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Mineral admixtures in mortars
Effect of inert materials on short-term hydration

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Abstract

This work is the first 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 separation of the different physical effects responsible for the modification of cement hydration, when chemically inert quartz powders are used in mortars, is presented. The phenomenological approach, based on semi-adiabatic calorimetry, is only associated with first-order phenomena, and the study excludes the complex physicochemical details involved in the chemistry of cement. The results, obtained for a wide range of fineness (between 180 and 2000 m^2/kg) and replacement rates (up to 75%), show that short-term degrees of hydration in mortars containing a chemically inert mineral admixture (quartz) are always higher than for a reference mortar. This study confirms that cement hydration is enhanced by inert mineral admixtures. The two main physical effects responsible for the modification of the hydration of cement are identified as the dilution effect and heterogeneous nucleation. The dilution effect of the cement is highlighted with a coarse mineral admixture. The heterogeneous nucleation effect, although it increases with fineness of mineral admixtures, presents an optimum depending on the replacement rate. In the following part of this work, these results will be used for the development of an empirical model allowing us to quantify both physical effects.

Keywords: Calorimetry; Degree of hydration; Dilution; Fineness; Heterogeneous nucleation; Mineral admixtures; Mortar; Specific surface

1. Introduction

It has been known for many years that mineral admixtures, chemically inert or not, modify the physical and mechanical properties of concrete when they are used as cementitious materials. These modifications must be taken into account if a correct concrete mix is to be designed.

The work presented here is 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 can be achieved by applying a global and phenomenological approach, which allows us to propose 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 analysis are intentionally omitted in order to develop empirical relations between the macroscopic properties and the basic characteristics of mineral admixtures. The main physical property used is the specific area which, when coupled with an efficient function, can be used to describe the increase of degree of hydration or compressive strength of mortars resulting from the physical effects of mineral admixtures.

The different phases of the overall project are outlined in Fig. 1. In the first part, the physical effects of chemically inert mineral admixtures on the short-term hydration of cement are separated and quantified by means of calorimetry. This analysis leads, in the second part, to the development of an empirical model, which can be used for the prediction of 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 involve the development of the empirical model from compressive strength tests up to 6 months. Finally, the last part takes into account the effect of pozzolanic admixtures on compressive strength evolution.

This paper presents the first stage of the project, concerning the separation of the different physical effects responsible for the modification of cement hydration when chemically inert mineral admixtures are used in mortars.

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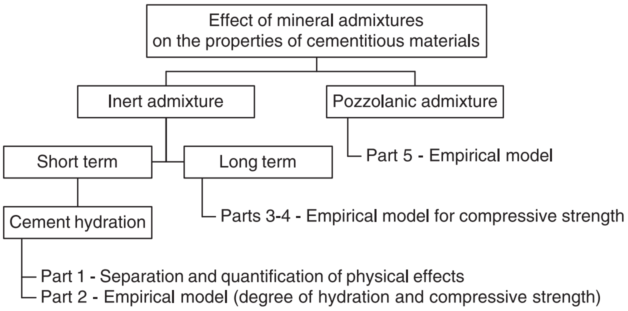


Fig. 1. Phases of the overall project.

The choice of chemically inert materials, composed of pure minerals, is required in order to avoid any chemical reaction which could lead to unsuitable analysis.

2. Background

Many papers in the literature report that mineral admixtures, chemically inert or not, modify the hydration kinetics of cement, especially in the short term. In most cases, the results are expressed as variations of the degree of hydration, bound water or total heat evolved between mixes with and without mineral admixtures.

Some mineral admixtures enhance cement hydration. It is often the case of inert, pure materials such as powders of quartz [1], calcite [1–4], rutile [4,5] and alumina [1]. Moreover, a few authors report the same effect for pozzolanic admixtures such as silica fume [6–9], fly ash [10–12], natural pozzolans [13] and colloidal silica [14]. This enhancement, which tends to increase with powder fineness, usually counteracts a part of the negative effect of cement dilution resulting from the replacement of cement by mineral admixtures.

On the other hand, some powders decrease the hydration rate, which could lead to setting delay and then affect the development of short-term compressive strength. This effect mainly concerns fly ash [8,12,15–20] or silica fume [21].

These enhancements or delays of cement hydration are the consequences of various physical and chemical phenomena, which are difficult to dissociate most of the time.

