Cement Additives Division

Strategies for the improvement of the cement workability

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Abstract

Everyone working in the construction industry knows very well which characteristics a good cement should have: compressive strengths that satisfy the correct standard and good workability. This term usually determines the ease of mixing and compaction of concrete and mortar. A cement with low mortar workability is not the best starting point for obtaining a concrete with the correct slump class with an acceptable quantity of water. On the other hand, the optimization of workability of cement simplifies the mix design of concrete. In this paper the main factors that can have negative influence on cements workability are reviewed and several strategies for the improvement of water request are described.

Introduction

From a practical point of view the workability of cements is measured in mortar through the flow determination. While flow is not usually included in hydraulic cement specifications, it is commonly used in standard tests that require the mortar to have a water content that provides a specified flow level and several test method (such as ASTM C1437 or EN 1015) are available. Regardless to possible differences in the expression of results or testing equipment, all the methods measure the ability of a mortar to spread over a surface. Alternatively, the amount of water needed to have a cement paste with the right consistency (measured through the penetration of a needle in a fresh cement paste) is another common way to assess the water request of cement (as described in ASTM C187 or EN 196-3).

Whatever is the method of practical evaluation, the workability and water request are directly linked to the early hydration behavior and to other characteristics such as particle size distribution. The presence of secondary additions (for example in pozzolan or fly ash blended cements) is another reason that can lead to workability decrease.

Factors influencing workability

The main factors influencing workability of cements are listed and described here below. Several times the reason for abnormal water request is a combination of different factors, rather than a single one.

Clinker reactivity

Early hydration of Portland cements is characterized by aluminate phases, basically C_3A. The reaction of tricalcium aluminate with water gives a wide range of products usually referred as calcium aluminate hydrates (C-A-H). The morphology, crystal structure and composition of these products can be very different, but generally they have a high water content and precipitate as a large plates on the grain surface giving workability decrease or other negative phenomena such as flash set. In figure 1 an images of C-A-H collected with Environmental Scanning Electronic Microscope (ESEM) is reported.

If sufficient gypsum is present, ettringite is the main hydration product. In favorable conditions, ettringite precipitates as a thin layer on the surface of clinker grains controlling clinker hydration and giving the best conditions for workability control.

In order to have the best workability, sulphate supply during clinker hydration should be optimized, especially in presence of clinker with high amounts of C_3A (evaluated through quantitative X-Ray diffraction analysis) and high fineness.

