ASIAN JOURNAL OF CIVIL ENGINEERING (BUILDING AND HOUSING) VOL. 8, NO. 1 (2007)
PAGES 13-24

EFFECT OF THE ADMIXTURES REACTIVITY ON THE STRENGTH OF MORTARS: APPLICATION OF THE PREDECTIVE MODEL FOR BOLOMEY

A. Boudchicha[a*], M. Cheikh Zouaoui[a], J.L. Gallias[b] and B. Mezghiche[c]
[a]Department of Civil Engineering, University of Larbi Ben Mehidi
04000 Oum Bouaki, Algeria
[b]Laboratory of Modelling, Materials and Structure LM²S
University of Cergy-Pontoise, 95031 France
[c]Department of Civil Engineering, University of Mohamed Khider
07000 Biskra, Algeria

ABSTRACT

The incorporation of admixtures in the cementing materials modifies their rheological and mechanical properties by a granular effect, a physicochemical and a chemical effect.

In order to evaluate the chemical reactivity of the admixtures, we used an approach which consists on the volume substitution of the cement by the admixture in mixtures of which the absolute volume of the whole constituents are preserved constant and the workability fixed by using superplasticizers. Under these conditions, the mixtures have a volume of the flexible phase and an initial porosity constant and then, only the clean chemical effect of the admixture is taken into account.

Keywords: Mortar, admixtures, mechanical strengths, chemical effect and predictive model for bolomey

1. INTRODUCTION

The recent studies which considered the influence of admixtures on the properties of the cementing materials showed that those, by their smoothness and their more or less significant reactivity with the cement, can generate significant modifications in the rheological and mechanical properties. The mechanisms at the origin of these modifications appear particularly complex, but several studies in this field [1-3] agree to distinguish three principal effects which are superimposed to influence the properties of the cementing materials: a granular effect, a physicochemical and micro-structural effect and a chemical effect.

The granular effect relates to all the modifications induced by the presence of the fine or ultra fine particles in the fresh cementing materials in presence of water and possibly

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[*] Email-address of the corresponding author: aboudchicha@yahoo.fr

additives. These modifications result from the capacity of arrangement of the particles of the admixture and the intensity of frictions with the other solid constituents of the melange. Several Studies [4,5] showed that according to the nature of the built-in admixture, this effect could be favourable or unfavourable and influences on the rheological properties and the compactness of the material in a fresh state and can influence the process of hydration of cement.

The physicochemical and micro-structural effect relates to the modifications induced by the presence of the particles of admixtures on the process of hydration of cement and on the structuring of the hydrated products. Several studies [6-8] showed that the admixtures allow a best repartition of the hydrated products and carry out to more effective structuring of the cementing matrix.

The chemical effect concern the capacity of the admixtures to react with water and the anhydrous or hydrated components of cement for forming new mineral phases which contribute to the mechanical strengths as well as the hydrated products of cement.

Pozzolanic reaction concerns mainly the silica fume, the siliceous fly-ashes, natural pozzolanas or calcined schist. The amorphous silica reacts in the presence of water with the formed portlandite during the hydration of cement to form the hydrated silicate of calcium according to the following reaction:

$$\mathrm{S + x\,C\,H + y\,H \rightarrow Cx\,S\,Hx + y}$$

For the limestone admixtures, the calcite ($CaCO_3$) reacts with aluminates of cement (C_3A, C_4AH_{13}) in presence of water to form a hydrated mono-carboaluminate of calcium of the type of $C_3A.CaCO_3.11H_2O$, crystallized in fine hexagonal plates [5].

Then, the chemical effect is complementary to the physicochemical effect; its action on the properties of the hardened material can be measured by the modification of the volume and the nature of the formed hydrated products. Nevertheless, the strong synergy between these two effects prevents any distinction, so that they can be associated in a single concept: the contribution to the flexible activity of cement [9].

To evaluate this chemical contribution of the admixtures to the flexible activity of cement, it is possible to determine the coefficient of reactivity of the admixtures by applying the concept of the equivalent binder and by using the predictive model of Bolomey for the calculation of the compressive strengths of the mortars and to analyze its variation according to the rate of the cement substitution.

