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The effect of fine mineral admixtures on water requirement of cement pastes

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Abstract

This paper deals with the effect of granular characteristics of fine minerals admixtures on the water requirement of a cement paste for constant workability without water-reducing admixtures. The contribution of the fine mineral admixtures in the granular packing is appraised by the variation of the water requirement as a function of the replacement of cement by the admixtures in the paste up to 100%. The water requirement of neat fine mineral admixture paste follows an increasing trend towards specific surface area. However, the irregular morphology of particles of some admixtures increases significantly the water requirements. For very low proportion of cement in the paste, the water requirement and, consequently, the porosity increase significantly in comparison to that measured on neat fine mineral paste preventing any optimization of the water requirement. Only admixtures with large particle size distribution could reduce the water requirement of blended cement pastes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Workability; Particle size distribution; Surface area; Mineral admixture; Cement paste

1. Introduction

The use of high-range water reducers (superplasticizers), condensed silica fume and other fine mineral admixtures has led to mix designs for high-strength concrete. Since condensed silica fume and fine mineral admixtures fill the porosity of the granular skeleton of the concrete, they improve the binding action of cement. However, most mix design methods for high-strength and ordinary concrete are not able to optimize the choice of the fine mineral admixtures and their proportioning in the mixtures. With the exception of condensed silica fume, the mineralogical, textural, and granular characteristics of the fine mineral admixtures are not taken into account in mix design [1]. Their use in concrete is based generally on trial and error, often leading to an excess of superplasticizer amount. Otherwise, it is believed that the presence of fine minerals could produce significant loss of workability or significant increase in the water quantity and consequently decrease in the concrete density [1].

As a first step to appraise the actual effect of fine mineral admixtures on concrete, the water requirement in cement pastes of fixed workability without use of superplasticizer is studied. The purpose is to define an overall criterion for the use of fine mineral admixtures in concrete. The results are compared to literature data.

2. Materials

For the experimental study, 14 fine mineral admixtures, different in origin, mineralogy, and fineness, were tested. Two common French cements are used (Table 1). The average particle size of the fine minerals varies between 0.07 and 60 μm, with Brunauer–Emmet–Teller (BET) specific surface areas between 0.3 and 40 m^2/g. Three groups may be distinguished as follows.

2.1. The natural carbonates

Calcite (CA1, CA3, and CA5), chalk (CH08, CH3, CH5, and CH60) and dolomite (DL3) are included. CA1, CA3,

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Table 1
Characteristics of fine mineral admixtures and cements

Fine mineral admixture	Origin	Mineral composition	Absolute density [kg/m^3]	Average particle size [μm]	BET specific surface area [m^2/g]
CA1	natural	calcite	2700	1.50	7.0
CA3	natural	calcite	2700	3.00	3.3
CA5	natural	calcite	2700	5.00	2.5
CH08	natural	chalk	2700	0.08	6.0
CH3	natural	chalk	2700	3.00	2.0
CH5	natural	chalk	2700	5.00	1.7
CH60	natural	chalk	2700	60.00	–
DL3	natural	dolomite	2860	2.50	4.5
QZ2	natural	quartz	2650	2.20	3.5
QZ50	natural	quartz	2650	53.00	0.3
DT12	natural	diatomite	2140	12.00	40.0
KA1	industrial	treated kaolin	2200	1.50	17.0
CP01	industrial	calcium carbonate	2710	0.07	20.0
SF01	industrial	silica fume	2340	0.15	15.0

Cement	Type	Absolute density [kg/m^3]	BET specific surface area [m^2/g]
CEM I	CEM I 52.5	3150	0.7
CEM II	CEM II/B 32.5	3100	1.0

and CA5 are derived from the same sedimentary limestone, with a crystallisation rate of 99%. Their average particle sizes are, respectively, 1.5, 3, and 5 μm. CH08, CH3, CH5, and CH60 are constituted of sedimentary cryptocrystalline fossil of coccoliths. Their average particle size varies between 0.8 and 60 μm. DL3 has the same average particle size as CA3 and CH3 and a similar specific surface area.

