevertheless, it seems that there is a general agreement about the importance of capillary porosity on the strength behavior of cement pastes [31,32]. Pores smaller than 200 Å probably do not affect the strength [33,34]. In spite of this, several authors have criticized these relations and point out the limited validity of the concept [26,35].

These models seem difficult to apply within this work because they do not take into account the fineness of mineral admixtures, an important parameter influencing the heterogeneous nucleation effect. As an example, Fig. 12 presents the compressive strength results versus the W/C ratio for quartz Q2, Q4, Q24 and Q61 in comparison with Féret's law, fitted using the reference mortar without mineral admixture. It can be seen that the calculated curve does not lead to a correct prediction of the compressive strengths of mortars containing mineral admixtures. In this case, the only

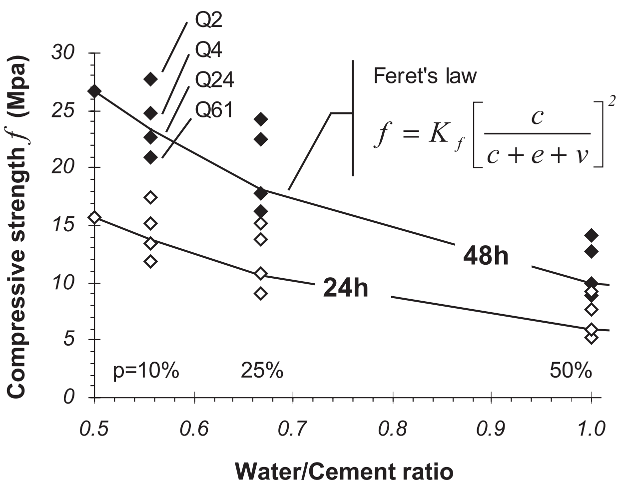


Fig. 12. Compressive strength vs. water/cement ratio for mortars with quartz Q2, Q4, Q24 and Q61 in comparison with Feret's law.

way to consider the presence and fineness of quartz is to include its effect in the coefficient K_f (Fig. 12). Then, it is necessary to calculate as many coefficients as there are admixture finenesses.

Many authors have reported a linear relation between the compressive strength and the degree of hydration (or related variables, e.g., heat of hydration) [36–42], while others found that a cubic or an exponential tendency was more appropriate [13,43,44]. In the range of strengths that are of practical interest (10–60 MPa), both approaches can be used [13].

In most cases, the W/C ratio significantly affects these relations, which is confirmed with our experimental values (Fig. 13), the replacement of p% of cement being equivalent to an increase of W/C. This effect of the water content was to be expected because a lower W/C ratio reduces the distances between cement grains and consequently decreases the degree of hydration required to bridge these distances with hydrated cement. According to some authors, the compressive strength does not depend on the degree of hydration alone [45,46].

Consequently, the degree of hydration is probably not the most pertinent parameter to be related to compressive strength because two mortars having the same degree of hydration do not have the same compressive strength if the initial amounts of cement are different, as is the case when mineral admixtures are used (dilution effect).

To avoid the effect of W/C, it is possible to relate the compressive strength to the amount of hydrated cement (C_h). Fig. 14 shows a single nonlinear relation between f and C_h. This kind of approach using the amount of hydrated cement is similar to the concept of the gel/space ratio, developed by Powers in the forties [47]. This concept and modified versions of it [48–50] have been widely used [33,41,51–53].

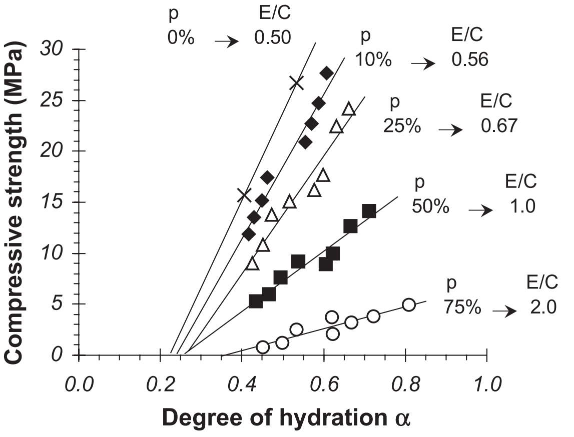


Fig. 13. Compressive strength vs. the degree of hydration of mortars with or without mineral admixtures.

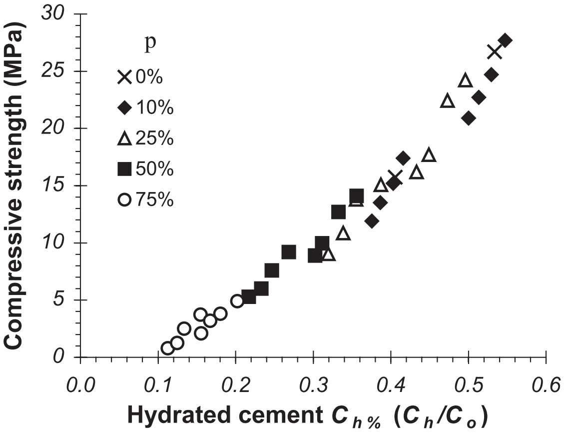


Fig. 14. Compressive strength vs. the amount of hydrated cement in mortars with or without mineral admixtures.