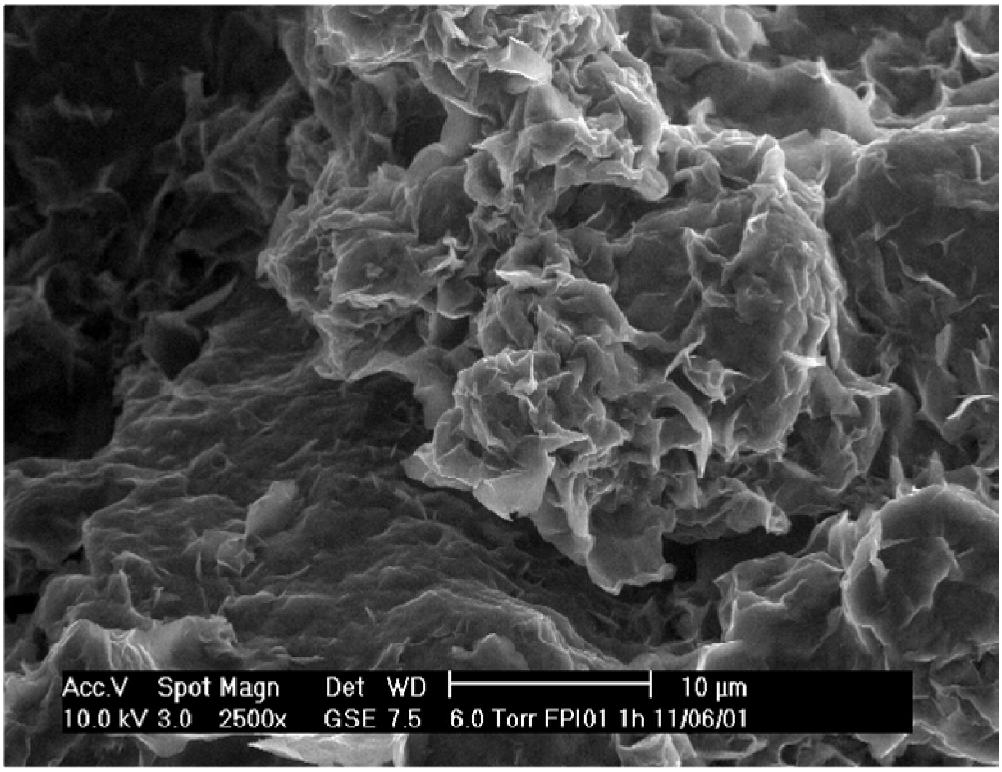


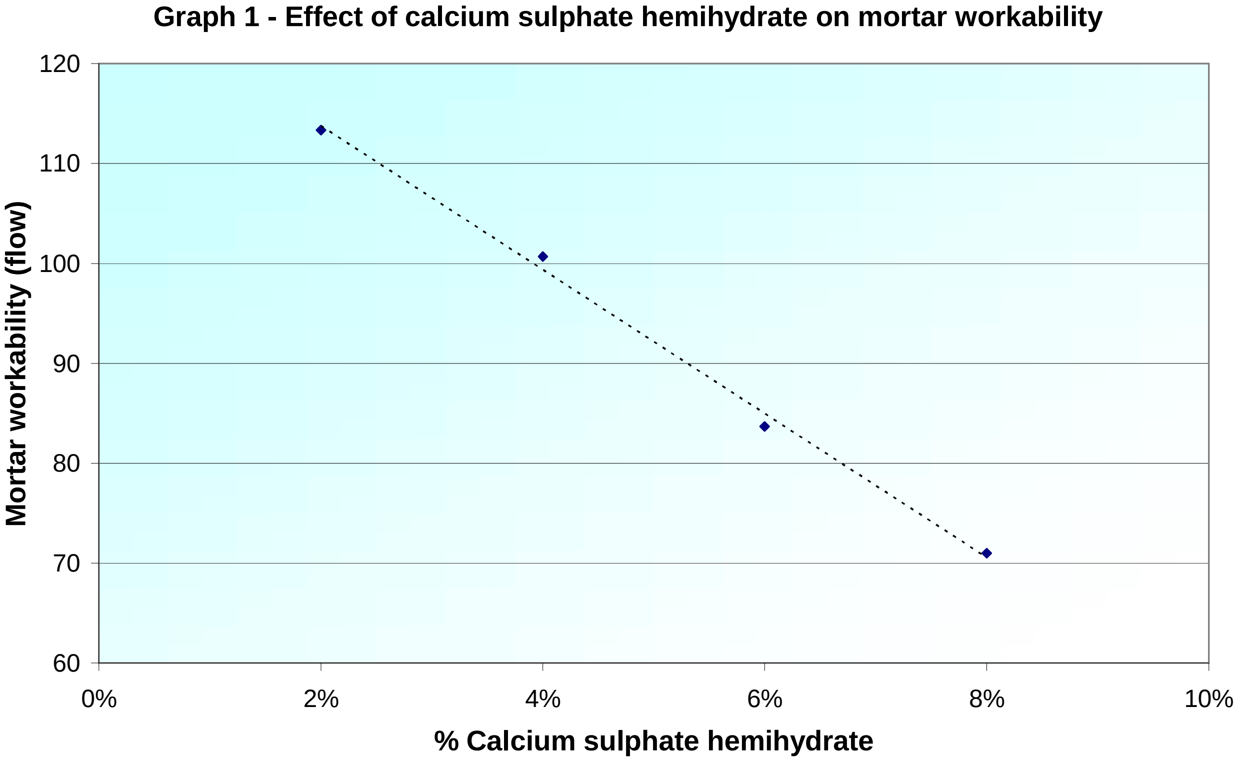
Figure 1: ESEM images of hexagonal hydrates on C_3A surface

Type of calcium sulphate

Calcium sulphate is added to cement with the purpose to control clinker reactivity. Sulphate ions react with calcium and aluminium coming from aluminate phases giving precipitation of ettringite on clinker grains slowing down the hydration and controlling the setting time.
Several forms of calcium sulphate exists:

- gypsum (calcium sulphate bihydrate $CaSO_4 \cdot 2H_2O$)
- bassanite (calcium sulphate hemihydrate $CaSO_4 \cdot 0{,}5H_2O$)
- anhydrite (anhydrous calcium sulphate $CaSO_4$)