2.1. Chemical behavior of mineral admixtures in cementitious materials

Pozzolanic activity, which modifies the chemical equilibrium of ionic species in pore solutions, can affect the short-term hydration of cement. This can occur for very active admixtures, when the rapid dissolution of silica leads to immediate consumption of calcium. It depends on the composition and solubility of the mineral admixtures and it has been shown that some materials, like colloidal silica, can modify the hydration kinetics of cement in the short term by chemical processes [14].

Other chemical activity on the hydration kinetics of cement can be observed between cement and some chemical elements, known as accelerators (e.g. Cl) or retarders (e.g. Zn [22]). These perturbing elements, sometimes found as impurities in admixtures from industrial by-products (e.g. fly ash and silica fume), probably explain several conflicting results on the effects of fine materials on cement hydration.

2.2. Physical behavior of mineral admixtures in cementitious materials

Three main physical effects are observed on cement hydration when mineral admixtures are used in cementitious materials. Two of these effects, i.e. cement dilution and modification of the particle size distribution, are the direct consequences of cement replacement by a mineral powder. The third effect is heterogeneous nucleation, which becomes significant for fine mineral admixtures.

The dilution effect, which is equivalent to an increase in the water–cement ratio, is inversely proportional to the replacement rate p: the increase of p involves a decrease of the amount of cement. Naturally, less cement implies less hydrated cement.

The effect of the particle size distribution, which depends on the fineness and on the amount of mineral powder used, is related to the modification of the initial porosity of the mix. Its influence on cement hydration does not seem to be well documented in the literature.

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. “Qualitatively, if the surface of the solid substrate matches well with the crystal, the interfacial energy between the two solids is smaller than the interfacial energy between the crystal and the solution, and nucleation may take place at a lower saturation ratio on a solid substrate surface than in pore solution” without mineral admixture [23]. The mineral powder used does not have to be reactive itself since its principal function is to provide nucleation sites for hydrates. Consequently, this effect 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 cement particles increases with the amount of foreign particles;
- the affinity of the mineral powder for cement hydrates [23], which is related to the nature of the mineral used.

3. Materials and mix design

The binder 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.

Table 1
Chemical and mineralogical composition of cement

Compounds	%	Minerals (Bogue)	%
SiO_2	19.8	C_2S	10
CaO	63.9	C_3S	61
Al_2O_3	4.5	C_3A	7
Fe_2O_3	3.2	C_4AF	10
MgO	1.1	Gypsum	7
Na_2O eq	2.5	Other	5
SO_3	3.1		
LOI	0.9		

The mineral admixtures used were five crushed quartz (Table 2), which were chosen in order to achieve a wide range of fineness. Their characteristics, independently of their fineness, were an angular shape, a density of 2.65 and a crystallized silica content of more than 99%. This last property allowed us to assume that this material was chemically inert, i.e. it did not react with hydrated phases of cement. The four finest powders were named by their mean diameter (μm): Q61, Q24, Q4 and Q2. The coarsest quartz powder, denoted as reference admixture (Q_{ref}), had a mean diameter of 215 μm, a specific surface (Blaine) of 23 m^2/kg and a narrow particle size distribution. These properties gave this powder very weak influence on cement hydration whatever the cement replacement rate used (see Results in this study).

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

Tests were carried out on mortars, which are more representative of concrete than cement pastes and more suitable than concrete regarding the large experimental program achieved. The reference mix without admixture, designed according to French standard NF EN 196-1, was composed, by mass, 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 of sand, powder (cement + mineral admixture) and water. The cement replacement by quartz powder was expressed as a mass fraction (p) of cement in the reference mix (C_0). Replacement rates were 10%, 25%, 50% and 75%.

The mix design parameters respected Relation (1)

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

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

4. Experimental method

4.1. Quantification of hydration

The aim of the experimental work was to evaluate the effect of mineral admixtures on cement hydration kinetics. Therefore, the indicator chosen to quantify the progress of hydration reactions was the "global degree of hydration" (α), defined (Relation (2)) as the ratio of the mass of hydrated cement (C_h) to the initial amount of cement (C). Relation (2) can also be used to characterize the degree of hydration in the case of the replacement of a fraction (p) of cement by a mineral admixture; thus, C_0 is the initial amount of cement in the reference without admixture.

$$\alpha(t) = \frac{C_h(t)}{C} = \frac{C_h(t)}{C_0(1-p)} \qquad (2)$$

From a theoretical point of view, it seems impossible to take into account the whole cement hydration process by means of a single degree of hydration, since all simultaneous reactions of the principal clinker minerals have different hydration kinetics [24]. Nevertheless, practice has shown that the global parameter α (Relation (2)) provides a reliable description of the hydration process of the whole cement [25–27].