The gel/space ratio is defined as the ratio of the volume of the hydrated cement paste (gel) to the sum of the volumes of the hydrated cement and capillary pores (Eq. 8). Taking v_c as the specific volume of anhydrous cement, α the degree of hydration of cement, w_0 the initial volume of water and c the mass of cement, and since 1 ml of cement produces 2.06 ml of gel [54], the gel volume is $2.06cv_c\alpha$, and the total space available to the gel is $cv_c\alpha + w_0$ [55]. Hence, the gel/space ratio is (Eq. 8):

$$X = \frac{\text{gel volume}}{\text{gel volume} + \text{volume of capillary}} = \frac{2.06 \cdot v_c \cdot \alpha}{v_c \cdot \alpha + \frac{w_0}{c}} \qquad (8)$$

The concept can be modified to take into account the effect of the volume of unhydrated cement [49].

Eq. (9) was suggested by Powers and Brownyard [47] to express the relationship between the cement strength (f) and the gel/space ratio (X):

$$f = F_0 \cdot X^n \qquad (9)$$

Where f_0 is the intrinsic strength of cement gel, or strength at zero capillary porosity, and n is a constant

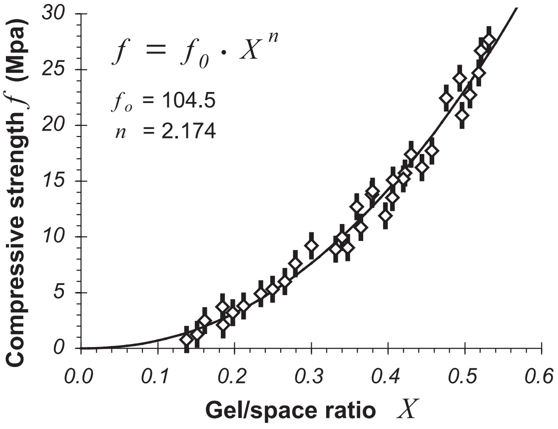


Fig. 15. Experimental values of compressive strength vs. the gel/space ratio X, calculated from the measured degrees of hydration, for 34 points obtained from the reference mortar and mortars with 10%, 25%, 50% and 75% of Q2, Q4, Q24 and Q61, at 24 and 48 h.

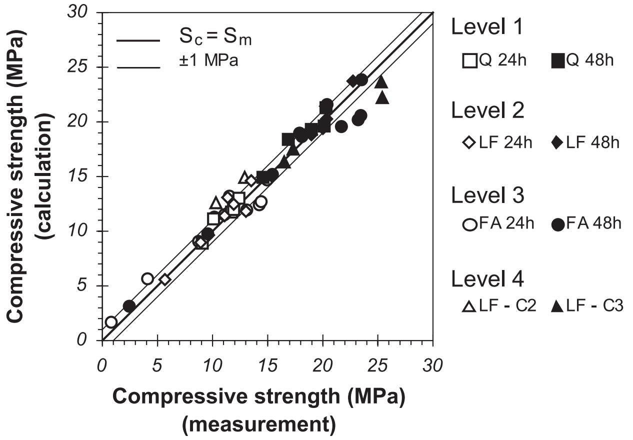


Fig. 16. Comparison between the measured and calculated compressive strengths for the levels of Table 3.

(usually between 2 and 3), depending on the type of cement. The constants can be varied to match the results of different compositions.

Fig. 15 plots the 34 experimental values (reference mortar and mortars with 10%, 25%, 50% and 75% of Q2, Q4, Q24 and Q61, at 24 and 48 h) of compressive strength versus the gel/space ratio X, calculated from the measured degrees of hydration. It can be seen that the fitted curve (Eq. 9) gives a correct approximation of compressive strength versus the gel/space ratio. This equation will be used to predict the compressive strengths of mortars containing mineral admixtures, using the calculated degrees of hydration from the empirical model (Fig. 9).

5.2.2. Application to prediction of compressive strength

The application of Eq. (9) to the prediction of the compressive strengths of the four levels of mortars (Table 3) is given in Fig. 16.

As was the case for the degree of hydration (Fig. 10), the prediction of the compressive strength is quite good for cement C1 because the values are within the limits of the 1-MPa error for inert mineral admixtures like quartz powders and limestone fillers. However, the results with fly ash are more dispersed. Concerning Level 4 (other cement and limestone filler as mineral admixture), better results should be obtained when the parameters from Eq. (9) are calculated to take the type of cement used into account.

6. Conclusion

This paper presented the development of an empirical model, based on semiadiabatic calorimetry measurements, which leads to the quantification of the enhancement of hydrated cement due to the heterogeneous nucleation effect.

An efficiency function $\xi(p)$ is introduced to quantify the effect of mineral admixture on the heterogeneous nucleation process. This function has notable properties: It is independent of time, independent of fineness and independent of the type of mineral admixture. The idea behind the efficient function is in accordance with the initial objective of our work, which was the development of general mix design rules for concrete containing different kinds of mineral admixtures.

The $\xi(p)$ is near 1 for low replacement rates and tends to 0 for high replacement rates: An efficiency near 1 means that all admixture particles enhance the hydration process of cement, while an efficiency near 0 indicates that, from the hydration point of view, the use of an inert powder does not lead to an increase in the amount of hydrates compared with the reference mortar without mineral admixture.

The empirical model developed allows us to quantify the variation of the degree of hydration induced by the use of inert mineral admixtures. The modifications are directly related to the specific surface of the admixtures.

One application of the model is the prediction of the degree of hydration of cement, which coupled with Powers' law, could lead to prediction of the short-term compressive strengths of mortars.

The forthcoming part of this work (Fig. 1) will:

- Deal with long-term action of inert admixtures.
- Focus especially on the compressive strength of mortars.
- Be divided in two parts:
  - Part 3, which will give the results and the qualitative analysis of a large experimental program showing the effect of inert mineral admixtures on compressive strength of mortars.
  - Part 4, which will be dedicated to quantitative analysis of the experimental results by the development of an empirical model comparable to the model reported in this paper.

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