Depending on temperature/humidity inside the mill, gypsum can lose water being converted to other forms. Among them, calcium sulphate hemihydrate is characterized by a higher immediate solubility: higher amounts of sulphate are supplied during clinker hydration. Sulphate in excess with respect to hydrating calcium aluminate precipitates as secondary gypsum, rather than producing ettringite. Secondary gypsum absorbs water reducing fluidity and increase viscosity due to the particular shape of secondary gypsum crystals [1]. The quantification of hemihydrate in cements requires specific X-ray diffraction analysis.
In graph 1 the results of a test performed in our lab showing the effect of hemihydrate are reported. A clinker was ground to a constant fineness and mixed with different amounts of ground calcium sulphate hemihydrate, obtaining several cement samples whose mortar flow was evaluated. As the content of hemihydrate increases the flow decreases linearly.



Particle size distribution

The expression particle size distribution (PSD) indicates the relative amount of each cement particle diameter. It is commonly evaluated through laser diffraction analysis and described with a graph reporting the % in volume or mass of each particle diameter. PSD can be narrow or broad, depending on relative diameter distribution: if dimensions of particles tend to extend over a short diameters interval (and thus particles have similar dimensions) the PSD is narrow. If there are higher relative amounts of fine and coarse particles the PSD is broad. The "broadness" or "narrowness" of a cement PSD is usually described with the uniformity constant, a parameter obtained from specific mathematical modeling, the most common being Rosin-Rammler-Bennet distribution [2]. Higher uniformity constant (narrow PSD) are associated to high water request. A simple model can explain the reason: if particle diameters tends to be similar there is a larger volume between particles that needs to be filled with water in order to get a movable paste. On the other hand, if there is a good proportion of fines and coarses the spaces between particles is lower and water requirement is lower [3].

Presence of mineral additions

The use of pozzolan or fly ash as mineral addition poses sometimes workability problems. Tuff or natural pozzolan cements, due to the higher porosity and to the ability of absorb water, represents a typical example of high water request binders. On the other hand, there are mineral additions (typical example is granulated blast furnace slag) with a positive effect of workability improvement.

Strategies to improve workability: the use of cement additives

Being related to several parameters (and sometimes to a combination of different parameters), the problem of high water request should be managed in several ways. Sometimes it is not practical to remove the reason for abnormal workability. For example, in case of high C_3A reactivity, the modification of clinker production or the coarse grinding of cement pose problems of kiln efficiency or lower cement performances. If particle size distribution is narrow, by reducing

the efficiency of separation it is possible to increase the amount of coarse particles and with overgrinding refinement (through an accurate control of recirculation) it is possible to increase the amount of fine material obtaining an improvement of water request. On the other hand this may have negative effect on strengths development.
The use of a cement additive is often the most simple way to eliminate the problem of a high water request. The advantages of the use of cement additives are the following:

- lower cost: in comparison to modifications in clinker production or in the use of secondary additions, the economical incidence of an additive on the cement produced is very low.

- Flexibility of use: while a modification of clinker chemistry or mechanical operations on the separator affect all the cements produced in the cement plant, a liquid additive can be used only on specific cements, where the workability problems are more evident.

- Possibility of having tailor made formulations: sometimes there is the need of a proper balance between retarding and dispersing effect and it is possible to formulate according to each specific case.

Cement additives with effect on workability can be divided in two main categories:

