

**“Improvement of mechanical strengths by the use of grinding aids:
optimisation of sulphate content in cement”**

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Abstract

A key point in cement technology is the improvement of mechanical properties, particularly in terms of compressive strengths. The use of grinding aids allows higher fineness to be obtained, together with interesting savings in the grinding energy costs, thus increasing the performances of cements. In addition, it is well known that grinding aids have a chemical effect on cement chemistry, that leads to higher degrees of hydration. In order to obtain the best results from the use of grinding aids, it is important to optimise all the parameters involved. In particular, the type and the amount of gypsum have a strong influence on the interactions between chemical additives and cement hydration. In this paper we present a study on the optimisation of gypsum content, showing the importance of taking into account this parameter when grinding aids are used.

Introduction

Even though from a technical point of view the Portland cement production process is well defined worldwide, there is still an increased demand for high quality and high performances cements. This is mainly due to the urgent needs of cost and energy savings, both for economical and environmental reasons [1]. In order to comply with the most advanced standard, during the last years the use of grinding aids has been spreading in several countries.

Grinding aids in cement production

The grinding process of cement absorbs 60-70% of the total energy employed. Finish grinding accounts for about 38% of specific electric power consumption [2]. The quantity of energy required by the process to obtain the correct fineness is only partially employed for the creation of new surface: in fact most of the total energy is lost as heat. Grinding efficiency rapidly decreases as fineness increases, mainly due to the agglomeration between the finest particles.

Grinding aids are organic substances that are strongly adsorbed on the surface of ground particles, so that preventing agglomeration and coating on ball and mill lining. Thanks to their dispersing effect, grinding aids also increase the efficiency of air separators because the finest particles are not carried along with the largest. The result is a reduction of circulating load and an improvement of particle size distribution. The advantages obtained by the use of grinding aids are the following:

- significant mill output increase at the same fineness. The increase in production can be used to reduce production costs or to cover market demand.
- Fineness increase at equal output, or both effects. In some cases very high fineness may only be obtained by using grinding aids.
- Improved particle size distribution at equal fineness. It is well known that the particle size fraction between 3 and 30 μm is directly related to the strengths development, and the fractions below 3 μm contributes to the early strengths [3]. The use of grinding aids allows higher mechanical strengths to be obtained thanks to a positive influence on particle size distribution.
- Higher separator efficiency.

- Improved flow characteristics of the cement during transport, silo storage and during loading/unloading operations.

The chemical effect of grinding aids

During the first stages of hydration of cement both crystalline and amorphous phases occur. In particular, the development of mechanical strengths is directly related to the hydration reaction of tricalcium silicate (C_3S) that leads to the formation of calcium hydroxide (portlandite) and to a complex family of amorphous products usually called calcium silicates hydrate (C-S-H) [4].

As soon as the cement is mixed with water, an amorphous and colloidal gel layer (rich in alumina, calcium, sulphate and silica) is formed. The nucleation and growth of the crystalline hydration products start from the gel itself and several parameters (according to thermodynamic and kinetic considerations: solubility products, solubility kinetics of the anhydrous phases, diffusion of ions through the gel) control type and morphology of the hydrates.

Among all the products that are formed during the early stage of hydration, ettringite nucleates from calcium, aluminium and sulphate ions in solution and grows in form of stubby rods from the first gel, according to the following reaction (see Figure 1):



Ettringite is probably the most important hydration product, because its morphology and microstructure are considered to have a great effect on cement hydration [4]. In our opinion an amorphous and thin layer of ettringite that covers the clinker grains can slow down the reaction rate of silicate by reducing the diffusion of water in the core of clinker grains. On the other hand a highly crystalline ettringite allows silicate minerals to react faster with water, leading to a better hydration and higher compressive strengths.

It is well known that grinding aids have a strong effect on the cement hydration, and this effect is probably based on their ability to affect the dissolution of clinker phases and the crystallisation of hydrated products [5, 6]. It has recently been demonstrated by X-ray diffraction analysis that grinding aids accelerate the hydration of aluminate phases [7] and this leads to higher mechanical strengths.

In particular, the amount and characteristics of ettringite produced during cement hydration are related to the availability of soluble ions and presence of chemical additives [8]. The availability of calcium, aluminium and sulphate ions depends on several parameters, ranging from clinker chemistry and mineralogical composition, particle size distribution of ground cement and type and amount of calcium sulphate. In our opinion, the latter is one of the most important, and needs to be carefully controlled, because there is a strong connection with the chemical effect of grinding aids on hydration.

