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Efficiency of mineral admixtures in mortars: Quantification of the physical and chemical effects of fine admixtures in relation with compressive strength

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Abstract

This work is the fourth part of an overall project the aim of which was the development of general mix design rules for concrete containing different kinds of mineral admixtures. The two first parts presented the separation and quantification, by means of an empirical model based on semi-adiabatic calorimetry measurements, of the different physical effects responsible for changes in cement hydration (short terms) when chemically inert quartz powders were used in mortars. Part three dealt with an intensive experimental program, presenting and commenting more than 2000 compressive strength measurements. This program concerned 1 day to 6 months old mortars containing up to 75% of inert and pozzolanic admixtures. All these compressive strength results are analyzed in this fourth part and the influence of three effects, namely dilution, heterogeneous nucleation and the pozzolanic effect, are discriminated and quantitatively evaluated. An efficiency concept is proposed in order to take into account the effect of mineral admixture in mortars from both the physical and chemical points of view. It uses an *efficiency function* $\xi(p)$ that has notable properties: it is independent of time, independent of fineness and independent of the type of mineral admixture.

Keywords: Heterogeneous nucleation; Fineness; Supplementary cementing materials; Specific surface area; Compressive strength; Fly ash; Limestone filler; Crushed quartz

1. Introduction

Many pozzolanic and chemically inert mineral admixtures have been used and studied over the years and it is well known that they modify the physical and mechanical properties of concrete. In order to understand their effect on the compressive strength of cement-based materials, experiments were carried out on mortars containing different kinds of fine materials. The aim of the overall project was to develop mixture proportion rules for cement-based materials containing mineral admixtures. This objective has been 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, in order to highlight the empirical relationships between macroscopic properties and the basic characteristics of mineral admixtures.

The different phases of the project are recalled in Fig. 1. The first two papers [1,2] studied the effect of mineral admixtures on the degree of hydration of cement. A decoupling process was proposed for dilution and heterogeneous nucleation effects [1], followed by the development of an empirical model [2] to quantify the amount of cement hydrated when inert mineral admixtures are used as cement replacement in mortars. Subsequent parts aimed to extend this approach to short- and long-term compressive strengths of mortars.

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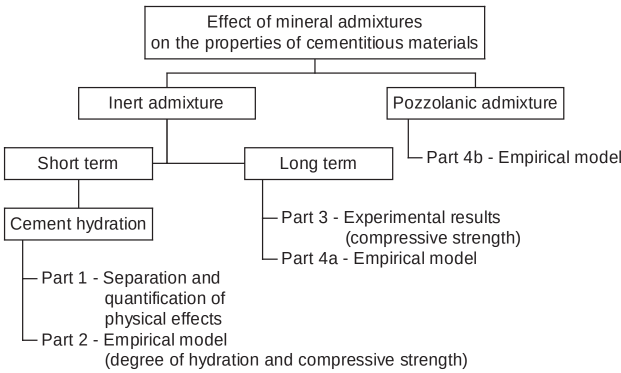

Fig. 1. Phases of the overall project.

So, the third part [3] presented the results of a large experimental program studying the compressive strength up to six months of mortars containing different types, amounts and finenesses of mineral admixtures. It included first order analysis of the results and a decoupling of the pozzolanic activity from the overall effect of the mineral admixture.

In this last part, these compressive strength results are separated into the fractions of strength related to the physical and chemical effects of mineral admixtures. Then, they are used in an empirical model in order to quantify the modification of compressive strength of mortars induced by mineral powders. The main property used is the specific area which, when coupled with an efficiency function, can be used to describe the increase in the compressive strength of mortars resulting from the physical and chemical effects of mineral admixtures.

2. Materials, methods and previous results

The materials and methods, which were exposed in a previous paper [3], are summarized in Table 1.

All compressive strength results have been reported in detail earlier [3]. These results highlight the significant effect of fineness and amount of mineral admixtures on strength, as summarized in Fig. 2.

It has been shown that:

- For short hydration times, the nature of the mineral admixture is not a significant parameter, since mortars containing the same amounts of crushed quartz, limestone filler and fly ash of equivalent finenesses present similar strengths.
- Strength increases 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 vary significantly for these mortars. Hence, it was concluded that this increase is due to the physical effect of heterogeneous nucleation.
- The increase 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.

The present paper proposes a quantitative analysis of the chemical and physical effects responsible for the modification of compressive strength of mortars containing mineral admixtures.

3. Quantitative analysis of the effects of mineral admixtures on compressive strength

3.1. Decoupling the effects of mineral admixtures on compressive strength

By analogy with the results of earlier works concerning the degree of hydration [1,2], the compressive strength of a mortar containing p% of a mineral admixture (f_p) is represented by the combination of different effects, each of them playing an additive role, as shown in Fig. 3.

These three effects can be quantified as fractions of strength related to the use of the mineral admixture:

- $f_{(dilution)}$ is the strength proportional to the amount of cement in the mixture ($C = C_0(100\% - p)$), without

Table 1
Materials, mixtures and methods

Materials		
Cements	OPC (NF P15-301)	C1: CEM I 42,5R, 280 m^2/kg (Blaine)
		C2: CEM I 52,5R, 400 m^2/kg (Blaine)
Aggregates	Normalized quartz sand (NF EN 196-1), particle size distribution: 0.08–2 mm	
Mineral admixtures	Crushed quartz	Q61 (187 m^2/kg), Q35 (257), Q24 (315), Q14 (474), Q11 (565), Q4 (1070), Q2 (2000)
	Limestone fillers	L19 (346 m^2/kg), L8 (497), L3 (782)
	Fly ash	FAC (384 m^2/kg), FAC11 (547), FAC7 (756), FAC5 (909), FAA (312)
Mixtures		
NF EN 196-1	Sand : cement : water (mass): 3 : 1 : 1/2	
Replacement rates (p)	5%, 10%, 17.5%, 25%, 35%, 50%, 75%	
Amount of cement (C)	$C = C_0$ (100% $- p$), where C_0 is the mass of cement in a reference mixture without mineral admixture	
Methods	Mixing, casting (4 × 4 × 16 cm prisms), storage (20 °C water) and compressive strength tests performed strictly in accordance with French Standard NF EN 196-1	
	Hydration times: 1, 2, 7, 14, 28, 90 and 180 days	