In this connection, we repeal that the European standard EN 206-1 defines a standard coefficient of reactivity *K* of certain admixtures like the silica fume and the fly-ashes used in concretes. In addition, French standard NF P 18-305 makes possible to extend the applicability of the coefficient of reactivity *K* to the slag of blast furnace and certain additions of the type 1 considered as quasi inert according to the standard EN 206-1.

2. METHODOLOGY

In the majority of the published studies and in accordance with the normative texts, admixtures were introduced in the mixture in a mass substitution of cement. In this case the absolute volume of the binder (cement + admixture) grows proportionally at the rates of the cement substitution and the modifications in the cementing matrix are more significant as this rate increases and the difference between the Specific gravity of cement and that of the admixture is significant. These modifications can influence the properties of the hardened mixtures and involve a bad evaluation of the different effects of the admixtures on the cementing materials.

Several studies showed that the incorporation of the admixtures in a cementing material had a favourable effect for the fine admixtures to weak rates of the cement substitution and an unfavourable effect for the ultra fine admixtures [4,10-12].

In order to allow more precise evaluation of the chemical effect of the admixtures in the cementing materials, it is necessary to control the granular effect and the maintenance of a constant compactness for all the formulations of mortars with the studied admixtures.

Then, the approach used consists of the progressive volume substitution of the cement by the admixtures in mortars of which the absolute volume of the whole constituents (solid components and water) and the workability are preserved constant [9,13]. The obtained mixtures have a volume of the flexible phase and porosity constant and consequently, only the clean chemical effect of the admixture in the cementing phase is taken into account.

To reach this purpose, we prepared a mortar of reference without admixtures whose composition is inspired by that of the normal mortar defined by NF EN 196.1 standard, with a quantity of water lower than that recommended by the standard norm so that all the formulations require a certain quantity of superplasticizer to obtain the reference workability, evaluated, by measuring the spreading of the mortar on the vibrating table.

We measured all the parameters which characterize the properties of mortars and we were interested in particular to:

- The superplasticizer requirement for mortars having constant workability:

The volume substitution of the cement by the admixture with preserving an absolute volume of the whole components constant, involves a variation of workability. To give to the mortar with admixtures the reference workability, the quantity of superplasticizer must be adjusted.

The superplasticizer requirement is expressed by the variation of the necessary quantity of superplasticizer in (Kg/m^3) according to the rate of the cement substitution by the admixtures (in %) for mortars having constant workability. The rate of substitution of cement by the admixtures varies between 0 and 50 %.

- The mechanical strengths:

For each mortar with the reference workability, 40x40x40 mm test cubes were used for the characterization of the mechanical strengths of the mortars at 7 and 28 days. The results are expressed by the ratio of compressive strength at the D-day of the mortar with admixture, by that of the mortar of reference at the same day, noted (Rc_j/Rcr_j), according to the rate of the cement substitution by the admixture in the mortar (in %):

Rcj: compressive strength at the D-day of the mortar with admixture.

$Rcrj$: compressive strength at the D-day of the mortar of reference.

The procedures of preparation of the mortars, the test cubes, storage, and measurement of strengths in compression are in conformity with NF EN 196.1 standard.

- Evaluation of the chemical reactivity of the admixtures on the compressive strengths:

As the granular effect is controlled, the variation of the mechanical strengths of the mortars is completely due to the chemical reactivity of the admixtures including the physicochemical effect and the chemical effect and which can be evaluated by the coefficient of reactivity K determined by applying to the studied mortars the principles of the predictive model of Bolomey [5] which expresses the compressive strength of a concrete to a given age by the following relation:

$$R_c = G_F f_c\left(\frac{C}{W+V} - 0.5\right) \quad (1)$$

Where:

C, W and *V* indicate respectively, the masses of cement, water and equivalent water of the occluded air in the mixture.

G_F indicates a coefficient which depends on the nature of the aggregates.

f_C indicates the compressive strength of the normal mortar at the same age.

To distinguish the chemical reactivity to each admixture, we can base on the concept of the equivalent binder *B* which is definite in NF P18 305 standard by the following relation:

$$B = C + KF \quad (2)$$

Where:

K indicates the coefficient of reactivity of the admixture

B and *F* indicate respectively, the masses of the binder and the admixture in the mixture.

