Grinding aids for high performance cements

M.Magistri, P.Recchi, Mapei SpA, Milan, Italy

Introduction

The interest in high performance cements has been growing in the last years, as a natural consequences of high performance concrete production. Cement producers are requested to offer in the market hydraulic binders with high early strengths, and this can be obtained by optimizing several parameters, ranging from clinker chemistry and reactivity to cement particle size distribution. The production of such high performing cements at a reasonable cost (from the point of view of clinker content and energy requirement for high fineness grinding) can be challenging and the use of suitable cement additives becomes mandatory. Several types of products can be found on the market. Whatever is the additive used (pure grinding aids, specifically designed to increase production and fineness, or performance enhancers with effect on cement hydration), the choice of the most appropriate relies on a detailed investigation that should consider all the characteristics of the cement.

Grinding aids for high performance cements

Grinding aids are organic compounds that are added to the mill during cement grinding. Their main purpose is to reduce the energy required to grind the clinker into a given fineness. In addition, some products (usually referred to as performance enhancers) provide positive effect on cement hydration improving strength development [1]. In this paper we present a typical example of full investigation about the possibility of producing high early strength type I cement, using an appropriate cement additive.

We were approached by a grinding plant with the target to produce a Portland cement (CEM I according to European standard EN 197-1) with early strengths as high as possible. The grinding plant has, for the production of high-performance cements, four different clinker sources available, here indicated as clinker 1, 2, 3 and 4. In our lab a detailed investigation was performed, consisting in the following main points:

1. clinkers characterization;
2. investigation about clinkers' grindability and reactivity;
3. optimum cement composition;
4. choice of the most appropriate cement additive, on the basis of the data collected.

Clinkers characterization

The four clinkers were characterized using the following techniques:

- X-Ray fluorescence (XRF);
- determination of loss on ignition and chemical analysis of free lime;
- X-Ray diffraction (XRD) with Rietveld refinement.

Results are reported in the table 1 (chemical composition) and table 2 (mineralogical composition).

	Clinker 1	Clinker 2	Clinker 3	Clinker 4
Loss on ignition	0,15 %	0,21 %	0,18 %	0,14 %
SiO_2	20,67 %	21,07 %	20,49 %	20,41 %
Al_2O_3	5,26 %	5,35 %	6,38 %	5,61 %
Fe_2O_3	3,18 %	3,85 %	2,18 %	2,89 %
CaO	65,12 %	64,51 %	64,46 %	65,43 %
MgO	2,10 %	1,61 %	3,09%	1,25 %
K_2O	0,68 %	0,71 %	0,48 %	0,93 %
Na_2O	0,12 %	0,13 %	0,48 %	0,11 %
SO_3	1,96 %	1,13 %	0,56 %	1,54 %
Free CaO	0,51 %	0,78 %	1,05 %	1,37 %

Table 1: chemical composition of clinkers according to XRF analysis

	Clinker 1	Clinker 2	Clinker 3	Clinker 4
Tricalcium aluminate C_3A	4,2 %	7,7 %	10,8 %	5,7 %
Tetracalcium aluminoferrite C_4AF	10,3 %	11,7 %	5,8 %	8,9 %
Alite C_3S	67,9 %	61,1 %	70,9 %	73,4 %
Belite C_2S	17,3 %	14,4 %	12,4 %	12,0 %

Table 2: mineralogical composition of clinkers according to XRD analysis with Rietveld refinement

Grindability

Several parameters affect difficulty or ease of clinker grinding. All of them should be taken into account, since it is not always possible to find a single correlation. In details, the main factors directly related to clinker grindability are the following:

- amount of belite (C_2S) and alite (C_3S): clinkers with high amount of C_2S usually present more difficulties in grinding, while as the C_3S increases the grindability increases [2];

- dimension of alite and belite crystals: bigger crystals (especially of belite) increase clinker hardness [3];

- impurities, such as magnesium (MgO), sulphate (SO_3) and potassium (K_2O), are reported to influence grindability, probably through a modification of crystalline structure of alite;

- tendency to pack-set and coating of grinding media and mill lining;

- porosity of clinker.