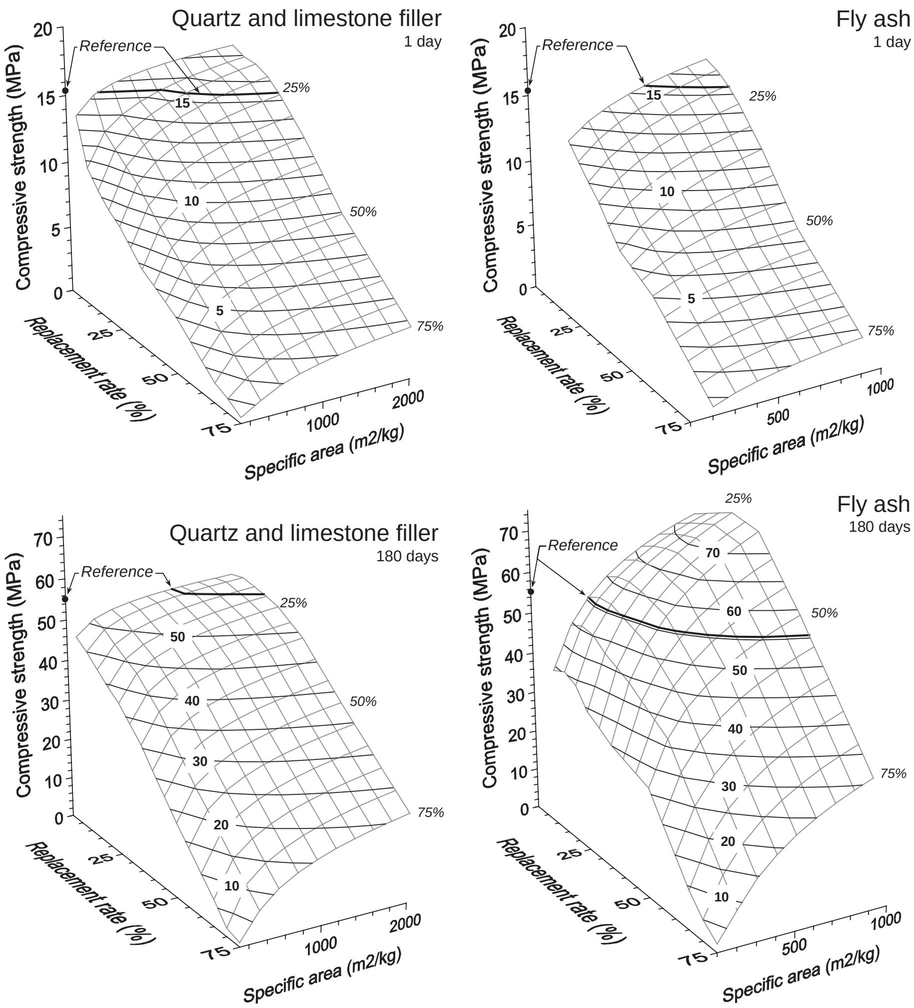

Fig. 2. Compressive strength at 1 and 180 days of mortars containing increasing proportions of inert (quartz and limestone) and pozzolanic (fly ash) mineral admixtures having different finenesses.

considering any physical or chemical effect of mineral admixture, except dilution;

- $\Delta f_{\varphi(physical)}$ is the increase in strength due to the physical effect of the mineral admixture. Previous work has shown that heterogeneous nucleation, which becomes significant for fine mineral admixtures [4], is probably responsible of a large part of the increase of strength [1–3] related to physical effects;
- $\Delta f_{pz(chemical)}$ is the increase in strength related to the pozzolanic reaction.

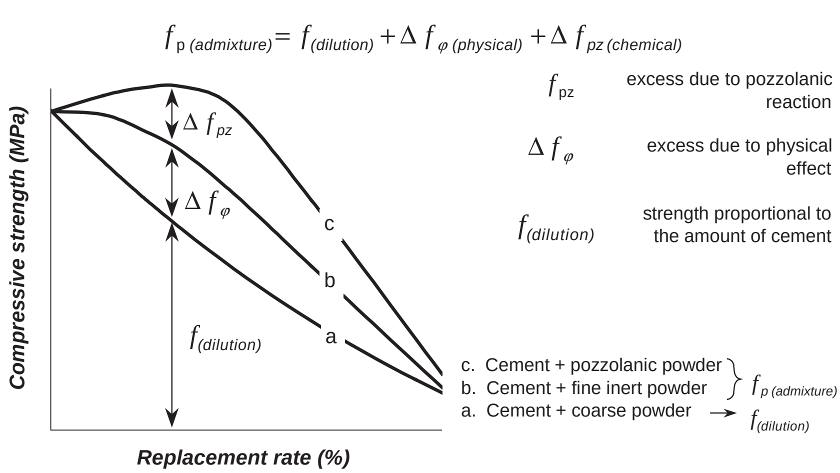

Fig. 3. Decoupling of compressive strength fractions due to physical and chemical effects of mineral admixture.

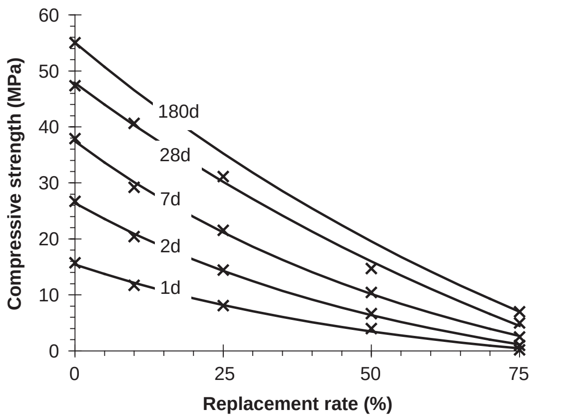

Fig. 4. Q_{ref} curves: Decrease of compressive strength with p, for mortars containing Q_{ref} (results at 14 and 90 days have been omitted in order to lighten the Figure).

The following sections of this paper deal with the quantification of all these terms. The decoupling process consisted in determining the proportions of compressive strength due to dilution ($f_{(dilution)}$), to heterogeneous nucleation (Δf_{φ}) and to pozzolanic (Δf_{pz}) effects (Fig. 3).

3.1.1. Dilution effect

The dilution effect is a consequence of the replacement of a part p of cement by the same quantity of a mineral powder. The increase in the amount of mineral admixture involves a decrease in the amount of cement and consequently an increase in the water/cement ratio. In its turn, less cement implies less hydrated cement and lower compressive strength compared to a reference without mineral admixture.

In order to quantify this effect, it was necessary to use a chemically inert mineral admixture, composed of particles large enough for it to be assumed that heterogeneous nucleation was not significant.

As for the quantification of the degree of hydration in an earlier paper [1], a coarse mineral admixture was used to dilute cement without producing significant surface effects. The powder used was a quartz (Q_{ref}) having a specific area of 23 m^2/kg, one eighth that of the fine Q61 (187 m^2/kg).

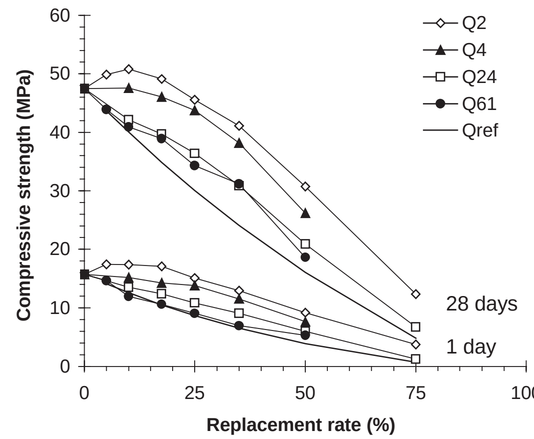

Fig. 6. Compressive strength at 1 and 28 days for mortars containing increasing proportions of mineral admixtures Q2, Q4, Q24 and Q61. Only curves at 1 and 28 days are shown. Comparison with the Q_{ref} curve characterizing the single dilution effect.

According to the literature [4], the mean diameter of Q_{ref} (215 μm) permitted us to presume that this admixture was large enough to exclude any heterogeneous nucleation effects. This assumption was verified with our own results, which showed that the degree of hydration of cement was not modified by Q_{ref} whatever the quantity used in replacement of cement [1,5].

Fig. 4 presents the variation of strength of mortars made with increasing proportions of Q_{ref} for hydration times up to 180 days.

Fig. 5 shows the fit of experimental data with three of the most popular empirical equations for compressive strength: Féret [6], Abrams [7] and Powers and Brownyard [8]. Among them, Powers' law leads to the best fit, even for high replacement.

3.1.2. Physical effects

Two main physical effects are often evoked when mineral admixtures are used in cementitious materials: the filler effect and heterogeneous nucleation.

