Influence of Grinding Aids

Matteo Magistri and Arianna Lo Presti, Mapei SpA, Italy, describe an X-ray diffraction experiment to study the effect of grinding aids on cement hydration.

Introduction

The use of grinding aids in cement production allows several advantages to be obtained, ranging from increased mill production, improvement of particle size distribution and reduction of pack-set[1]. It is also well known that several raw materials used in the formulation of a grinding aid have a strong chemical effect on cement hydration, leading to the possibility of formulating specific products for the enhancement of compressive strengths, the regulation of setting time and the improvement of workability. Despite its widespread use, the interactions between additive and cement hydration are not yet fully understood. Several papers have been published dealing with the effect of various chemicals[2,3].

From a kinetic point of view, the hydration of cement is often studied following the evolution of physical or chemical properties in time. In particular, the structural and microstructural modifications that take place when water gets in contact with cement are often investigated with X-ray powder diffraction (XRD), a powerful technique that helps to identify and quantify products that develop during the hydration process.

This article presents the results of an XRD experiment performed in order to understand how hydration is influenced by the presence of a grinding aid. The modification of the mineralogical composition of a Portland cement paste during the first 12 hours of hydration has been described and used to explain the observed improvement of mechanical strengths.

Experiment

Preparation of cement sample

An ordinary Portland cement (CEM I according to the European standard EN 197-1) was reproduced by grinding clinker and calcium sulfate (β–hemihydrate) in a laboratory ball mill to a given Blaine specific surface area. The characteristics of the prepared cement are reported in Table 1. The clinker was analysed by X-ray fluorescence and by X-ray diffraction/Rietveld refinement (GSAS software[4]). The chemical characterisation of clinker is reported in Table 2.

Mechanical tests

Compressive strengths after 24 and 48 hours of hydration have been evaluated according to European standard EN 196-1, without any additive and by adding in mixing water a typical grinding aid based on alkanolamines (0.05% on the weight of cement).

X-ray powder diffraction

The experiment was performed at the European Synchrotron Radiation Facility (ESRF) beamline BM08 (GILDA). The instrumentation has been described elsewhere in detail[5]. A sample of cement (100 g) was mixed with water (w/c = 0.4) and conserved in a sealed case, at a relative humidity of 100% and at room temperature. A second

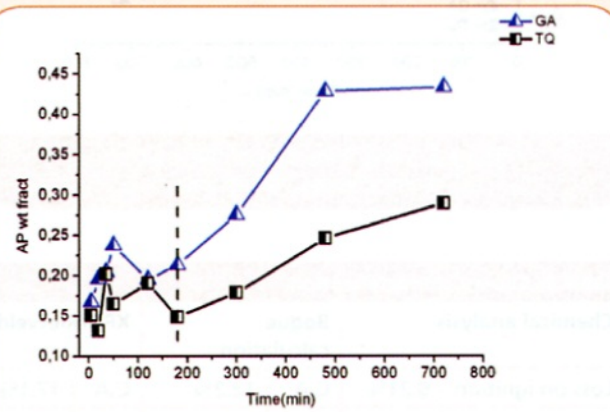

Figure 1. Weight fraction of amorphous phase versus time.

Table 1. Characteristics of prepared cement	
Cement composition	
Clinker	95%
Calcium sulphate (β–hemihydrate)	5%
Blaine specific surface (according to EN 196-6)	
375 m^2/kg	
Alpine granulometry	
Sieve	% residual
32 μm	16.5
40 μm	10.0
63 μm	3.0
90 μm	0.5
200 μm	0.0

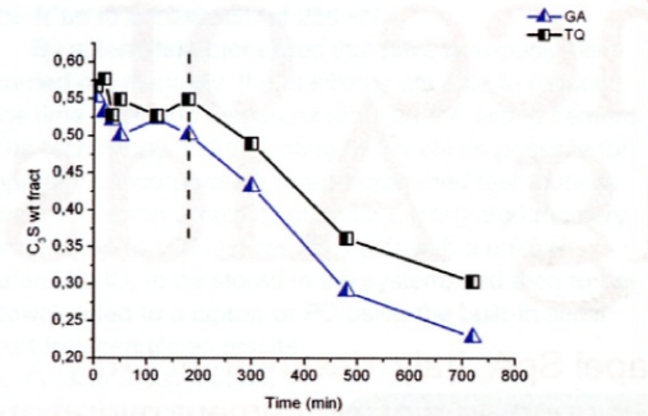

Figure 2. Weight fraction of tricalcium silicate versus time.

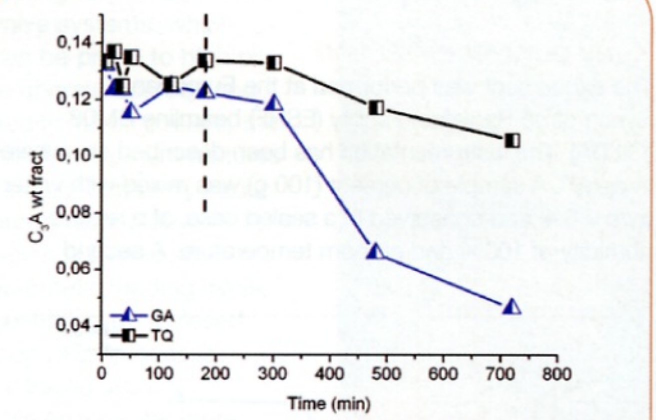

Figure 3. Weight fraction of tetracalcium aluminoferrite versus time.