4.2. Experimental method

Many methods are available for evaluating the degree of hydration of cement: X-ray diffraction (XRD) [28], nuclear magnetic resonance (NMR) [29], thermal analysis and measurement of bound water [12,30], image analysis [31], calorimetry, etc. Among them, semi-adiabatic calorimetry was chosen for our short-term study. The degree of hydration was then defined (Relation (3)) as the ratio of heat evolved $Q(t)$ at a time t to the total (and theoretical) heat of hydration of cement Q_∞.

$$\alpha(t) = \frac{Q(t)}{Q_\infty} \qquad (3)$$

The total heat of hydration Q_∞ is the quantity of heat in joules per gram of unhydrated cement (J/g), evolved upon complete hydration. It was estimated (Relation (4)) from the mineral composition of the cement (m_i in %, obtained from Bogue calculation or by quantitative XRD) as the relative sum of the heats of hydration of the individual compounds (Q_i in J/g) when hydrated separately. Typical values of the heat of hydration of pure compounds are to be found in the literature [32–36]. Mean values used for the calculation of Q_∞ are 510 J/g for C_3S, 260 J/g for C_2S, 1100 J/g for C_3A and 410 J/g for C_4AF.

Table 2
Physical properties of mineral admixtures (quartz)

Name	Mean diameter (μm)	Specific area (m^2/kg)
Q_{ref}	215	23
Q61	61	187
Q24	24	315
Q4	4	1070
Q2	2	2000

The application of Relation (4) leads to a total heat of hydration of 450 J/g for the cement used in this study.

$$Q_\infty = \sum m_i Q_i \tag{4}$$

The heat evolved $Q(t)$ at a time t was measured by semi-adiabatic calorimetry using the Langavant calorimeter (NF P 15-436) [37], which can handle large amounts of material (1.6 kg).

In this apparatus, the mortar was put into a well, but not perfectly, thermally insulated bottle placed in an airconditioned room at 20 ± 1 °C. The calibration of the bottle allowed us to calculate the heat lost by the tested mortar. The heat evolved $Q(t)$ at a time t is the sum of the heat accumulated in the calorimeter and the heat dissipated (Relation (5)):

$$Q(t) = \frac{\mathrm{HC}}{C} T + \frac{1}{C} \int_0^t \beta T \mathrm{d}t \tag{5}$$

where C is the mass of cement in the bottle (g), t is the hydration time (h), HC is the total heat capacity of the calorimeter and the mortar (J/°C), β is a thermal coefficient (J/h °C) and T is the relative temperature of the mortar at time t (°C).

Tests lasted for up to 48 h, in order to minimize the uncertainties on heat evolved when long-term heating decreased.

However, the experimental heat evolved can be used to compare the progress of reaction between the different mortars only if the mixes have a similar degree of maturity, i.e. they have been subjected to the same temperature variations. Fig. 2 shows that this is not the case when the cement is replaced by a mineral admixture. Since cement hydration is a thermoactivated reaction, the comparison of heat evolved at a given time requires a correction of the raw experimental results in order to reach similar degrees of maturity in all mortars.

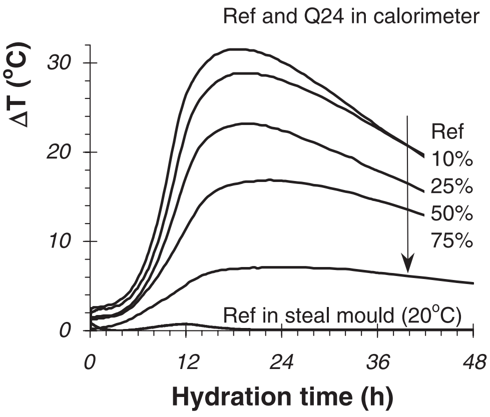


Fig. 2. Evolution of temperature in calorimeter of reference mortar and mortars containing increasing proportions of admixture Q24. Comparison with the variation of temperature when the reference mortar is cured at 20 °C in a steel mould.

The correction uses the concept of equivalent age for the evaluation of the degree of maturity of the mortars [38,39]. It is based on Hansen's hypothesis [40], which assumes that the hydration speed depends only on the variation of the temperature of the mix at time t. The Arrhenius law [41] was chosen since it seems to be the most accurate law for describing the effect of temperature on simultaneous chemical reactions, as is the case for cement materials [25–27,42].