The filler effect implies a modification of the initial porosity of the mix, and it results in an increase or a

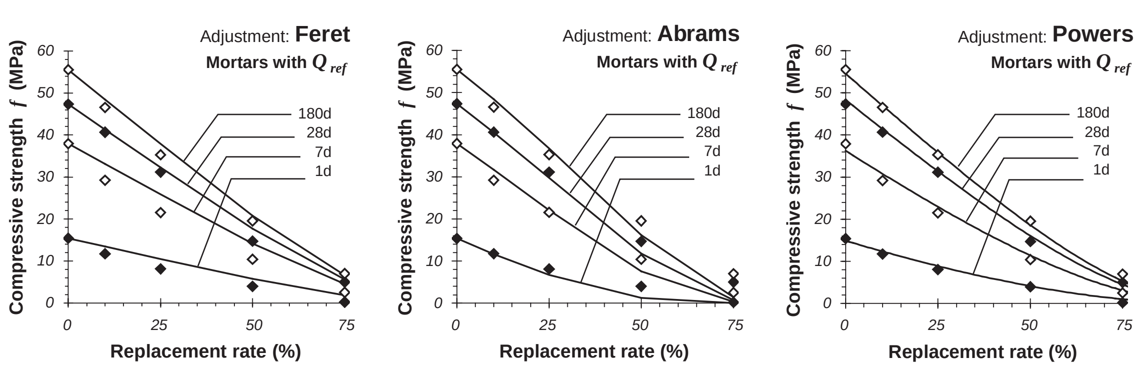

Fig. 5. Fitting of Féret, Abrams and Powers laws to compressive strength results of mortars containing admixture Q_{ref}. Only results at 1, 7, 28 and 180 days are presented.

decrease in the water required to maintain a constant workability. In the present case of a constant amount of water in mortar mixtures, the total initial porosity should be independent of the replacement rate. Measurements of the density and air content of fresh mortar mixtures showed that these properties did not vary significantly for mortars containing inert powders. Thus, it was deduced that the filler effect was not significant, meaning that it cannot explain the increase in strength of the mortars.

Heterogeneous nucleation is a physical process leading to a chemical activation of the hydration of cement and is related to the nucleation of hydrates on foreign mineral particles. Since heterogeneous nucleation leads to an enhancement of cement hydration, its effect at a given time is an increase in the compressive strength. This physical effect depends essentially on the fineness and the amount of the powders used [1–3].

The enhancement effect of inert mineral admixtures (or pozzolanic powders before the onset of the chemical reactions) on cement hydration is often mentioned in the literature from a qualitative point of view for various types of mineral admixtures but its consequences on compressive strength are rarely quantified. In the context of the present program, Δf_φ can be deduced from the difference between f_p and $f_{Q_{\mathrm{ref}}}$ (Eq. (1)), since these values were measured by compressive strength tests.

$$\Delta f_\varphi(p, S_\mathrm{s}, t) = f_p(p, S_\mathrm{s}, t) - f_{\mathrm{Qref}}(p, S_\mathrm{s}, t) \quad (1)$$

Fig. 6 shows compressive strength at 1 and 28 days for mortars containing increasing proportions of crushed quartz

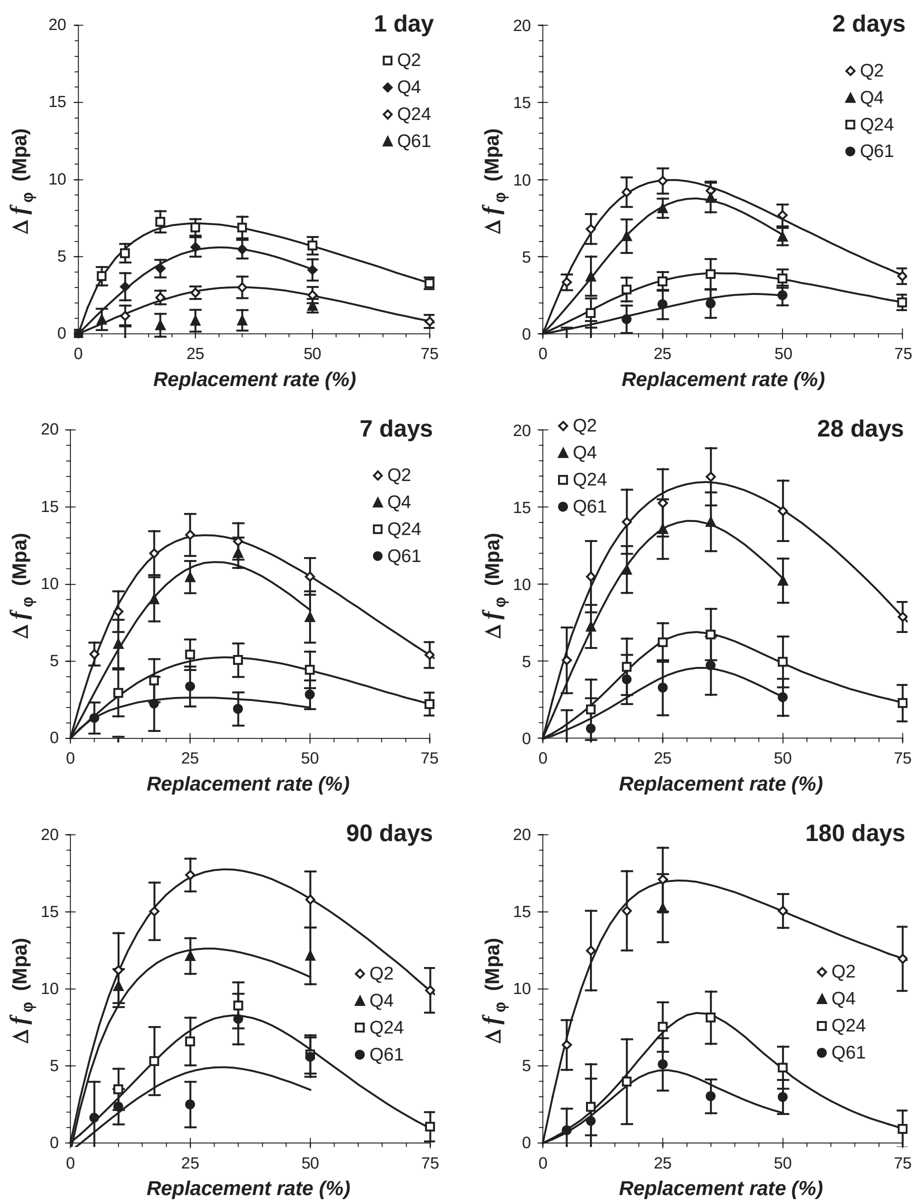

Fig. 7. Increase in compressive strength Δf_φ at 1, 2, 7, 28, 90 and 180 days of mortars containing increasing proportions of mineral admixtures Q2, Q4, Q24 and Q61.