2.2. The natural silicates

Well-crystallized quartz (QZ2 and QZ50) derived from the same deposit and a natural diatomite (DT12) are included. Their particle size and specific surface area vary substantially.

2.3. The industrial admixtures

Thermally treated kaolin clay (KA1) and carbonate precipitate (CP01) obtained from a controlled reaction between CO_2 and $Ca(OH)_2$ producing very fine particles (average particle size of 0.07 μm), are included. A condensed silica fume (SF01), composed of amorphous silica and commercialized as admixture for high-strength concrete, was used. The specific surface area of silica fume is close to that of the carbonate precipitate and the treated kaolin.

Two common French cements, CPA-CEM I 52.5 and CPJ-CEM II/B 32.5, according to European standards were used for the tests. CEM II is blended 25% by mass carbonate filler.

3. Methods

According to European standard EN-196.3, the water requirement of the cement is determined as necessary quantity to obtain a neat cement paste of standard consistency. The standard consistency is obtained when the 10-mm needle of the Vicat apparatus penetrates 34 ± 1 mm into the paste. The same method was used to measure the water requirement of the fine minerals and of the mixtures with cement.

The water requirement of the pastes is determined as the ratio of W/C when only cement is used in the paste, as W/F when only fine mineral admixture is used in the paste, and as $W/(C+F)$ when the fine mineral admixture is mixed with cement, where:

W is the water content by volume of the paste for standard consistency;
C is the cement content by volume of the paste; and
F is the fine mineral content by volume of the paste.

The proportion in percentage of fine mineral in the cement paste is determined by the volume ratio $F/(C+F)$ in percentage. All the fine mineral admixtures were tested in various proportions from 0% to 100%. In order to appraise the packing effect of the fine mineral admixture, the absolute volume of solids in the pastes is kept constant.

Also determined was the porosity of the pastes as the ratio of the absolute volume of solid to the apparent volume of the paste.

4. Results and discussion

4.1. Influence of granular characteristics of the fine mineral admixtures

The water requirement and the porosity, as measured on a 100% fine mineral admixture paste, are shown in Table 2

Table 2
Water requirement and porosity of fine mineral admixture and cement pastes

Fine mineral	*W*/*F* [v/v]	Porosity [%]
CA1	0.89	49
CA3	0.84	48
CA5	0.79	46
CH08	0.90	49
CH3	0.72	44
CH5	0.59	39
CH60	0.77	44
DL3	0.93	50
QZ2	1.09	55
QZ50	0.67	43
DT12	4.19	82
KA1	2.12	69
CP01	2.06	68
SF01	1.39	62
Cement	***W*/*C* [v/v]**	**Porosity [%]**
CEM I	0.91	49
CEM II	0.79	47

and compared to those obtained on 100% cement paste. This comparison leads to the classification of the fine mineral admixtures in three groups:

- fine mineral admixtures with water requirement lower than cement, in the order CH5, QZ50, CH3, and CH60;
- fine mineral admixtures with water requirement similar to cement as CA5, CA3, CA1, and CH08; and
- fine mineral admixtures with water requirement higher than cement, in the order DL3, QZ2, SF01, CP01, KA1, and DT12.

This classification of the water requirements of the fine mineral admixtures could not be correlated with the mineralogy or the average size of particles (Fig. 1). Natural fine minerals have water requirement decreasing with the average size of particles (with an exception for CH60), but industrial fine minerals as such SF01, KA1, and DT12 follow an opposite trend. Considering the porosity of the pastes (Table 2), the correlation is weaker.

The relation between the water requirement and the BET specific surface area (Fig. 2) shows an increasing trend. Generally speaking, water requirement is increasing with the specific surface area. But this tendency is not strong enough to assess the water requirement of fine mineral admixtures in pastes. Other parameters, like the morphological character of the mineral admixtures (particle shape and surface texture), should be taken into account.