Type and amount of calcium sulphate

The amount of gypsum strongly affects setting time, compressive strengths and volume stability [4]. During industrial grinding, due to the high temperature in the mill, conversion of gypsum in anhydrite or hemihydrate is possible, and it is well known that different types of calcium sulphate are characterized by different solubility kinetics. The quantity of ions (Ca^{2+} and SO_4^{2-}) that goes into water solution in function of the time is different, and in our opinion this strongly affects the nucleation rate of ettringite [9]. The fineness of calcium sulphate obviously has an influence on the rate of dissolution. During industrial grinding, due to the fact that clinker and calcium sulphate have very different hardness, their relative fineness are in fact more difficult to control.

It is important to point out that grinding aids and amount, type and fineness of calcium sulphate affect the ettringite nucleation and growth and their relative effect should be considered together when the target is the improvement of mechanical strengths.

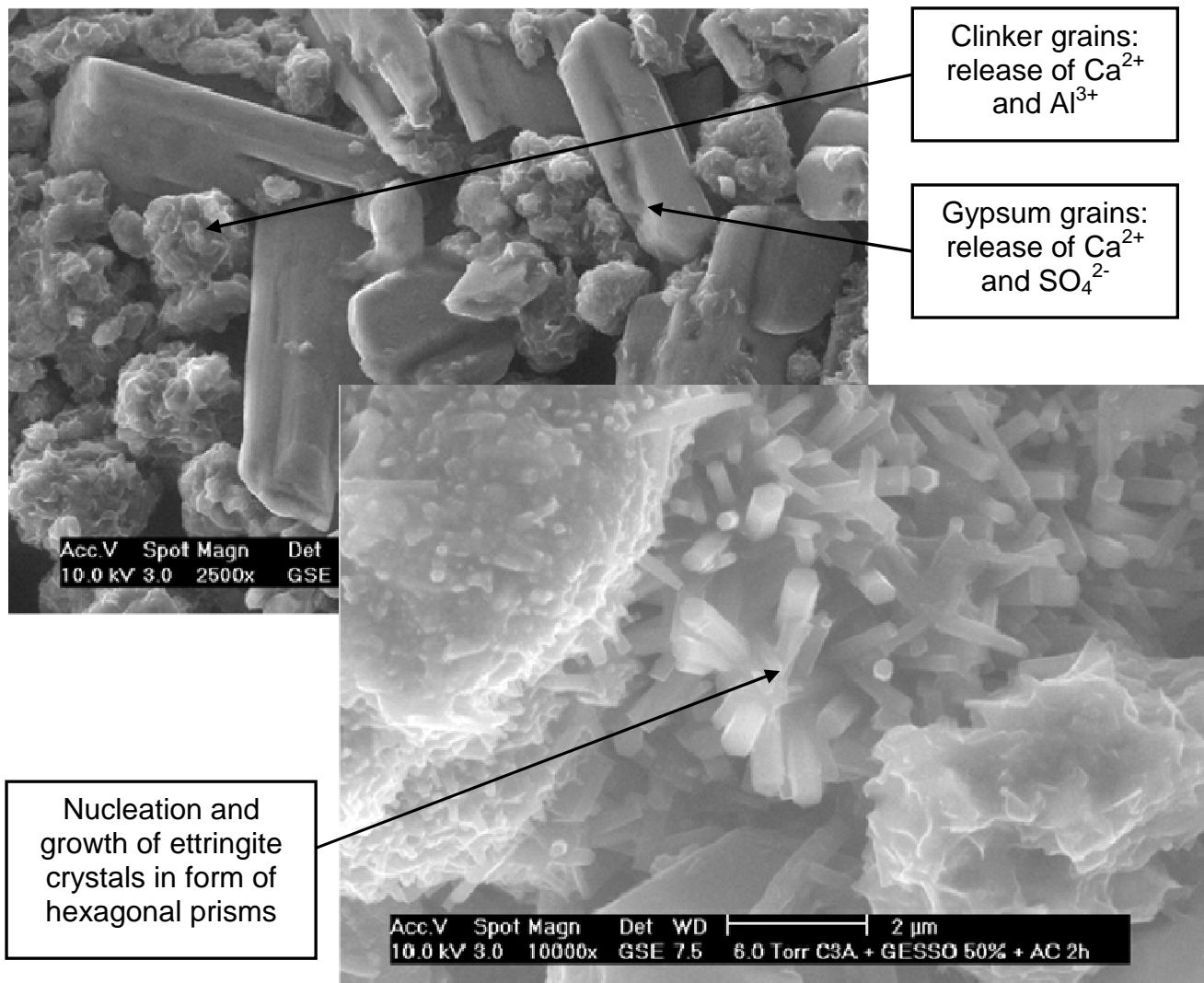


Figure 1: ESEM-FEG images showing ettringite during cement hydration

Optimisation of gypsum content with grinding aids

The results of a long term industrial trial with MA.G.A./C type of grinding aids are reported here. A cement type CEM I 52,5 R (according to European Standard EN 197-1) was produced in a 2 chamber mill (3,4 m x 13,0 m), with a 2nd generation separator (4 cyclones). Considering that the main target of the cement plant was to increase the production, we decided to use a grinding aid maintaining the same Blaine fineness, and increasing early strengths relying only on the chemical effect of the additive. A detailed study of the optimum gypsum was performed, by grinding several hours with different amounts of gypsum (2%, 4%, 6% and 8%), with MA.G.A./C type of grinding aids dosed at 300 g/t, keeping the same Blaine fineness.

The results are reported in the graph (Figure 2). In the case of cement ground without additive, the gypsum was optimised at 4%. With the introduction of MA.G.A./C, in order to obtain the best performances, the optimum gypsum was shifted to 6%, allowing a 20% gain in 1 day strengths to be obtained.

In Figure 3 the percentage increase of 1 day strengths obtained with the use of MA.G.A./C is reported: it can be clearly seen that if the amount of gypsum is different, the efficacy of grinding aid ranges from 10% to more than 40%, and the maximum effect is obtained with 6% gypsum.