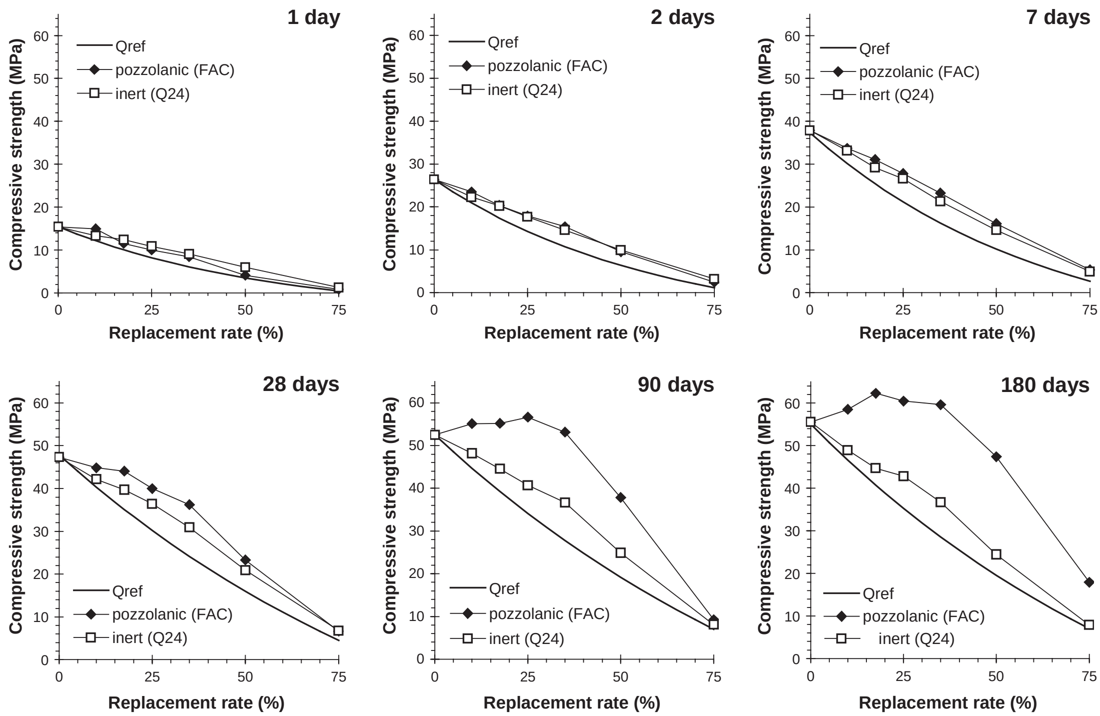

Fig. 8. Compressive strength between 1 and 180 days for mortars containing increasing proportions of mineral admixtures Q24 (inert) and FAC (pozzolanic), both having almost the same fineness. Comparison with the Q_{ref} curve characterizing the dilution effect alone.

Q2, Q4, Q24 and Q61. The comparison of these curves with the Q_{ref} curves characterizing the dilution effect alone highlights the increase in compressive strength due to fine mineral admixtures. Similar results, not presented here, were obtained for other hydration times (2, 7, 14, 90 and 180 days).

The increase in compressive strength is illustrated in Fig. 7. From a qualitative point of view, it can be seen that:

– Δf_{φ} increases with the fineness of the mineral admixture. These experimental results confirm that the greater the specific area, the easier the germination.
– The different curves of Fig. 7 highlight the optimal replacement rate (between 25% and 35%) which does not vary much between 1 and 180 days. The left part of the curves is characteristic of a lack of mineral particles, which leads to an insufficient area available for the precipitation of hydrates. On the other hand, the right part of the curves is characteristic of an excess of mineral particles, which contributes to the dispersion of the cement grains. In this situation, a fraction of the mineral particles are too far from cement particles to serve as nuclei for the hydration process.

3.1.3. Chemical effect

Pozzolanic activity enhances the compressive strength of cement based materials. Its effect is noticed after

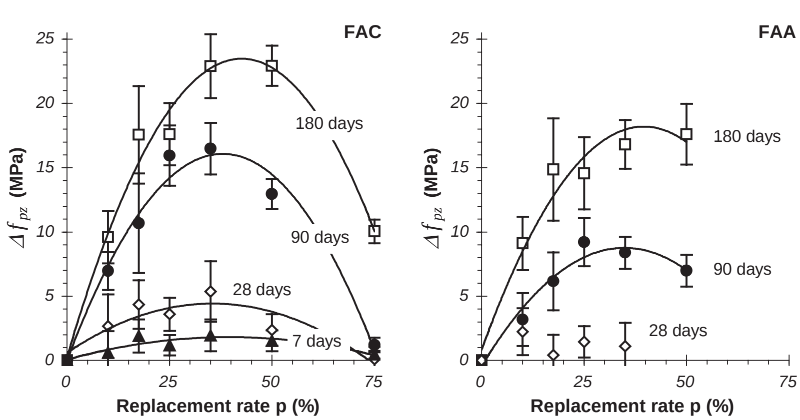

Fig. 9. Increase in strength (Δf_{pz}) due to pozzolanic effect of mortars containing up to 75% of fly ash (FAC or FAA) in cement replacement.

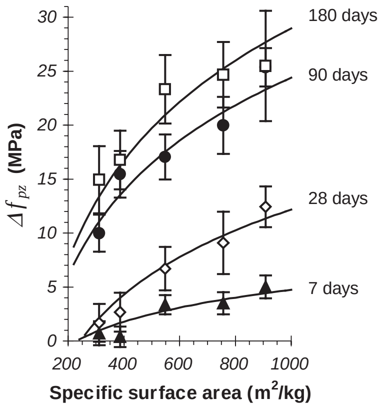

Fig. 10. Increase in strength (Δf_{pz}) versus specific surface area due to pozzolanic effect of mortars containing 25% of five fly ashes (FAC, FACx and FAA) as cement replacement.

periods of a few days (e.g., silica fume) to several months (some fly ash or natural pozzolans), depending principally on the amount and solubility of amorphous silica in the material.

Other chemical activities which modify the hydration kinetics of cement affect compressive strength. This is the case of some chemical elements, known as accelerators (e.g., Cl) or retarders (e.g., Zn [9]). It is generally known that the use of an accelerator gives high early strength but it can also reduce long term compressive strength [10]. These effects may be difficult to quantify, especially when the perturbing elements are found as impurities in admixtures from industrial by-products (e.g., fly ash and silica fume). The effect of minor elements was neglected for this work.

The increase in compressive strength due to pozzolanic activity of fly ash in mortars was evaluated in the precedent paper [3] by comparing their strengths with the strengths of mortars containing chemically inert powder (Fig. 8).

The increase in strength Δf_{pz} due to pozzolanic reaction is deduced from the difference in strength between fly ash mortars f_{FA} and inert quartz mortars f_Q (Eq. (2)). This contribution Δf_{pz} was calculated at the same hydration time t, at the same replacement rate p and at the same fineness S_s of mineral admixture.

$$\Delta f_{pz}(p, S_s, t) = f_{FA}(p, S_s, t) - f_Q(p, S_s, t) \quad (2)$$

Fig. 9 shows the increase in compressive strength due to pozzolanic reaction for FAA and FAC relative to Q24, which has a fineness equivalent to that of the two raw fly ashes. Δf_{pz} became significant after 7 and 28 days for FAC and FAA, respectively, and it increased significantly over time. The curves present maximum values around replacement rates of 35% to 40%. This optimum content of fly ash leads to the highest excess strength due to a pozzolanic effect.

Fig. 10 shows Δf_{pz} for different finenesses of fly ash (five raw and ground admixtures all together). The strength of mortars containing inert materials (quartz) having an equivalent fineness to fly ash was calculated using a logarithmic evolution of data (Fig. 11 of Ref. [3]). The pozzolanic activity calculated using this method is also displayed from 7 days and subsequently it increased to 180 days. Whatever the hydration time, pozzolanic activity increased with the fineness of the fly ash, showing the importance of particle size on the pozzolanic reaction.

3.2. The role of amount and fineness of mineral admixture

After having quantified the increase in strength due to physical and chemical effects, an empirical model is proposed below to improve the understanding of the behavior of mineral admixtures used in mortars. The model is developed using a procedure similar to the one presented in a previous paper dealing with the degree of hydration [2].

The model is based on the assumption that surface effects, related to the fineness of the admixture, are the main phenomena involved in heterogeneous nucleation and pozzolanic reaction. So, the model aims to correlate the increase in strength to specific surface area and quantity of powder, which are identified, as stated earlier, as simple and measurable influencing parameters.

This approach should constitute a generalization of the way of taking into account the effect of inert and pozzolanic

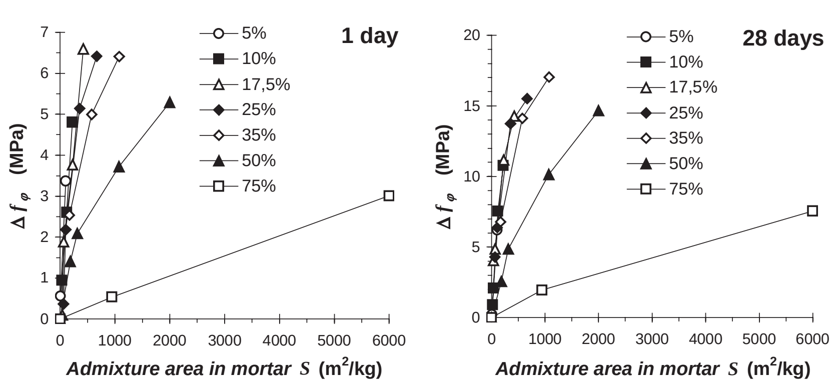

Fig. 11. Increase in compressive strength Δf_{φ} due to quartz powder at 1 and 28 days, as a function of the mineral admixture surface area S in mortars.

powders in mortars, and eventually should lead to the development of mix design rules for cement based materials containing mineral admixtures.