Table 2. Clinker characterisation

Chemical analysis		Bogue calculation		XRD/Rietveld	
Loss on ignition	0.21%	C_3A	12.2%	C_3A	17.1%
SiO_2	20.60%	C_4AF	7.8%	C_4AF	2.2%
Al_2O_3	6.26%	C_3S	63.8%	C_3S	69.2%
Fe_2O_3	2.57%	C_2S	10.9%	C_2S	8.7%
CaO	65.83%				
MgO	1.30%				
Free CaO	0.46%				
SO_3	0.73%				

Table 3. Mechanical tests

	24 h compressive strengths (MPa)	% improvement
No additive	21.2	-
0.05% grinding aid	24.4	+ 15.1
	48 h compressive strengths (MPa)	% improvement
No additive	30.8	-
0.05% grinding aid	36.6	+ 18.8

sample was mixed with the same amount of water and with the grinding aid (0.05% on the weight of cement).

During a period of 12 hours, several samples were taken from both batches of cement and the X-ray diffraction patterns collected. The wavelength used was 0.489197 Å calibrated against standard LaB_6. The angular range explored was 1 - 32° 2 theta corresponding to a d-spacing interval of 14 - 0.89 Å.

The collected spectra were elaborated with Rietveld method using the GSAS software[4] to obtain quantitative information. The refinements were performed using structural models, for all the phases, taken from Inorganic Crystal Structure Database (ICSD).

Results and discussion

The results of mechanical tests are reported in Table 3. The alkanolamines based grinding aid has a positive effect on cement hydration and leads to an increase in mechanical strengths. This could be explained by taking into account the results of the XRD experiment.

It is known that during the first stages of hydration of a cement paste, both crystalline and amorphous phases occur[6]. In particular, the development of mechanical strengths is directly related to the hydration reaction of tricalcium silicate (C_3S), which leads to the formation of calcium hydroxide (Portlandite) and to a complex family of amorphous products usually called calcium silicates hydrate (C-S-H)[6]. X-ray powder diffraction is perhaps the most powerful method of obtaining quantitative phase information from multicomponent mixtures. Nevertheless, if an amorphous phase is present, it cannot be directly measured and all the results obtained are overestimated, since the Rietveld method constrains the sum of the crystalline phases to be equal to 1. Considering that dicalcium silicate (C_2S, belite) has a contribution to hydration that shows up over a long period (after the 12 hours studied), the belite was used as an internal standard. Data was normalised by taking the crystalline content and subtracting from 1 to obtain the weight fraction of the amorphous material and to measure how it changes during the hydration process.

In Figure 1, the weight fraction of the amorphous phase (AP) is plotted versus time. It shows that the C-S-H is higher in the sample of cement hydrated with grinding aid and this could explain the better mechanical performances. Calcium hydroxide can be revealed in the XRD patterns 180 minutes after mixing (dashed line). This indicates that the hydration of C_3S and the hardening of cement paste have started. In Figure 2 the weight fraction of crystalline tricalcium silicate as a function of time is reported: the effect of the grinding aid is to accelerate the hydration. The C_3S is converted to C-S-H and portlandite and its weight fraction decreases more rapidly than in the absence of the grinding aid.

It is also important to observe the effect of GA on the aluminate phases of cement. As can be seen in Figure 3 and in Figure 4 (that show respectively the weight fraction of C_3A and C_4AF in function of time), the decreasing rate of the crystalline content of C_3A and C_4AF changes in the presence of a chemical additive. This could be explained by considering a possible influence of the grinding aid on the rate of conversion of the aluminate phases. Since it is well known that the hydration of C_3S depends on the hydration of tricalcium aluminate and tetracalcium

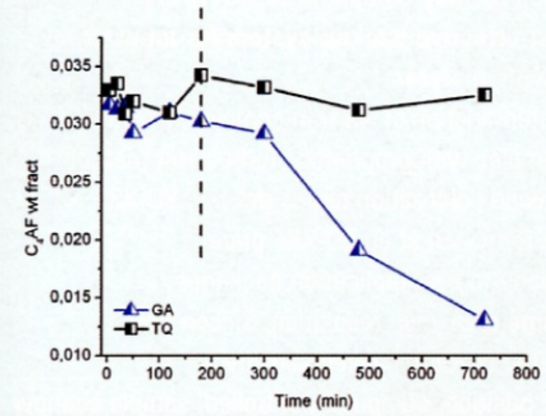

Figure 4. Weight fraction of tetracalcuim aluminoferrite versus time.

aluminoferrite[6], it can be supposed that the chemical effect of a grinding aid is to accelerate the reactivity of aluminate phases, allowing a better hydration of silicates, as reported by several authors[7].

Conclusion

The quantitative X-ray diffraction with Rietveld refinement is a powerful technique that allows the modifications in complex systems to be followed. The application to the study of cement hydration can be very useful, especially in order to clarify the interaction with chemical additives.

Alkanolamines-based grinding aids have a strong chemical effect on cement hydration: the improvement of compressive strengths usually observed by adding a chemical additive in mixing water can be explained in terms of acceleration of the hydration of aluminate phases that drives the reaction of silicates and the development of mechanical strengths.

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