For a mortar subjected to a temperature variation $T_1(t)$, the correction allows us to estimate the corrected time t_c (Relation (6)) [43] corresponding to a temperature variation $T_2(t)$, in order to reach the same heat evolved. Then, it is possible to present the variation of the degree of hydration of a mortar subjected to a virtual curing variation $T_2(t)$, whatever the real curing conditions $T_1(t)$ of the test.

$$t_c = \int_0^t \exp\left(-\frac{E}{R}\left(\frac{1}{273 + T_1(t)} - \frac{1}{273 + T_2(t)}\right)\right) \mathrm{d}t \tag{6}$$

where $T_i(t)$ are the temperature variations (K), E is the apparent activation energy of the mortar (J/mol) and R is the gas constant (8.314 J/mol/K).

If $T_1(t)$ is the temperature variation in the calorimeter, $T_2(t)$ can be chosen as an isothermal condition (e.g. 20 °C) like the one when the mortar is cured at 20 °C in a steel mould (Fig. 2). This choice allows us to compare the results obtained by calorimetry measurements with the compressive strength of mortars having the same composition.

The use of the Arrhenius law requires the knowledge of the activation energy E, which is a parameter depending on the overall chemical reactions of hydration. The activation energy can be estimated experimentally (see, for example, the values reported from Ref. [35]) or by the use of numerical models [44]. Although some authors have observed that E can vary with α and T [44,45] and in the absence of consensus on the subject, a constant value of $E = 43$ kJ/mol was chosen for all the mortars tested [46].

5. Experimental results

Figs. 3 and 4 give the evolution of the degree of hydration α during the first 2 days of hydration (expressed as corrected time), calculated from calorimetry results corrected for isothermal conditions (20 °C). Fig. 3a, which presents the results for the mineral admixture Q24, shows that the degree of hydration increases with the replacement rate. Similar results at 1 and 2 days were obtained with mineral admixtures Q2, Q4 and Q61 (Fig. 3b). Fig. 4a gives the results for one replacement rate ($p = 25\%$). It can be seen that the degree of hydration is significantly enhanced when fine particles are added to the mixture. Fig. 4b summarizes the effect of mineral admixture fineness for all replacement rates.

The overall results presented here confirm the enhancement effect of inert mineral admixtures (like quartz) on the hydration of cement. At a given time, the relative amount of

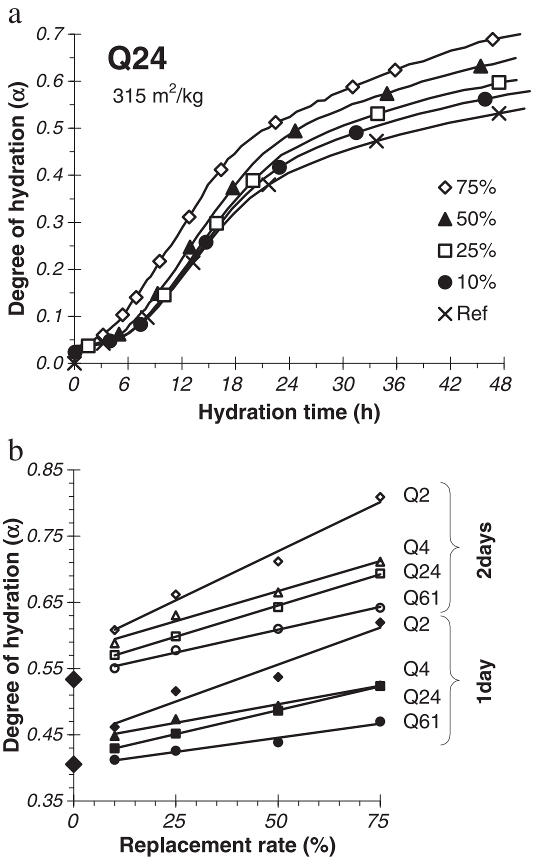


Fig. 3. (a) Degree of hydration up to 48 h (corrected time) of mortars containing mineral admixture Q24 (0, 10%, 25%, 50% and 75% in replacement of cement). (b) Degree of hydration of mortars, at 1 and 2 days, as a function of the replacement rate of cement by mineral admixture Q2, Q4, Q24 and Q61.

hydrates is higher in a mortar containing crushed quartz than in the reference mortar without mineral admixture. This phenomenon depends on the fineness and on the quantity of the admixture used.