3.2.1. Total surface of contact of mineral admixture in mortars

The simplest approach for taking account of the fineness and amount of inert or pozzolanic powder is to use the total surface of contact S (per unit mass of cement) of the mineral admixture in the mortar (Eq. (3)):

$$S = \frac{S_S \cdot A}{C} = \frac{S_S \cdot pC_0}{(100\% - p)C_0} = S_S \frac{p}{100\% - p} [\text{m}^2 \text{ of mineral admixture/kg of cement}] \quad (3)$$

where C_0 is the mass of cement in admixture-free mix, A and C are the masses of mineral admixture and cement respectively in the mix with mineral admixture, S_s is the specific surface area (m^2/kg) of the mineral admixture and p is the replacement rate.

Fig. 11 presents the increase in compressive strength Δf_φ as a function of the admixture area S in mortars, at 1 and 28 days, for all replacement rates and for quartz powders. It can be seen that the experimental points $\{S, \Delta f_\varphi\}$ are not lifted by one single curve but lie on individual curves characterized by the replacement rate p. Similar results are obtained for fly ash (Fig. 12). Thus, the effect of mineral admixtures on heterogeneous nucleation or pozzolanic reaction is not a function of the total admixture area S alone. This parameter does not meet the stated objective of developing a single generalized relation for the effect of powders on the increase of strength.

3.2.2. Physical and chemical efficiency of mineral admixtures

Figs. 11 and 12 show that a given surface of contact S does not involve the same increase of strength for various proportions of admixture within the range studied. This means that particles of admixture do not have the same efficiency regarding compressive strength when small or large quantities of powder are used: a small amount of powder has an optimum efficiency and results in a large increase in compressive strength while the use of a large amount of powder has a smaller effect.

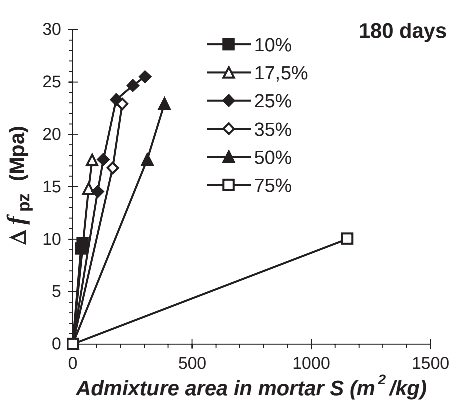

Fig. 12. Increase in compressive strength Δf_{pz} due to fly ash at 180 days, as a function of the mineral admixture surface area S in mortars.

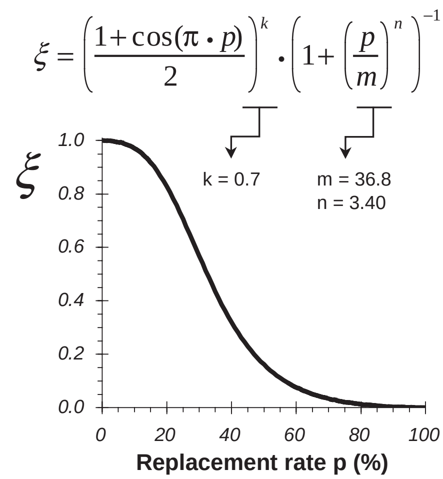

Fig. 13. Efficiency function $\xi(p)$, which is independent of S_S.

An efficiency concept has already been defined in earlier work concerning the degree of hydration of mortars with inert admixtures at young ages [2]. An efficiency function $\xi(p)$ (Fig. 13), which had the specificity of being independent of time, independent of fineness and independent of the type of mineral admixture used, was proposed. This concept will now be extended to the analysis of compressive strength results at any hydration time. $\xi(p)$ is close to 1 for low replacement rates and tends to 0 for high replacement rates:

- An efficiency close to 1 means that almost all admixture particles enhance the cement hydration process or react with cement hydrates;

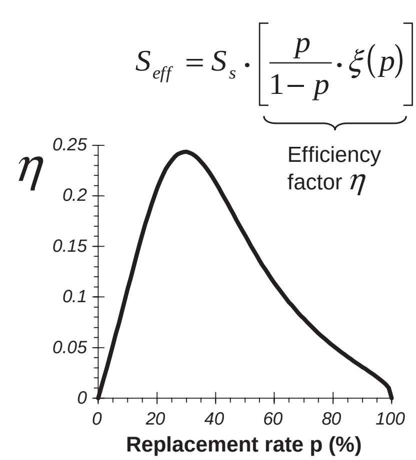

Fig. 14. Efficiency factor $\eta(p)$, used in the concept of efficient surface area S_{eff}.

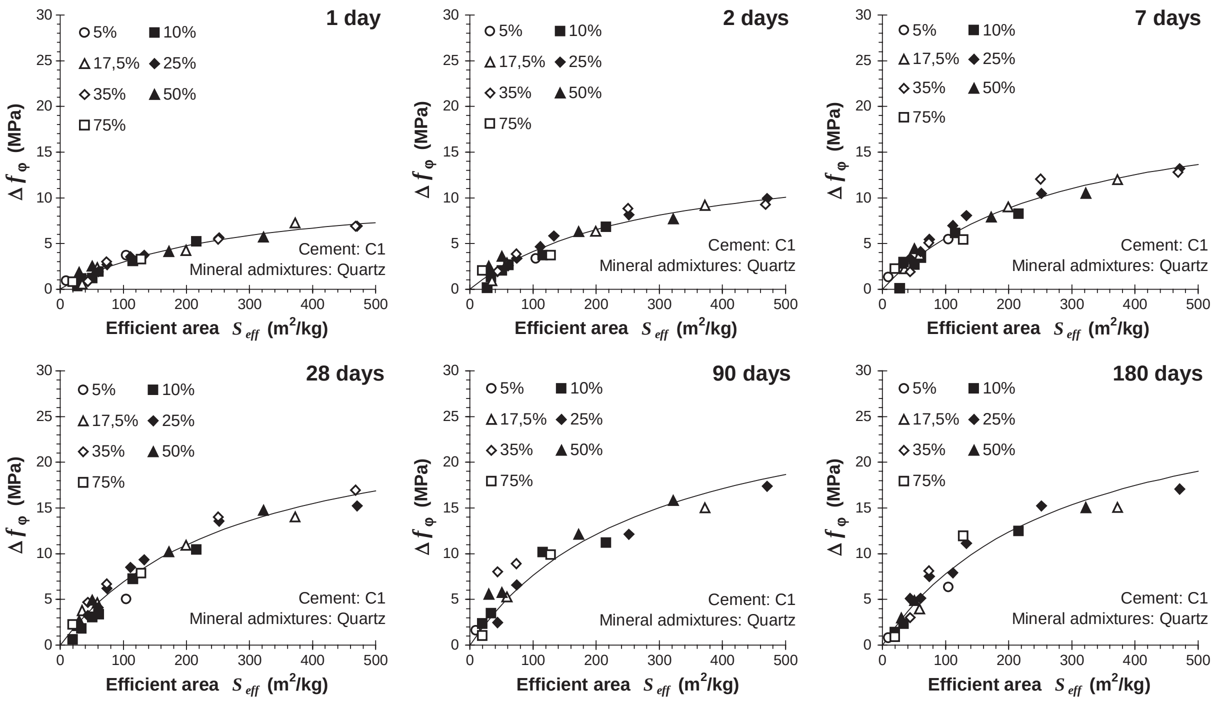

Fig. 15. Increase in compressive strength Δf_{φ} due to physical effect between 1 and 180 days, as a function of the efficient surface area of mineral admixtures.