By applying this concept to the studied mortars, the relative compressive strength can be deduced by the predictive model of Bolomey:

$$\frac{R_c}{R_{cr}} = \frac{\left(\frac{B}{W+V} - 0.5\right)}{\left(\frac{C_r}{W_r+V_r} - 0.5\right)} \quad (3)$$

Where:

C_r, W_r and V_r indicate respectively, the masses of cement, water and the equivalent water of the occluded air in the mortar of reference.

Then, the coefficient of reactivity *K* can be written with the following relation:

$$K = \frac{R_c}{R_{cr}}\left(\frac{C_r}{F} - \frac{W_r+V_r}{2F}\right) + \frac{W_r+V_r}{2F} - \frac{C}{F} \quad (4)$$

With:

$$C_r = \rho_C.c_r \quad C = \rho_C.c \quad F = \rho_F.f$$

Where:

ρ_C *and* ρ_F indicate respectively, the absolute densities of cement and admixture.

c, c_r and *f* indicate respectively, the volumes of cement and admixtures in the mortar.

The analysis of the variation of the coefficient of reactivity *K* according to the rate of the cement substitution can inform us on the specific chemical reactivity to each studied admixture.

3. MATERIALS

3.1 Cement

Current cement used for the manufacturing of the ordinary concretes in Algeria.

- Designation: Cement CPJ, CEM II/A 42.5.
- Production: Cement factory of Ain Touta, Department of Batna, Algeria.
- Specific gravity = 3100 kg/m³
- Specific Surface (Blaine) = 3200 cm²/g

Table 1. Chemical composition of clinker

Components	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**L.I.**
%	64.36	22.0	5.02	2.94	2.07	1.94	0.64

Table 2. Mineralogical composition of clinker (Bogue)

Minerals	**C_3S**	**C_2S**	**C_3A**	**C_4AF**
%	51.28	24.68	8.33	8.94

3.2 Sand

Current sand of river used for the manufacturing of the ordinary concretes in Algeria.

- Designation: Sand of river.
- Origin: Lioua Department of Biskra, Algeria.
- Specific gravity = 2600 kg/m³
- Fineness modulus = 2.5
- Equivalent of sand = 78 %

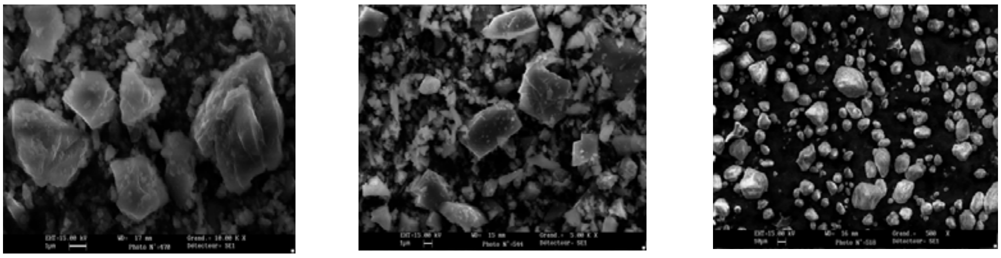
3.3 Admixtures

For this study, we considered four fine admixtures (three kind of limestone different by their smoothness, and one quartz) and one ultra fine admixture (Silica fume) currently used for new concretes in developed countries.

The limestone admixtures are obtained from the crushing of a natural calcite layer crystallized with more than 99 %. Their particles are rather of polyhydric form without grooves nor arises, comparable to round forms (Figure 1a).

The admixture of quartz is obtained from the crushing of a quartzes sand layer. Its particles are of an angular form and their surface present of grooves and arises (Figure 1b).

The silica fume is obtained from the arc furnaces of the ferro-silicon industry. It consists of submicron spheroids of amorphous silica condensed in agglomerates of some micrometers (Figure 1c)



a. Limestone b. Quartz c. Silica fume

Figure 1. Morphology of the studied admixtures grains

Table 3. Physical characteristics of the admixtures

Admixture	**Designation**	**Specific gravity (Kg/m^3)**	**Specific Surface Blaine (cm^2/g)**
Limestone 1	Ca1	2700	18500
Limestone 2	Ca2	2700	10500
Limestone 3	Ca3	2700	8000
Quartz	QZ	2650	11200
Silica fume	SF	2240	15 (*)

(*): The smoothness of the silica fume was provided by the BET test and was given in m^2/g.