6. Decoupling and quantification of physical effects of inert mineral admixtures on cement hydration

The enhancement effect of inert mineral admixtures is often mentioned in the literature from a qualitative point of view for different types of mineral admixtures but its consequences (for example on the degree of hydration of cement) are rarely quantified. To develop an empirical model leading to a quantification of the effects of inert mineral admixtures on cement hydration, it is necessary to separate the different physical effects involved.

6.1. Reference admixture Q_{ref}—dilution effect and modification of the particle size distribution

The first step of the process to decouple physical effects was based on the use of a chemically inert mineral admixture, composed of particles large enough for it to be assumed that heterogeneous nucleation was not significant. Then, the only conceivable physical effects were cement dilution and the modification of the particle size distribution.

The coarse mineral admixture used to reduce surface effects was the quartz Q_{ref}, which had a specific area of 23 m^2/kg, eight times smaller than that of the fine Q61 (187 m^2/kg). The large mean diameter of Q_{ref} (215 μm) allowed us to presume, according to the literature [47], that this admixture was large enough to exclude any heterogeneous nucleation effects.

Table 3 presents the degrees of hydration at 1 and 2 days, calculated from the corrected results for the heat released, for mortars containing increasing contents of Q_{ref} (between 10% and 50%). The experimental results show that the degree of hydration is almost constant. Consequently, the admixture Q_{ref} did not modify the global hydration process, whatever the quantity used in replacement of cement.

Assuming that the heterogeneous nucleation effect is excluded and that the rules of additivity can be applied, the

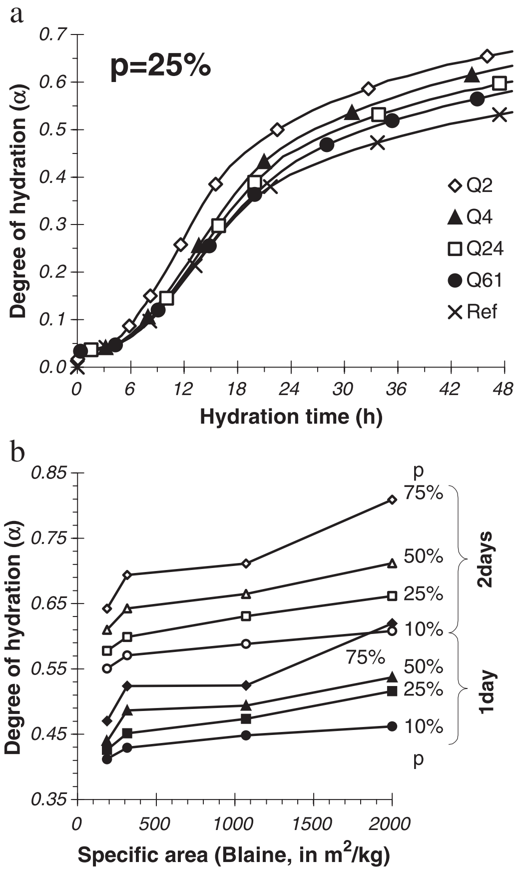
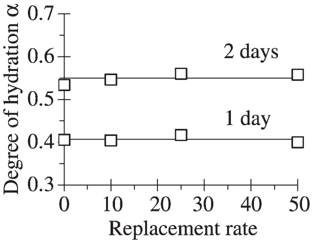


Fig. 4. (a) Degree of hydration up to 48 h (corrected time) of mortars containing 25% of mineral admixtures (Q2, Q4, Q24 and Q61) having different fineness. (b) Degree of hydration of mortars, at 1 and 2 days, as a function of the fineness and replacement rate for mineral admixtures Q2, Q4, Q24 and Q61.

Table 3

Degree of hydration α_{ref} at 1 and 2 days of mortars containing increasing amounts of admixture Q_{ref} in replacement of cement

	Degree of hydration (α_{ref})	
	1 day	2 days
Reference	0.406	0.534
10% Q_{ref}	0.404	0.546
25% Q_{ref}	0.417	0.560
50% Q_{ref}	0.404	0.563



overall effect of Q_{ref} on the degree of hydration can be expressed as the sum of the respective parts of the two remaining physical effects (cement dilution and modification of the particle size distribution).