- An efficiency close to 0 indicates that the use of an inert or pozzolanic powder does not lead to an increase in compressive strength compared to the reference mortar without mineral admixture. Practically, for very high replacement rates, most particles do not influence the hydration reactions of cement (or do not react with hydration products) and the overall increase in compressive strength remains negligible.

One possible physical interpretation in the case of inert powder is that a particle of admixture should influence the hydration kinetics of a cement grain only if both particles are close enough to interact with each other. When the amount of mineral admixture is small, the admixture particles have a high probability of being near one or more cement grains. On the other hand, when the amount of admixture increases, this probability decreases, since some particles can be isolated from cement grains. In the latter case, only a small fraction of the mineral admixture is efficient in the heterogeneous nucleation process by supplying mineral surfaces on which hydrates can precipitate. A similar assumption can be made for pozzolanic admixture, since the probability of a particle of fly ash reacting with hydrated phases of cement is higher when the particle is near cement grains.

Considering the efficiency of an inert or pozzolanic powder leads to the concept of efficient area S_{eff} (expressed per unit mass of cement), as defined by Eq. (4)

$$S_{\mathrm{eff}} = S \cdot \xi(p) = S_{\mathrm{S}}\left[\frac{p}{100\% - p} \cdot \xi(p)\right] = S_{\mathrm{S}} \cdot \eta(p) \tag{4}$$

where S is the total area of contact (Eq. (3)), S_{s} is the specific surface area of the admixture, $\xi(p)$ is the

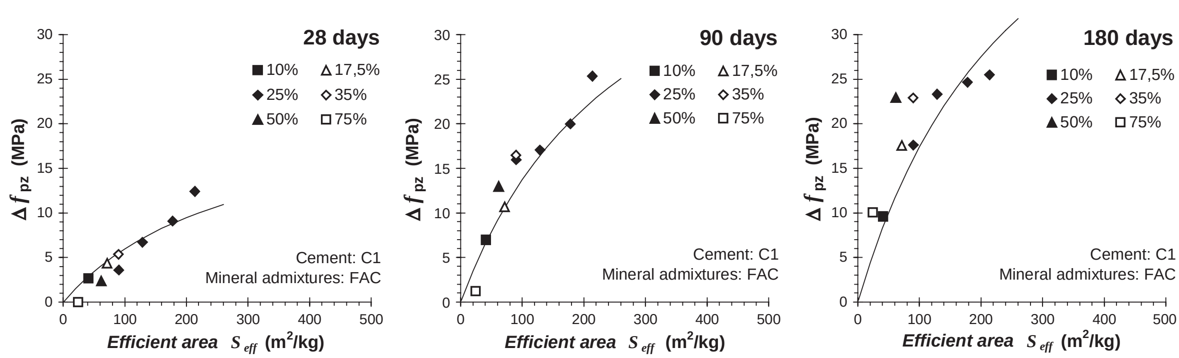

Fig. 16. Increase in compressive strength Δf_{pz} due to pozzolanic effect of FAC between 28 and 180 days, as a function of the efficient surface area of mineral admixtures.

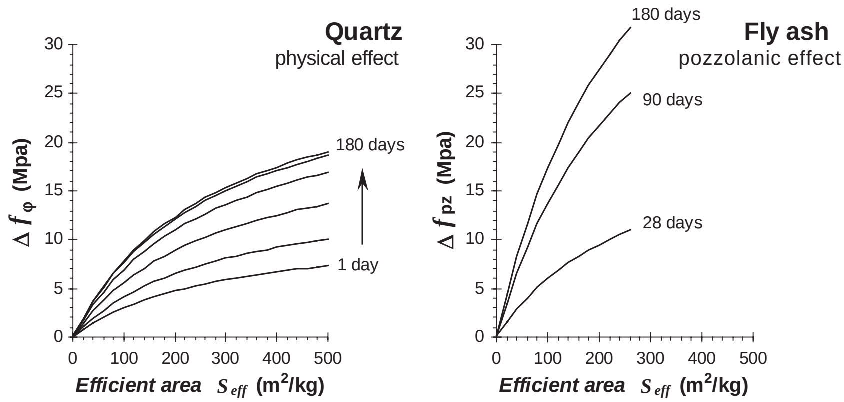

Fig. 17. Increase in compressive strength Δf_{φ} (between 1 and 180 days) and Δf_{pz} (between 28 and 180 days), as a function of the efficient surface area of mineral admixtures.

efficiency function (Fig. 13) and $\eta(p)$ is the efficiency factor (Fig. 14).

According to Eq. (4), the efficient area of a mineral admixture tends to 0 in three cases: when the replacement rate is close to 0 ($p \to 0$) or close to 100% ($\xi(p)/(100\% - p) \to 0$) (Fig. 14), or for coarse powders for which the specific surface areas S_S are very low.

The application of the efficiency concept to the experimental points is given in Figs. 15 and 16 for inert (quartz) and pozzolanic (FAC) powders, respectively. The increase in compressive strength as a function of the efficient surface area is characterized by a series of single curves that only depend on time i.e., on the age of the mortar. The increase of strength is negligible when the efficient surface area is near 0, corresponding to the case for which the strengths of mortars with and without mineral admixtures are the same. It can be seen that the most significant increases in strength are obtained for the finest admixture (Q2 and FAC5) and for the replacement rate of 25%.

A formula can be proposed (Eq. (5)) to express the increase in strength (Δf_{φ} or Δf_{pz}) depending on the efficient surface area S_{eff},

$$\Delta f_{\varphi,pz}(t) = \frac{a}{1 + \left(\frac{b}{S_{eff}}\right)^c} \quad (5)$$

where a, b and c are empirical parameters; of course this formula is valid only when the specific surface area of mineral admixture is greater than the specific surface area of Q_{ref}.

Fig. 17 summarizes the curves calculated for ages between 1 and 180 days and Fig. 18 gives the parameters of Eq. (5) obtained by means of least squares analysis. For the experimental conditions of this study, it was found that b and c were constant values: b was close to the specific surface area of cement and c was equal to 1. Only parameter a depended on the time of hydration of the mortars. It can be seen from Fig. 18 that the pozzolanic effect goes beyond the physical effect after 28 days.

3.3. Validation of the model for other cement and mineral admixtures

Fig. 19 summarizes the decoupling process of the empirical model to separate the physical and chemical effects of mineral admixtures in mortars.

This synthetic chart distinguishes:

– the dilution effect caused by the variation of the water/cement ratio, which can be evaluated by using Powers' law;
– the physical and chemical effects, which are taken into account in very similar ways. For each of them, the efficient surface area S_{eff} is calculated from the specific surface area of the admixture, S_s, and its replacement ratio, p, by means of the efficiency factor (Fig. 14). The contribution of the physical or pozzolanic effects derives from a simple equation in which two coefficients out of three are identified either as a constant ($c = 1$) or as the specific surface area of the cement itself (b). The third coefficient (a) is time dependent and characterizes the interaction between the cement and the admixture (Fig. 18). For the case of the physical effect, the curve $a(t)$ looks like a typical hydration curve (e.g., compressive strength over time).

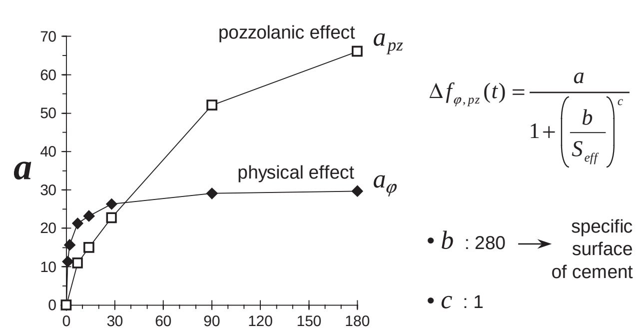

Fig. 18. Numerical values of parameters of Eq. (5).