4.2. Influence of morphological characteristics of the fine mineral admixtures

Aoune-Seghir et al. [2] have shown that fine mineral admixtures for concrete could be classified in three morphological categories according to their shape: rounded, angular, and irregular.

In this case, the natural carbonates (CA, CH, and DL series) and the silica fume (SF01) are round-shaped and close to spherical-shaped. They show the lowest water requirements because of the small roughness of the surface diminishing the friction between particles. So the packing of particles in the paste is denser in this case.

On the contrary, irregular-shaped particles of diatomite (DT12), and, to a lesser extent, industrial calcium carbonate (CP01) and treated kaolin (KA1) have high water requirements. Water requirement of diatomite is six times higher than that of natural carbonates with the same range of particle size. It is two times more important than that of the other industrial admixtures as CP01 and KA1 with close-set specific surface area. The irregular-shaped particles of diatomite create low-density structures leading to very high water requirement. Angular-shaped quartz parti-

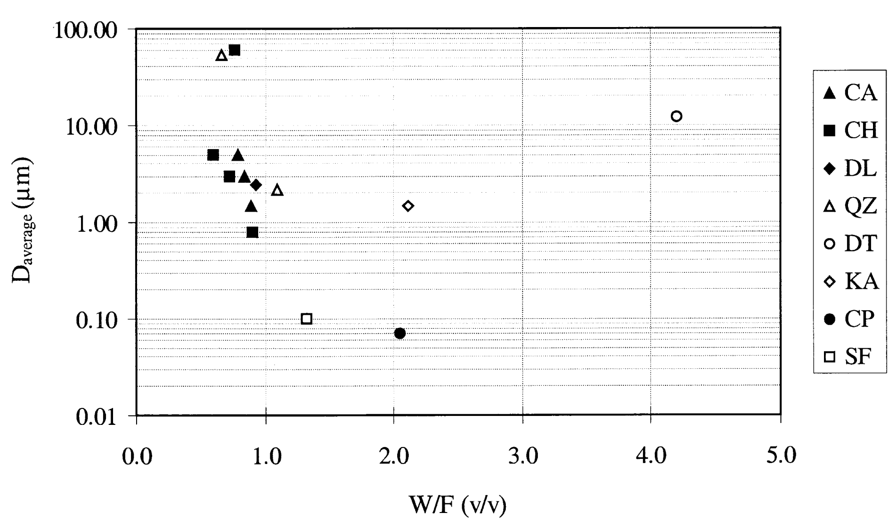

Fig. 1. Water requirement of fine mineral pastes vs. average size of particles.

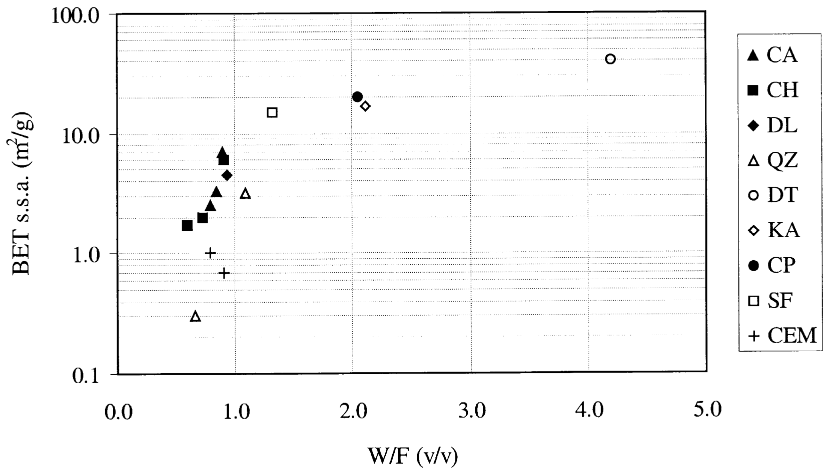

Fig. 2. Water requirement of fine mineral pastes vs. BET specific surface area.

cles (QZ2, QZ50) have an intermediate behavior. Cement particles, with angular-shaped particles, have a behavior similar to quartz.