The degree of hydration may not be the more suitable indicator for evaluating the cement dilution effect since it does not take into account the decrease in cement content. Thus, instead of the degree of hydration, the relative amount of hydrated cement $C_{h\%}$ was used. This parameter is defined (Relation (7)) as the ratio of hydrated cement (C_h) to the total amount of powder, i.e. the mass of cement C_0 in the reference mortar or the sum of cement C and admixture A masses in mortars containing mineral admixtures. It can also be evaluated from Relation (2) with the degree of hydration α and the replacement rate p.

$$C_{h\%} = \frac{C_h}{C_0} = \frac{C_h}{C + A} = \alpha(1 - p) \tag{7}$$

Table 4 shows the experimental points calculated from Table 3, compared to the theoretical curve characterizing a simple dilution effect of cement. This curve was obtained from Relation (7), considering α to be independent of p. Since the experimental points coincide with the dilution curve, it may be reasonable to consider that the dilution effect explains the overall decrease of the amount of hydrates. Consequently, the modification of the particle size distribution when Q_{ref} replaces increasing amounts of cement is not critical. The latter result will be extended to other mineral admixtures.

6.2. Surface effect due to heterogeneous nucleation

Considering the results presented previously, the overall effect of an inert mineral admixture on the degree of hydration is the combination of two antagonistic effects:

- cement dilution, which leads to a decrease of the total amount of hydrates without significantly changing the degree of hydration; its effect can be quantified theoretically or with the help of Q_{ref};
- heterogeneous nucleation, which leads to an excess of hydrates at a given time and for a given amount of cement.

Assuming these effects to be additive, the amount of hydrated cement in a mortar containing p% of inert powder ($C_{h\ p\%}$) is equal (Relation (8)) to the sum of the hydrated cement in a mortar having p% of Q_{ref} ($C_{h\ ref\%}$) and the excess of hydrated cement coming from the heterogeneous nucleation effect ($\Delta C_{h\ \varphi\%}$).

$$C_{h\ p\%(\mathrm{admixture})} = C_{h\ \mathrm{ref}\%(\mathrm{dilution})} + \Delta C_{h\ \varphi\%(\mathrm{nucleation})} \tag{8}$$

The decoupling process, which consists in the determination of the proportions of hydrates due to dilution and to heterogeneous nucleation effects, is given in Fig. 5. Since $C_{h\ p\%}$ and $C_{h\ ref\%}$ can be measured by calorimetry, $\Delta C_{h\ \varphi\%}$ can be deduced from the difference.

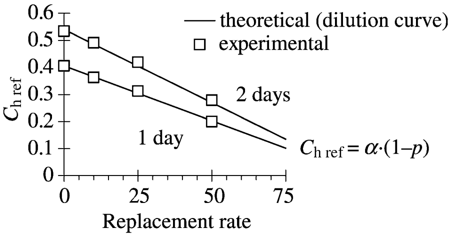
Fig. 6 shows the relative amounts of hydrated cement for mortars containing increasing proportions of mineral admixtures Q2, Q4, Q24 and Q61. The comparison of these curves with the Ref curve characterizing the dilution effect alone highlights the excess of hydrated cement due to fine mineral admixtures. This excess is quantified in Fig. 7. From a qualitative point of view, it can be seen that:

- $\Delta C_{h\ \varphi\%}$ 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 present optimal replacement rates (between 25% and 35%), which do not vary much between 1 and 2 days. The left part of the curves is characteristic of a lack of mineral particles, which has the consequence of decreasing the available surface area,

Table 4

Amount of hydrated cement ($C_{h\ ref}$) at 1 and 2 days in mortars containing the mineral admixture Q_{ref}. Comparison with the theoretical curve considering the dilution effect

	Hydrated cement ($C_{h\ ref}$)	
	1 day	2 days
Reference	0.406	0.534
10% Q_{ref}	0.364	0.491
25% Q_{ref}	0.313	0.420
50% Q_{ref}	0.200	0.279



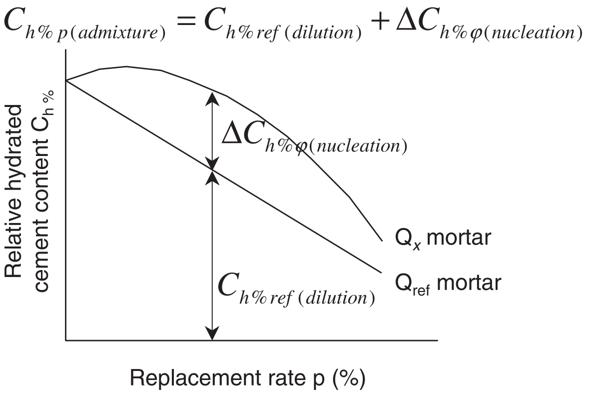


Fig. 5. Quantification of the amount of hydrates due to heterogeneous nucleation.

reducing the precipitation of hydrates. On the other hand, the right part of the curves is characteristic of an excess of mineral particles, which has the effect of dispersing the cement grains. Consequently, a fraction of mineral particles is too far from cement particles to serve as nuclei for hydration process.