3.4 Superplasticizer

In order to provide the various mortars with admixtures the reference workability in maintaining a constant quantity of water for all the formulations, it was necessary to use a superplasticizer high water reducer containing sulfonic polynaphthalene (MEDAPLAST SP 40), used in aqueous form, manufactured and marketed in Algeria.

Table 4. Chemical compositions of the admixtures

Admixtures	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**K_2O**	**L.I.**
Limestone	55.5	-	-	0.03	0.8	-	43.6
Quartz	0.03	98.9	0.6	0.06	-	0.35	-
Silica Fume	20	79	-	-	-	-	1

Table 5. Characteristics of the used superplasticizer

Characteristics	Form	Density	pH	Chlorine	Dry extract
SP 40	Liquid	1.22±0.01	8.2	< 1 g/l	40 %

4. TESTS AND RESULTS

4.1 Making of the Mortar of Reference

A mortar of reference is made on the basis of the composition of the normal mortar defined by NF EN 196.1 standard, by using 450 g of cement, 1350 g of ordinary sand (0-5) instead of standardized sand and a quantity of water lower than that recommended by the standard so that all the formulations require a certain quantity of superplasticizer to obtain the reference workability.

The reference workability was selected equal to a spreading of 111±1 mm on the vibrating table, which required a quantity of water equal to 164 ml and a quantity of superplasticizer equal to 3.62 kg/m^3 in the making of the mortar of reference.

The results obtained for the mortar of reference are:

- Compressive strength at 07 days: Rc_7 = 39.25 MPa
- Compressive strength at 28 days: Rc_{28} = 56.68 MPa

4.2 Effect of the Admixtures on the Superplasticiser Requirement of Mortars

The analysis of figure 2 shows that the variation of the superplasticizer requirement for the mortars with admixtures varies appreciably with the quantity, the mineralogical nature and the granular characteristics of the built-in admixture. For the studied mortars with fine admixtures (Ca1, Ca2, Ca3 and Qz), the superplasticizer requirement is more or less close to that of the mortar of reference and remains weaker for rates of the cement substitution lower than 17 %. This reduction indicates an optimization of the space arrangement of the particles in the mixture and/or a reduction of the inter-particulates frictions. In this case the fine particles present a favourable granular effect while succeeding in dispersing and placing themselves in the vacuums of the Granular structure . But the mortar with silica fume (ultra fine admixture), presents the strongest superplasticizer requirements in agreement with its large smoothness. This increase in the superplasticizer requirement can be allotted to the phenomenon of flocculation which requires significant quantities of additives to lubricate the whole of the ultra fine particles and to ensure their dispersion in the granular structure. In this case the ultra fine particles present an unfavourable granular effect. This difference in behaviour confirms the results of several works [9,12,14].

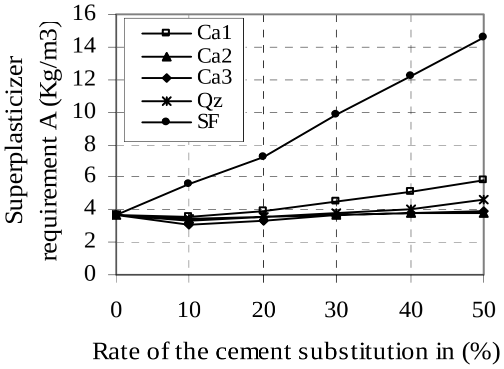


Figure 2. Variation of the superplasticizer requirement of mortars having constant workability

It is also noticed that, the superplasticizer requirement for the three kind of limestone admixtures is more important as the smoothness is large and that with comparable smoothness, the superplasticizer requirement of the particles of quartz of angular form (irregular morphology: Figure 1b) is more significant than that of the limestone particles of almost round form (regular morphology: Figure 1a). These conclusions join the results of certain researchers who considered the morphology of the particles of admixtures [9,15].