A compilation of 30 published experimental data [3–5] in Fig. 3 confirms that the morphological classification of the fine mineral admixtures determines three independent areas corresponding to the water requirement values. The water requirements of round-shaped and angular-shaped admixtures present a strong correlation with the BET specific surface area of the particles. This is not true for irregular-shaped particles.

4.3. Water requirement optimization

Geometric packing models [6,7] foresee denser arrangement of fine particles with significant difference on granular grading in good accordance with experimental data on pastes and mortars [8,9]. The finest particles fill the voids between the coarsest particles. Optimum packing is obtained for fixed proportions. Mixtures of two mineral admixtures at varying proportions were characterized with the aim to determine influence of optimum packing on water requirement. QZ50 and CH3 with water requirement lower than cement and CA5 with equal to CEM II water requirement were selected (Fig. 4). The results show that a minimum water requirement for the proportions of 60% QZ50 + 40% CH3 and 70% QZ50 + 30% CA5 is obtained for the mixtures of the finest CH3 or CA5, with the coarsest QZ50. These optima blends are called OptA and OptB, respectively. Their calculated specific surface area is about 1 m^2/g similar to CEM II cement, but the water requirement is about 40% lower than CEM II in the first case and 30% in the second, showing that a large particle size distribution reduces water requirement.

On the other hand, the results show (Fig. 4) that when the fineness of the fine minerals are equivalent, as the case of

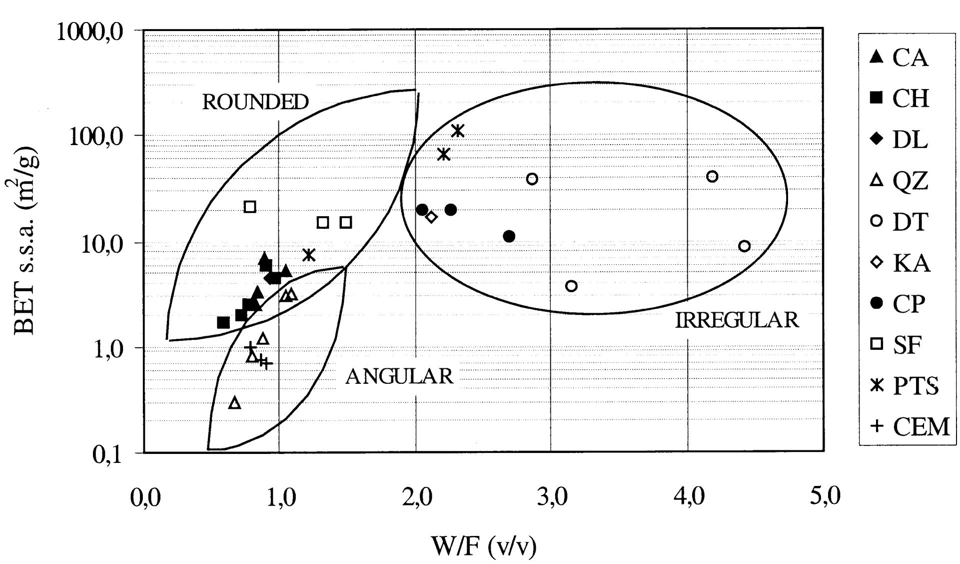

Fig. 3. Influence of the morphological classification in the variation of the water requirement of fine minerals as a function of the BET specific surface area.