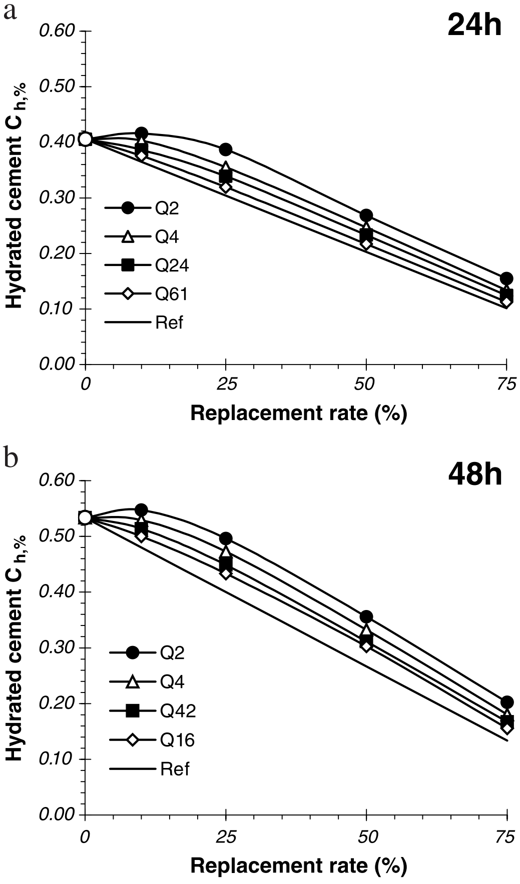


Fig. 6. Amount of hydrated cement relative to C_0 ($C_{h\%} = C_h/C_0$) at (a) 24 h and (b) 48 h, as a function of replacement rate, of mortars containing increasing proportions of mineral admixtures Q2, Q4, Q24 and Q61.

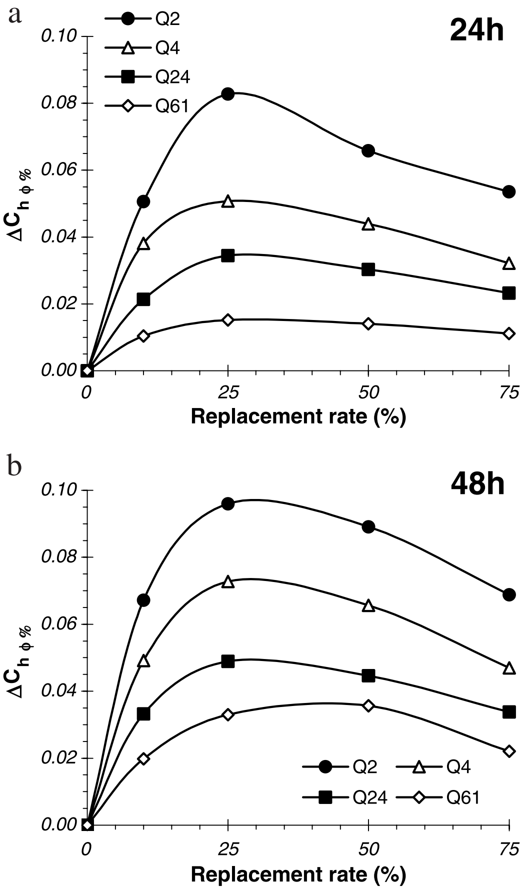


Fig. 7. Excess of hydrated cement $\Delta C_{h\ \varphi\%}$ relative to C_0 ($\Delta C_{h\ \varphi\%} = \Delta C_{h\ \varphi}/C_0$) at (a) 24 h and (b) 48 h, as a function of replacement rate, of mortars containing increasing proportions of mineral admixtures Q2, Q4, Q24 and Q61.