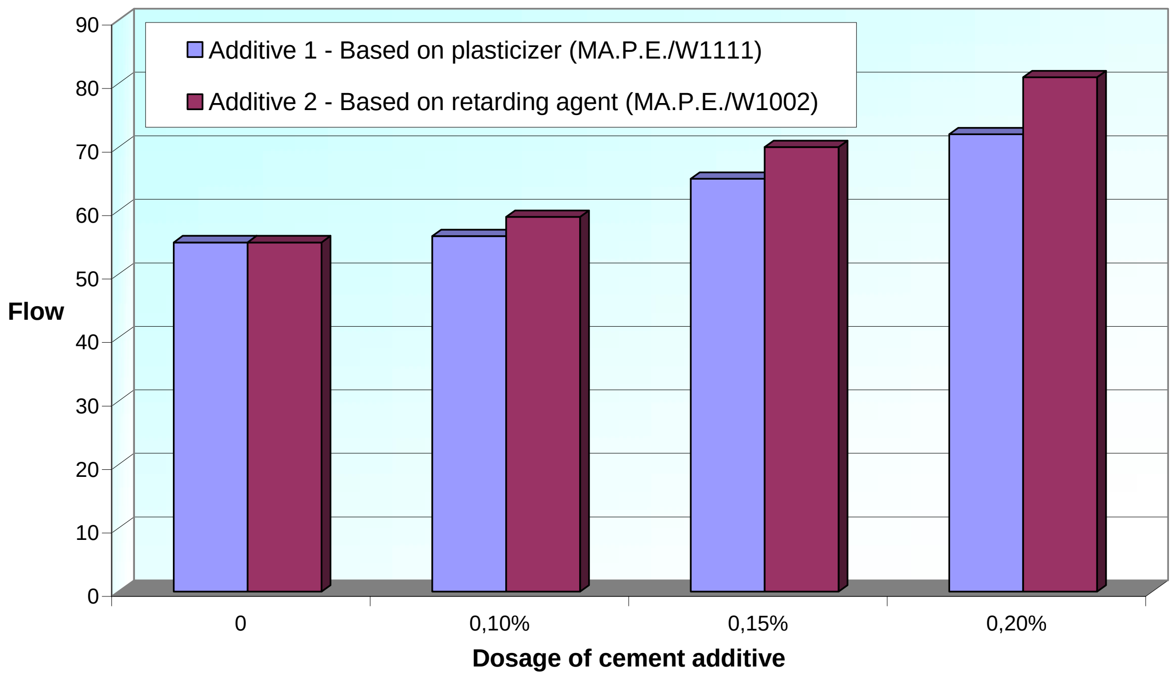
- dispersing agents, such as plasticizers/superplasticizers: the action is to disperse the flocculated cement particles through a mechanism of electrostatic repulsion. These additives are supposed to be adsorbed on to the cement particles, giving them a negative charge which leads to repulsion.

- retarding agents: their action is to slightly retard the hydration of aluminate phases, slowing the formation of calcium aluminate hydrates and allowing a high water amount available during the early hydration, thus improving workability.

Of course, different reasons for abnormal workability require different types of cement additives. In case of high reactivity of C_3A the use of dispersing agent can be useless, while the proper retarding agent can give interesting benefits. On the other hand, in case of not correct particle size distribution or in case of natural pozzolan the use of a dispersing agent is the most correct. The following example clarifies the situation.

Example
Graph 2 reports the results of an industrial test carried out on a type I cement characterized by high water request. X-Ray diffraction and laser diffractometry show that high water request is probably due basically to high clinker reactivity and also to a not optimized particle size distribution. Two additives were tested at different dosages: additive 1 (MA.P.E./W1111) based on a typical plasticizer and additive 2 (MA.P.E./W1002) with formulation corrected with the addition of a retarding agent. Results are reported in the graph 2 and show that the addition of a retarding agent in the formulation allows improvement of workability at dosages lower than pure plasticizer. This means that the clinker reactivity was the main factor and the use of retarding agent is crucial.

Graph 2 - Comparison of cement additives for flow improvement



The following table summarizes the reason for high water request of cements and the strategies for workability improvement.

Reason for high water request	Details	Evaluation methods	Strategies for workability improvement
Clinker reactivity	High C_3A levels, high fineness	Quantitative X-Ray Diffraction	Modification of clinker quality, gypsum optimization, use of suitable retarding additives
Type of calcium sulphate	Presence of calcium sulphate hemihydrate	Quantitative X-Ray Diffraction	Use of different gypsum sources, control of grinding temperature
Particle size distribution	Narrow particle size distribution	Laser diffraction analysis with calculation of RRB-line slope	Modifications in grinding/separation, use of suitable additives with dispersing/plasticizing effect
Mineral additions	High water request due to porosity or water absorption	-	Use of different secondary additions, use of suitable additives with dispersing/plasticizing effect

Conclusions

The water request of cements can be related to several factors ranging from clinker chemistry to particle size distribution and sometimes a combination of different parameters can not be excluded. The development of a specific cement additive for workability improvement should take into account a detailed investigation about the reasons of unusual water request and the proper balance between retarding and dispersing effect should be carefully investigated.

Bibliography

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