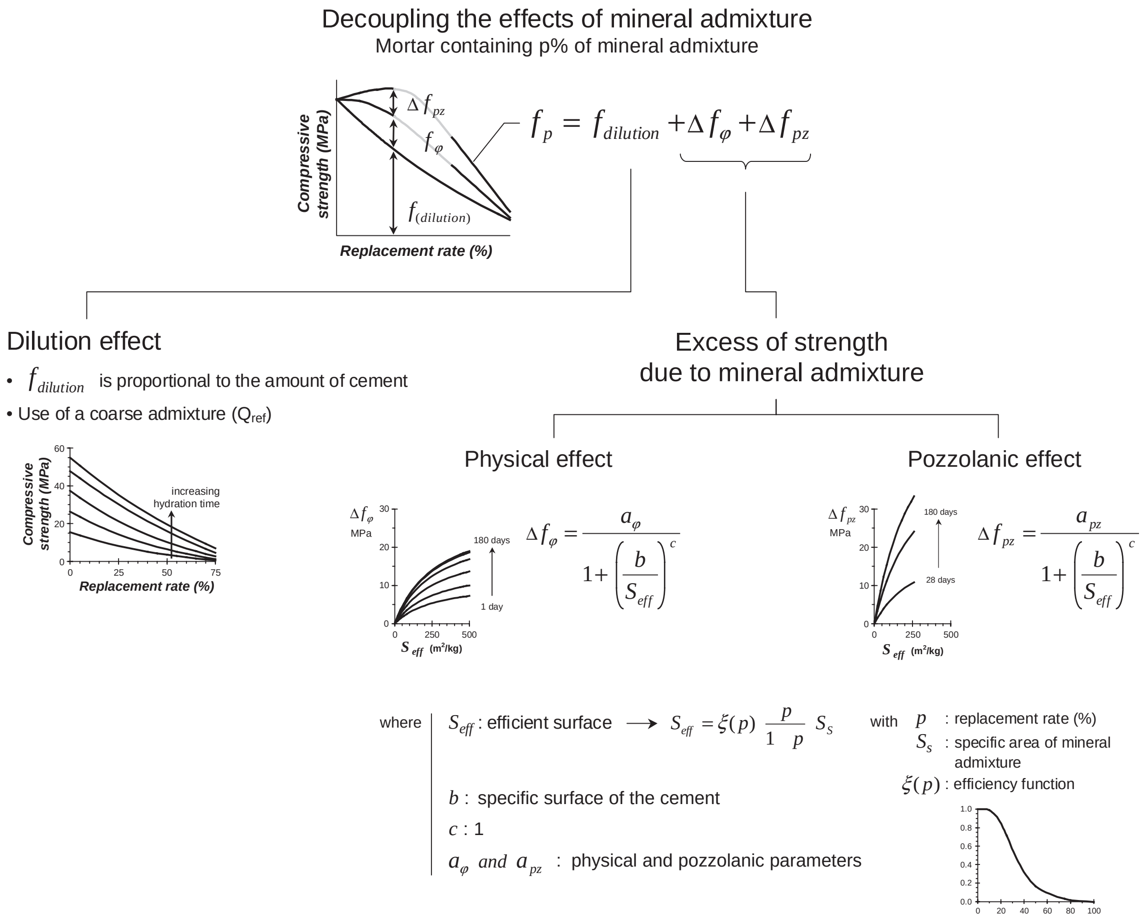

Fig. 19. Schematic representation of the decoupling process of physical and chemical effects of mineral admixtures in mortars.

In order to validate this decoupling approach for other materials, three levels of experimental data, taken from the results presented in the previous paper [3], were used.

- Testing other non-pozzolanic mineral admixtures (Fig. 20) Mortars with cement C1 and 10%, 17.5%, 25% and 50% of limestone filler (L19, L8 and L3), were tested between 1 and 180 days. Parameter values of Eq. (5) were $c = 1$, $b = 280$ m^2/kg and $a(t)$ was taken from Fig. 18 (curve a_φ).

The role of calcium carbonate as a nucleating agent in cement systems has been thoroughly discussed elsewhere [11]. For our work, it was decided to treat limestone filler as an inert material and its contribution was included in the physical term of the model, considering that this powder was only a nucleating agent. This is probably the predominant effect in this study as the surface area is relatively low. Nevertheless, it should be noticed that limestone filler is not totally an inert material, since it reacts with C_3A and C_4AF to form carbo-aluminates [12,13]. Our previous work showed an increase in strength

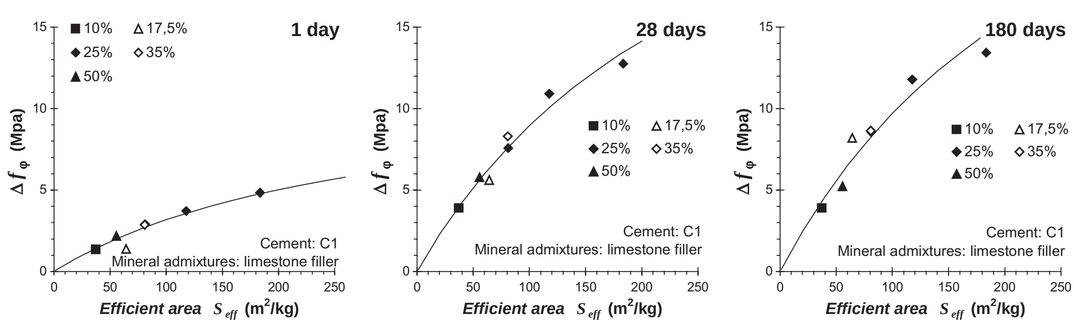

Fig. 20. Increase in compressive strength Δf_φ in mortars containing cement C1, due to physical effect at 1, 28 and 180 days, as a function of the efficient surface area of limestone admixtures. Same curves were obtained at 2, 7, 14 and 90 days.

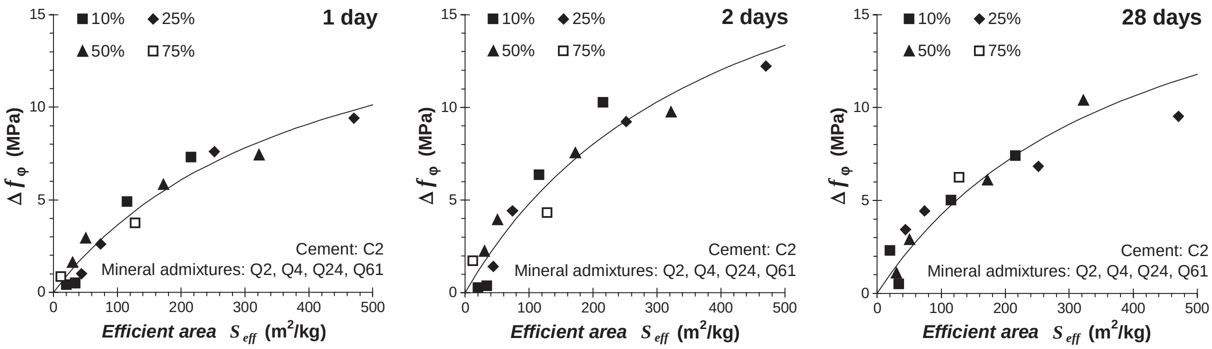

Fig. 21. Increase in compressive strength Δf_φ in mortars containing cement C2, due to physical effect at 1, 2 and 28 days, as a function of the efficient surface area of quartz admixtures.

between 7 and 28 days for mortars containing limestone fillers compared to mortars with quartz powders. This increase was neglected since it was not significant compared to other physical effects.