One hypothesis explaining the enhancement of cement hydration is that the thickness of the hydrated layer formed around cement grains is reduced when mineral particles are present (Fig. 8). The hydration of the anhydrous part, which rapidly becomes related to diffusion phenomena, is then facilitated. Consequently, if the particles of mineral admix-

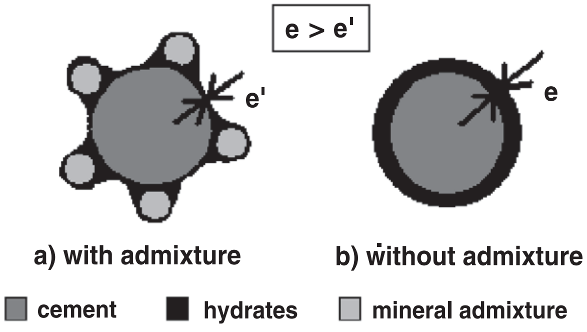


Fig. 8. Schematic representation of a hypothesis explaining the enhancement of cement hydration.

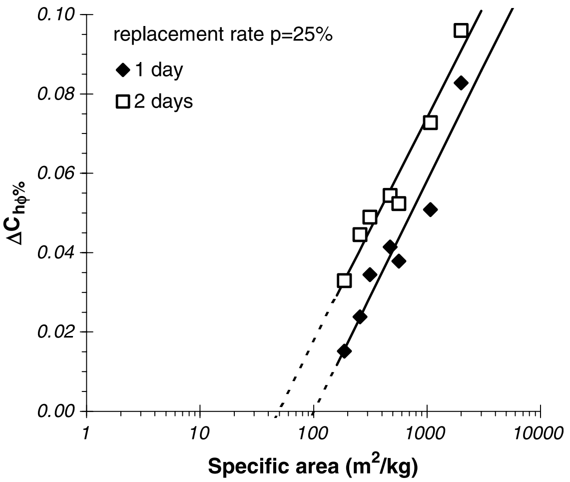


Fig. 9. Excess of hydrates due to heterogeneous nucleation ($\Delta C_{\mathrm{h}\ \varphi\%}$) relative to C_0 ($\Delta C_{\mathrm{h}\ \varphi\%} = \Delta C_{\mathrm{h}\ \varphi}/C_0$) as a function of the specific area of mineral admixtures used ($p = 25\%$).

ture are sufficiently fine and near the cement particles, this leads to an enhancement of cement hydration.

Fig. 9 shows the dependence of the excess of hydrates $\Delta C_{\mathrm{h}\ \varphi\%}$, due to heterogeneous nucleation, on the specific area of the mineral admixtures used ($p = 25\%$). For these experiments, it can be seen that the heterogeneous nucleation effect becomes insignificant for specific areas lower than 50 to 100 $\mathrm{m^2/kg}$. This result confirms the assumption made earlier about the absence of a heterogeneous nucleation effect when the admixture $\mathrm{Q_{ref}}$ was used in mortars.

7. Conclusion

In this paper, the separation of the different physical effects responsible for the modification of cement hydration at young ages have been described for the case when chemically inert quartz powders are used in mortars.

Here, the phenomenological approach only describes the first-order phenomena and excludes the complex physicochemical mechanisms involved in the chemistry of cement. The state of hydration of the different mortars is compared at the same maturity by the means of semi-adiabatic calorimetry.

This study shows that the degrees of hydration in the short term of mortars containing a chemically inert mineral admixture (quartz) are always higher than those for the reference mortar. The results have been obtained for a large range of fineness (between 180 and 2000 $\mathrm{m^2/kg}$) and replacement rates (up to 75%).

In conclusion, this study:

- confirms the enhancement of cement hydration with inert mineral admixtures,
- identifies and quantifies, from a phenomenological point of view, the two main physical effects responsible for the modification of the hydration of cement,
- characterizes the dilution effect of the cement through the use of a mineral admixture coarse enough for it to be assumed that heterogeneous nucleation is not significant,
- shows that heterogeneous nucleation, even if it increases with fineness of the mineral admixtures, presents an optimum depending on the replacement rate.

The following part of this work:

- will show that these concepts are verified, at early ages, for other mineral admixtures like limestone filler and fly ash,
- will extend the results to another cement,
- will propose an empirical model allowing us to quantify the heterogeneous nucleation effect. To this end, it will be shown that the 'efficiency' ξ of an admixture depends on the replacement rate according to the relation

$$\xi = \left(1 + \left(\frac{P}{m}\right)^{n}\right)^{-1} \text{ by}$$

$$\xi = \left(\frac{1 + \cos(\pi \cdot p)}{2}\right)^{k} \cdot \left(1 + \left(\frac{P}{m}\right)^{n}\right)^{-1}$$

(m and n being two constant values). This empirical model will be used to predict the degree of hydration of cement and will be extended, in some cases, to the prediction of the short-term compressive strength of mortars.

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