Figure 2 - Modification of optimum gypsum with grinding aids

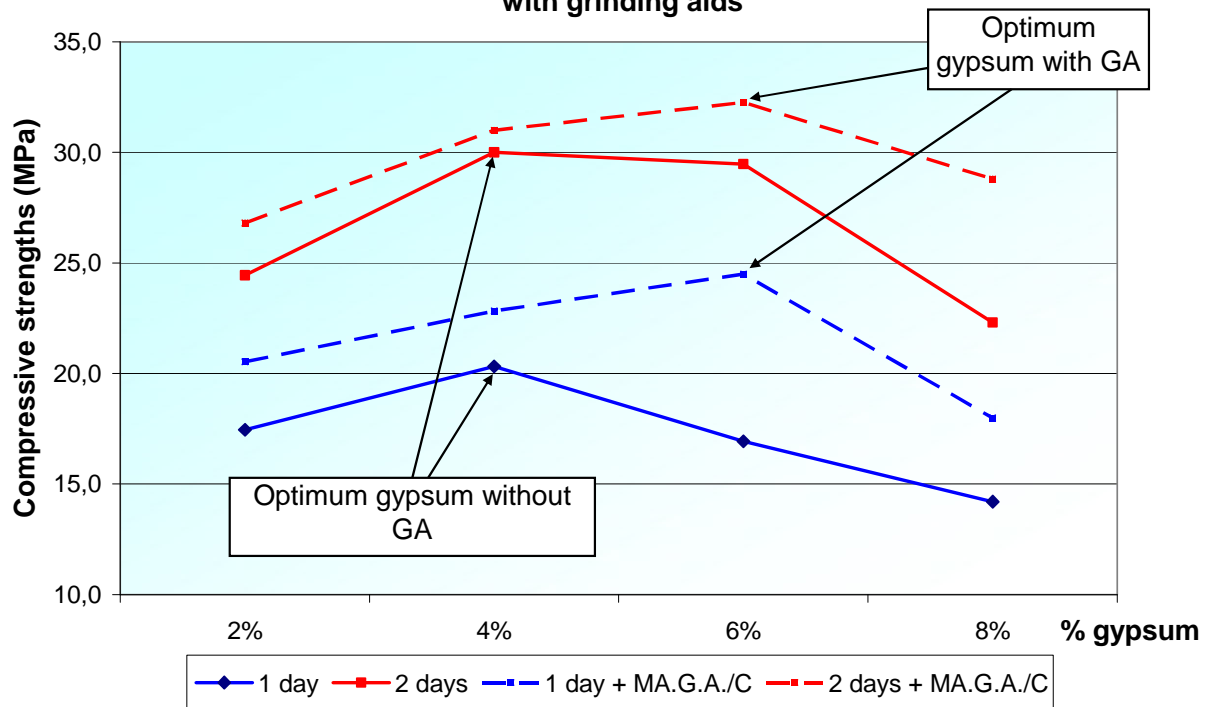
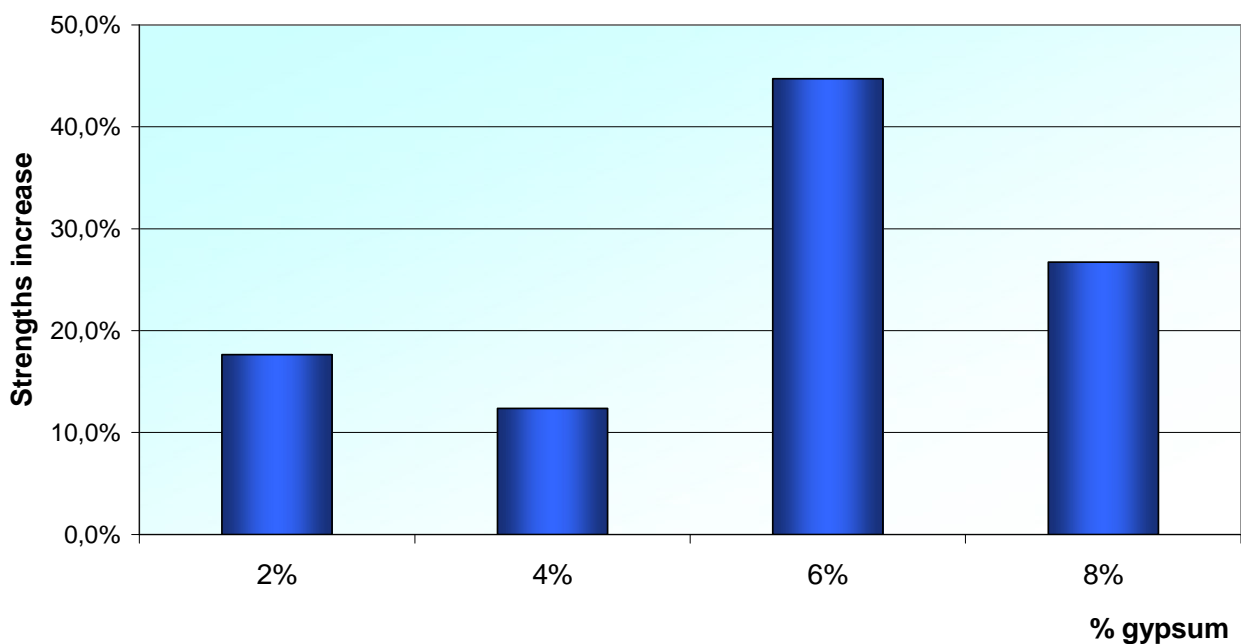


Figure 3 - Percentage increase of 1 day compressive strengths



The final results obtained (summarized in Table 1) were the following:

- increase of production from 31,5 to 39,5 t/h;

- increase of 1 day compressive strengths from 20,3 to 24,5 MPa;
- increase of 2 days compressive strengths from 30,0 to 32,3 MPa;
- reduction of clinker content from 93,0% to 91,0%.

Table 1: final results		
	No grinding aid	300 g/t MA.G.A./C
Cement type	CEM I 52,5 R	CEM I 52,5 R
Fineness	4700 cm ² /g	4710 cm ² /g
Mill output	31,5 t/h	39,5 t/h
% clinker	93,0 %	91,0 %
% gypsum	4,0 %	6,0 %
% limestone	3,0 %	3,0 %
1 day compressive strengths	20,3 MPa	24,5 MPa
% increase	-	20,7 %
2 days compressive strengths	30,0 MPa	32,3 MPa
% increase	-	7,7 %

Conclusions

1. The use of grinding aids allows interesting results to be obtained, in terms of production cost reduction and improvement of cement properties.
2. Beside the positive effects on reduction of agglomeration and improvement of mill efficiency, grinding aids have a strong chemical effect on cement hydration, probably related to a modification of microstructure of hydration products (ettringite).
3. In order to optimize the efficacy of grinding aids, the amount of gypsum is probably one of the most important parameters to be taken into account.
4. The optimum gypsum can be very different if a grinding aid is used during cement production. This allows interesting results to be obtained, in terms of higher compressive strengths and better performances.

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