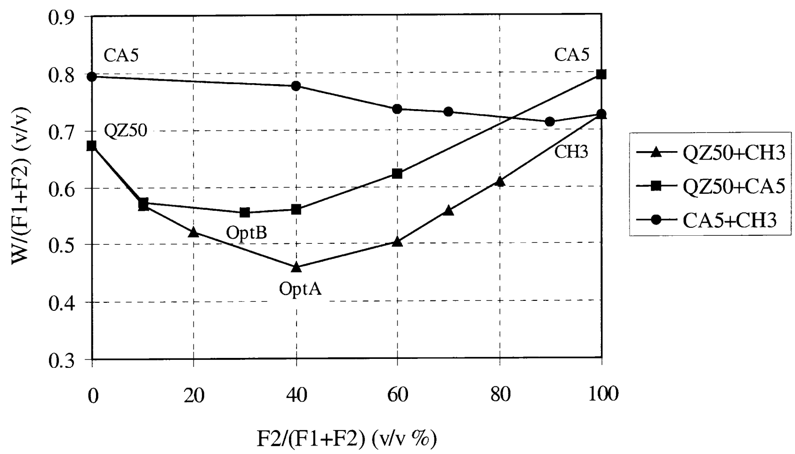

Fig. 4. Water requirement of pastes with two fine minerals as a function of proportioning.

the CA5–CH3 mixture, the water requirement does not change significantly for the blends. The mix of granular materials with similar sizes of particles cannot lead to a denser arrangement.