- Testing another cement (Fig. 21)
Tests were also made on mortars containing cement C2 and 10%, 25%, 50% and 75% of quartz (Q61, Q24, Q4 and Q2), at 1, 2 and 28 days. Here the coefficient b was 400m^2/kg (Table 1) and $a_\varphi(t)$ had been adjusted so that the model curve fitted the experimental data (increase in strength).
- Testing another pozzolanic admixture (Fig. 22)
Mortars with cement C1 and 10%, 17.5%, 25% and 50% of fly ash FAA were tested between 28 and 180 days. Only one specific surface area was available with this non-ground fly ash (312 m^2/kg) so that efficient surface areas extended only from 0 to 100 m^2/kg. Once again, c was set to 1, b to 280 and a_{pz} was adjusted according to the experimental data.

For all these tests, the application of the decoupling process including the efficiency concept led to a series of single curves that only depended on the age of the mortar. This demonstrates that the model can be used with other cements and mineral admixtures.

4. Conclusion

This paper has presented the quantitative analysis of the effects of mineral admixtures on compressive strength by means of an empirical model. More than 2000 compressive strength results between 1 day and 6 months for mortars containing up to 75% of inert and pozzolanic admixtures were analyzed. Some of them were used to develop this empirical model and some were used to check its validity.

A decoupling process of the main effects of mineral admixtures on compressive strength has been proposed. It consists in determining the contributions to compressive strength due to dilution ($f_{(dilution)}$), to heterogeneous nucleation (Δf_φ) and to pozzolanic (Δf_{pz}) effects.

- The dilution effect was evaluated from mortars containing an inert mineral admixture composed of particles large enough for it to be assumed that heterogeneous nucleation was not significant (quartz Q_{ref}). This effect is also correctly fitted by Powers' law.
- The increase in strength due to physical effects (Δf_φ) was deduced from the difference between the strength of mortars with fine inert admixtures and the strength of mortars with Q_{ref}.

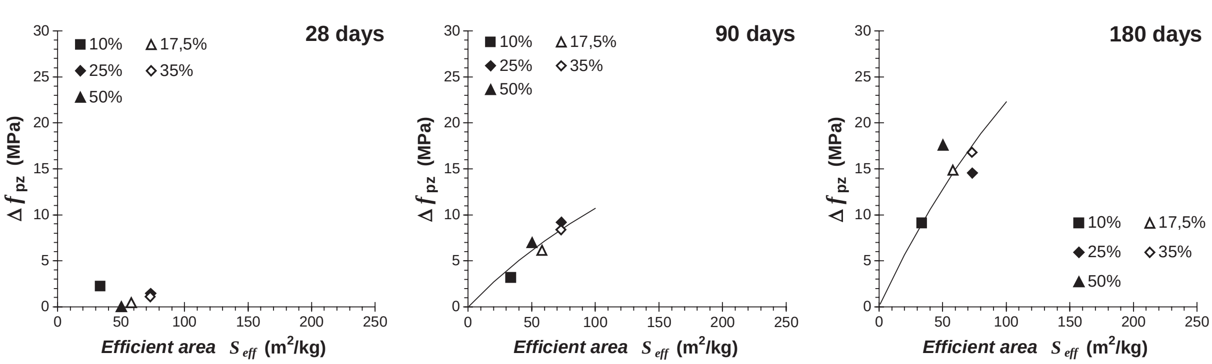

Fig. 22. Increase in compressive strength Δf_{pz} in mortars containing cement C1, due to pozzolanic effect at 28, 90 and 180 days, as a function of the efficient surface area of mineral admixture FAA. Comparison with the FAC curves (Fig. 16).

- When pozzolanic admixtures were used, the increase in strength due to chemical reactions (Δf_{pz}) was obtained by the difference in strength between fly ash mortars f_{FA} and inert quartz mortars f_Q of same fineness.

Finally, an efficiency concept has been proposed in order to take account of the effect of mineral admixture in mortars from both the physical and chemical points of view. In this approach, an *efficiency function* $\xi(p)$ is used to quantify the effect of mineral admixture on the heterogeneous nucleation and pozzolanic processes. $\xi(p)$, which was already defined in earlier work concerning the degree of hydration of mortars with inert admixtures at young ages [2], has notable properties: it is independent of time, independent of fineness and independent of the type of mineral admixture. The empirical model developed allows us to quantify the increase in strength induced by the use of inert and pozzolanic mineral admixtures. The modifications are directly related to the specific surface areas of the admixtures.

5. General conclusion

Four papers have been proposed on the subject of the efficiency of mineral admixtures in cement based materials. A large and rigorous experimental program has been performed, presented and commented in order to highlight the effects of the mineral admixture whatever its nature, quantity or fineness. Two experimental approaches were considered: (i) semi-adiabatic calorimetry (papers 1 [1] and 2 [2]) was used to investigate the physical effects in the short term; (ii) compressive strength tests (papers 3 [3] and [4]) enabled both short and long terms to be studied.

The aim of the whole program was to find the bases on which to build a method for the design of concrete with mineral admixtures. To that end, general rules would be found to facilitate the work of engineers who need straightforward methods. The main result of this study is an empirical decoupling model.

Replacing cement by mineral admixture causes an increase in the water/cement ratio. In this situation, all well known laws (Féret, Abrams, Powers) predict a decrease in the compressive strength of mortars but none of them correctly fit the experimental data. In fact these laws do not take into account the strength contribution of the mineral admixture. This is the reason why it is necessary to distinguish the "dilution" effect from other "physical effects" and "chemical effects". So the dilution effect was evaluated by using a particular mineral admixture with a small fineness (S_s=23 m^2/kg). It was shown that this "reference admixture Q_{ref}" did not contribute at all to the hydration of cement (as proved by calorimetry tests, [Table III of Ref. [1]]) whatever its substitution ratio. The compressive strength data of mortar mixed with this reference admixture are well fitted by Powers' law (Fig. 5 of this paper).

The replacement of cement by mineral admixtures having a specific surface area over 100 m^2/kg [1] revealed other phenomena, in addition to the dilution effect, leading to an increase in the degree of hydration [1,2] and compressive strength [2,3]. When the admixture is chemically inert, these increases can be attributed to heterogeneous nucleation (globally named "physical effect"). This effect consists of an increase in hydration [Fig. 4 of Ref. [2]] which in turn leads to an increase in compressive strength (this paper, Fig. 7). Both the increase in hydration and the increase in strength can be described by a single approach in which the "increase" is expressed as a function of the fineness and the replacement rate, leading to the concept of "efficient surface area". It is noteworthy that the latter concept requires the definition of an "efficiency coefficient", $\xi(p)$, which is independent of fineness, mineral nature and time. Time appears implicitly in one of the coefficients used in the model.

When the mortar contains a pozzolanic admixture, it combines two effects: the physical effect (as describe above) and a chemical effect which contributes to the compressive strength. This increase can be accurately represented using the same model as for the physical effect, but with another, time-dependent parameter (a_{pz}), which takes into account the reaction kinetics of the admixture.

Finally, the compressive strength of mortars, and so of concrete, can be simply expressed as the sum of three effects: $f_p = f_{dilution} + \Delta f_\varphi + \Delta f_{pz}$ (this paper, Fig. 19). Based on tests involving a great variety of materials, this decoupling approach has been tested and validated on several mortars including different cements, and inert or reactive admixtures.

This approach is intended for the engineers and a physicochemical approach would still have to be developed in order to further explain the phenomena involved in the use of mineral admixtures. In particular, it would be interesting to explain the sigmoid shape of the efficiency function $\xi(p)$ or to connect the time-dependent coefficient to the hydration properties of cement. This will be the purpose of further research work.

Acknowledgments

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