4.3 Effect of the Admixtures on the Mechanical Strengths of Moratrs

The analysis of figures 3 and 4 shows that for the studied fine admixtures (Ca1, Ca2, Ca3 and Qz), the variation of the relative strength at 07 days grows for the weak rates of substitution and reaches a maximum in the vicinity of 10 % of the rate of the cement substitution, then starts to decrease. For the mortar with silica fume (ultra fine admixture), it decreases directly without any improvement, but become more significant than that of the fine mineral admixtures, at strong rates of the cement substitution.

The improvement of the strengths at 07 days for the fine admixtures which reaches rates of 18, 12, 08 and 06 % for the mortars with Ca1, Ca2, Ca3 and Qz respectively didn't reproduce for the strengths at 28 days and all of them are decreasing. For the mortar with silica fume, the relative strength presents an improvement of 15 % in the vicinity of 10 % of the rate of the cement substitution.

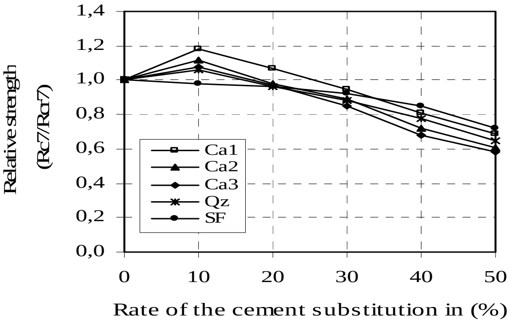


Figure 3. Variation of the relative compressive strength at 07 days for mortars having constant workability

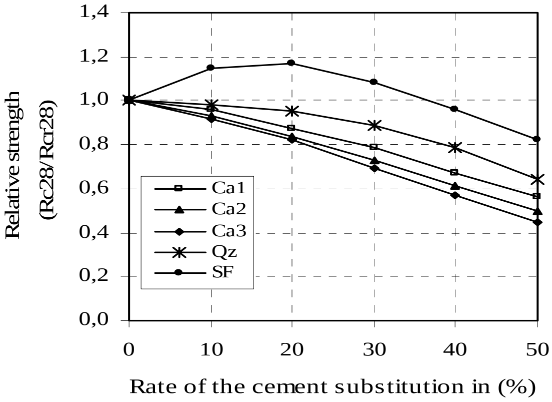


Figure 4. Variation of the relative compressive strength at 28 days for mortars having constant workability

We can thus deduce that the action of the fine admixtures on the cement is limited to an acceleration of the process of hydration at the youth ages. This acceleration is more or less equivalent for all of them and it is stronger as the particles are fine; but becomes negligible at 28 days of age. The opposite action of the silica fume is probably due to the relatively late pozzolanic reactions with the cement.

This analysis confirms the results obtained by several studies on the limestone admixtures [16], and on the siliceous admixtures [2,7,17,18]; because, for the limestone admixtures, the presence of the carbonate of calcium ($CaCO_3$) make better the hydration of the C_3S at the first moments, especially when the particles are fine and the quantity of $CaCO_3$ is large. In addition, the calcite ($CaCO_3$) reacts with the aluminates of cement in presence of water to form a hydrated mono-carboaluminate of calcium. For the siliceous admixtures, the quartz particles constitute preferential sites of nucleation especially for the crystallization of the crystals of portlandite. For the silica fume, the amorphous silica reacts chemically in the presence of water with the formed portlandite during the hydration of cement to form the hydrated silicate of calcium.

4.4 Evaluation of the Chemical Reactivity of the Admixtures in Mortars

The analysis of figures 5 and 6 makes possible to note that the coefficients of reactivity of the studied admixtures are very variable and depend on their mineralogical and chemical nature, the rate of the cement substitution and the age of the mortar with admixtures. Indeed the coefficients of reactivity of the silica fume increase with time whereas they decrease for all the other studied admixtures. These coefficients of reactivity present maximal values at 10 % of the rate of the cement substitution by reaching 2.69 for the limestone admixtures at 07 days and 2.94 for the silica fume at 28 days, and minimal values at 50 % of the rate of the cement substitution. At 7 days and at weak rate of the cement substitution, the limestone admixtures present the most significant coefficients of reactivity and are stronger as their smoothness is large. At more significant rates of the cement substitution, the silica fume becomes more active chemically and the quartz presents intermediate coefficients of reactivity between the calcites and the silica fume. At 28 days, the silica fume presents more significant coefficients of reactivity than those of the limestone admixtures which are stronger as the smoothness is large. The quartz presents intermediate coefficients of reactivity between the silica fume and the calcites.