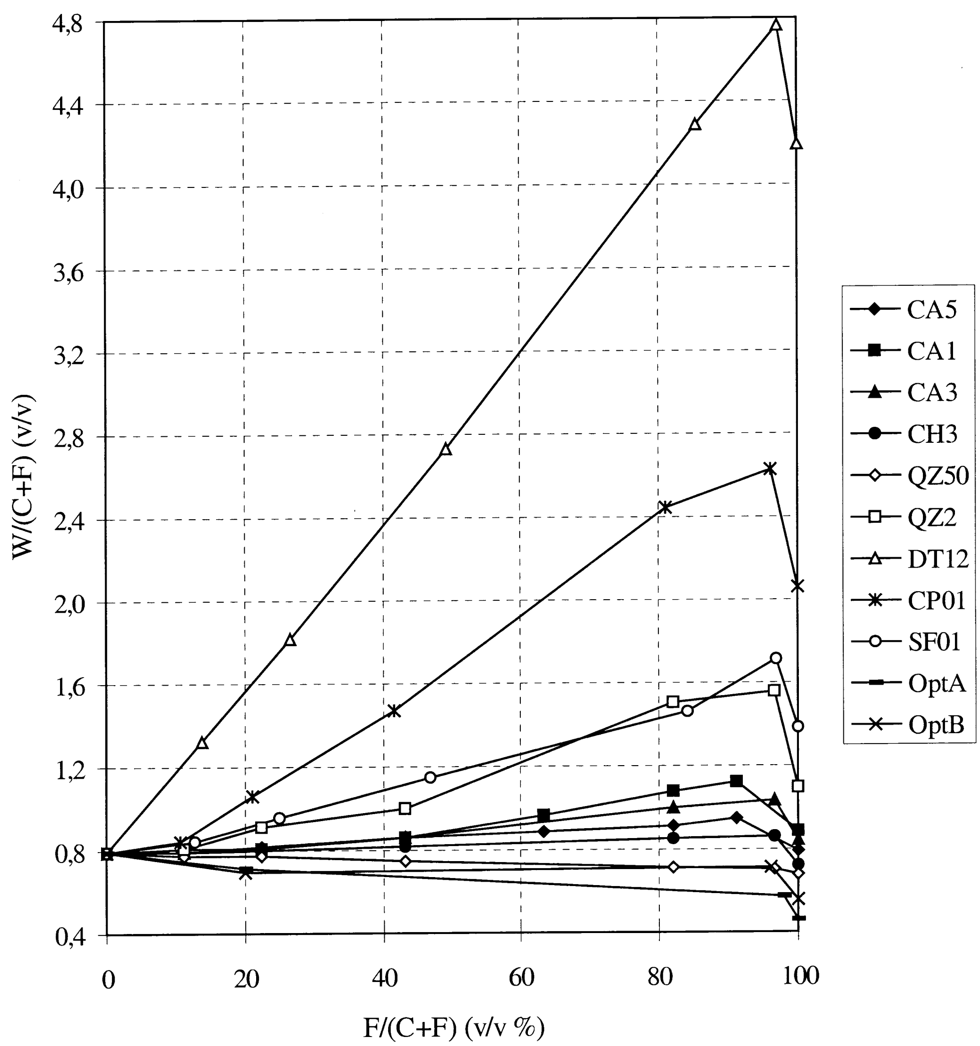

Fig. 5. Water requirement of CEM II cement pastes as a function of the fine mineral admixture proportion.

4.4. Effect of the fine mineral admixtures on the cement pastes

Fig. 5 shows the variation of the water requirements of pastes with CEM II cement as a function of the increasing proportion of the fine mineral admixture.

The results show that cement fine mineral admixture blended mixtures do not present any optimization of the water requirement. On the contrary, the water requirement is higher than expected regarding the proportion of cement and fine mineral admixture and the water requirement of neat pastes. The difference between the experimental data and the linear behavior of the water requirement between neat cement paste and neat fine mineral admixture paste is more important for high mineral admixture proportion with a maximum in the range of 90–98%.

This particular behavior of fine mineral admixture cement pastes follows a trend opposite to the geometrical packing models valid in the case of two fine mineral admixture mixtures as seen before (Fig. 4). The looser arrangement of the particles in the cement-blended pastes probably results from the repulsion between particles or gathered particles in the absence of superplasticizer. It seems that the finest particles (of the fine mineral admixture, in general) do not fill the voids between the coarser particles (of cement) in the paste.

In the case of optimized blends of fine mineral admixtures (OptA and OptB), the water requirement in the presence of cement is lesser than that observed for each of their components. The advantage of the denser packing of the optimized admixture is maintained. However, for high proportioning of optimized admixture, the water requirement of the paste presents the same particular behavior as in the case of the other fine mineral admixtures.

The water requirement of mixtures with low fine mineral proportion, corresponding to usual field concrete mixture, is controlled by the excess in water requirement observed for high fine mineral proportion in the paste. The results show that up to 20% fine mineral admixture, the water requirement of the paste could be approached by the linear behavior of the water requirement between neat cement paste and neat fine mineral admixture paste. Beyond 20%, the water requirement of the paste is higher than the linear behavior between neat pastes; the resulting excess of porosity could have disastrous consequences on mechanical and physical performances of the mixture.

By changing the cement type (CEM I instead of CEM II), the water requirement of pastes varies in the same way. It seems that the cement type has no major influence on the loose particle arrangement in the pastes. However, the presence of cement is the essential factor determining the very loose granular packing of mixtures with high fine mineral proportion.

Kara-Ali and Gallias [10,11] have shown that the low density of the packing for high proportion of fine mineral admixture is independent of the experimental methodology and of the consistency of the mixtures.

5. Conclusions

The water requirement of fine minerals is the main factor for their use as admixture in concrete without superplasticizer. The specific surface area of the admixture is the major granular parameter to evaluate the water requirement, but not enough to explain the measured differences. The morphology (shape and texture) of the particles has to be taken in account. Irregular-shaped particles require two to four times higher the amount of water than rounded or subangular-shaped ones. Increased particle size distribution of fine minerals blended mixtures leads to denser packing and optimized water requirement.

The water requirement of cementitious pastes is higher than expected regarding the proportion of cement, of fine mineral admixture, and the water requirement of neat pastes. The excess in water requirement is very significant for high proportion of fine mineral admixture resulting probably from the repulsion between particles. The water requirement of mixtures with low fine mineral proportion, corresponding to usual field concrete mixture, is controlled by the excess in water requirement observed for high fine mineral proportion in the paste. Without superplasticizer, the fine mineral admixtures do not contribute to a denser granular packing of the cementitious matrix.

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