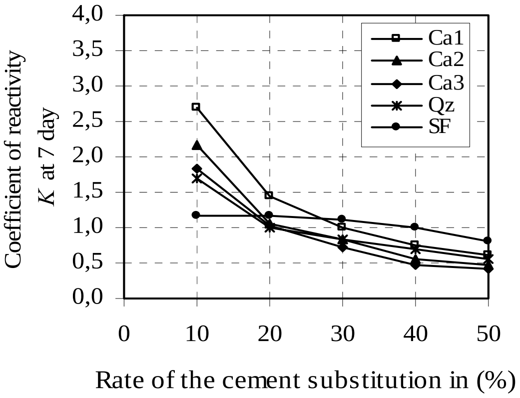


Figure 5. Variation of the coefficient of reactivity at 07 days, calculated on the basis of the predictive model of Bolomey for mortars having constant workability

It thus results that the coefficients of reactivity of the studied admixtures are very sensitive to the parameters of formulation of the mortars (nature, proportions and time) and consequently these analysis differ from the concept of the equivalent binder recommended by the standard of the ready-mixed concretes which are based on a coefficient of reactivity with contractual values.

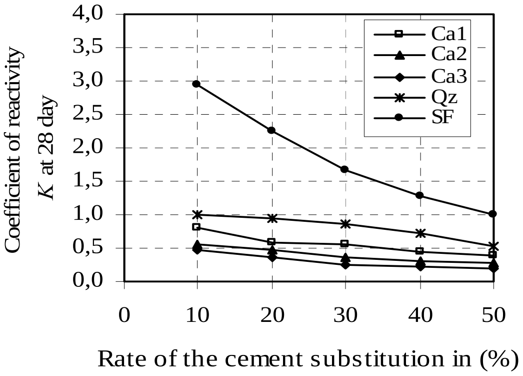


Figure 6. Variation of the coefficient of reactivity at 28 days, calculated on the basis of the predictive model of Bolomey for mortars having constant workability

5. CONCLUSIONS

The approach used made possible to distinctly quantify the chemical contribution of admixtures on mortars. It consists of the progressive volume substitution of the cement by the admixtures in mortars of which the workability and the absolute volume of the whole constituent phases (solid components and water) are preserved constant.

The analysis of the variation of the superplasticizer requirement showed that:

- The superplasticizer requirement varies appreciably with the quantity, mineralogical nature and the granular characteristics of the built-in admixture.
- The fine particles present a favourable granular effect at weak rates of the cement substitution, whereas the ultra fine particles present an unfavourable granular effect.
- The superplasticizer requirement is more important as the smoothness of the admixture is large.
- The superplasticizer requirement is more important as the particles of admixtures are of irregular morphology.

The analysis of the variation of the relative strength showed that:

- The action of the fine admixtures on the cement is limited to an acceleration of the process of hydration at the youth ages, and it is more or less equivalent for all of them.
- The opposite action of the silica fume (ultra fine admixture) is probably due to the relatively late pozzolanic reactions with the cement.

The specific chemical action to each admixture had been evaluated by analyzing the variation of the coefficient of reactivity K, by applying the concept of the equivalent binder and by deducing the coefficient of reactivity K from the predictive model of Bolomey. The analysis of the variation of the coefficients of reactivity shows that:

- The coefficients of reactivity are very sensitive to the parameters of formulation of the mortars and depend on their mineralogical and chemical nature, the rate of the cement substitution and the age of the mortar with admixtures.
- Consequently, the coefficients of reactivity differ from the concept of the equivalent binder recommended by the standard of the ready-mixed concretes which are based on a coefficient of reactivity with contractual values.

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