Since energy requirement for high fineness grinding is crucial in developing high performance cements, a preliminary investigation on clinker grindability were carried out.
The grindability of clinkers is usually compared on a lab scale by using a lab ball mill. By grinding several clinkers using the same procedure (same amount of material and identical grinding time), harder clinkers reach lower fineness (expressed as Blaine specific surface or residual on sieve) than softer. Even though such lab tests hardly allow to forecast the energy requirement for cement production in industrial mills, a general indication of difficulties in grinding different clinkers in the same mill can be obtained.

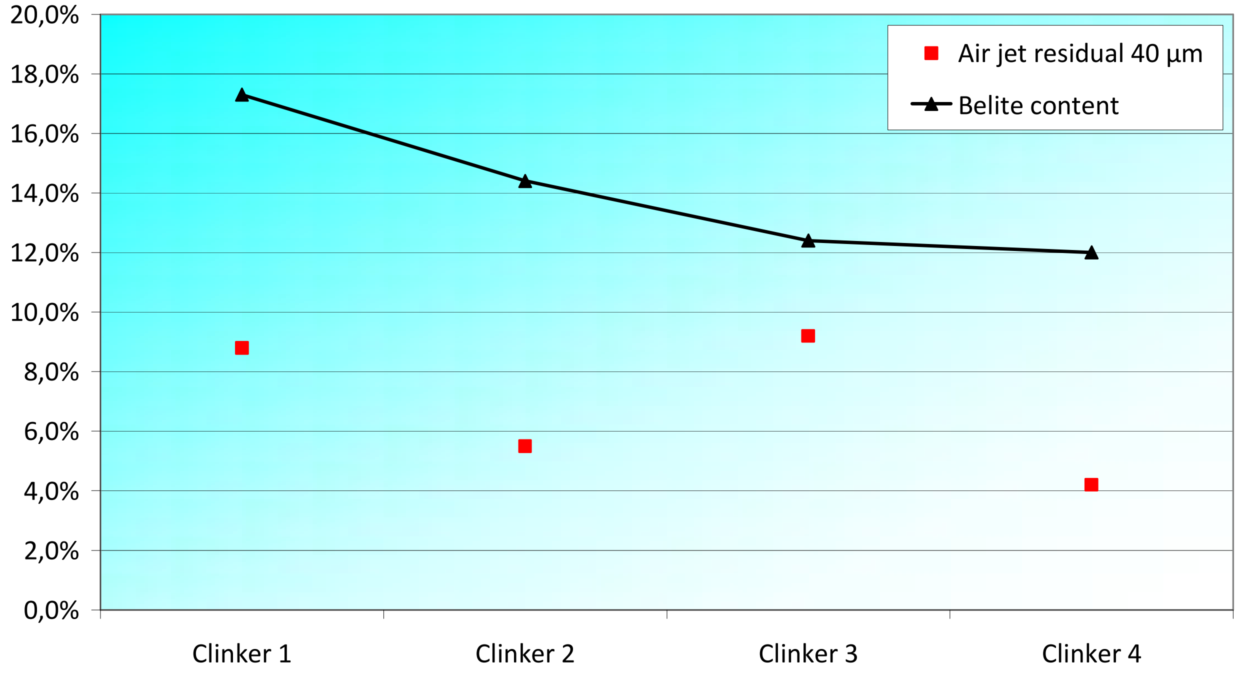
The clinkers received were compared according to the following protocol:

- All the clinkers were crushed to a particle size totally passing through a 3 mm sieve;
- 5 kg of each clinker were ground in a lab ball mill;
- Blaine specific surface and air jet residual (Alpine) of ground material were checked.

Graph 1 reports the 40 µm air jet residual and the belite content of each clinker. The grindability of clinkers 1, 2 and 4 is directly related to the C_2S amount, while clinker 3 resulted more difficult to grind, without direct correlation to C_2S content. Anyway it has to be pointed out that this clinker has the highest content of MgO and the lowest content of SO_3, both factors influencing the formation of specific polymorphic modifications of alite [4].

Graph 1

Clinker grindability: air jet residual versus belite content



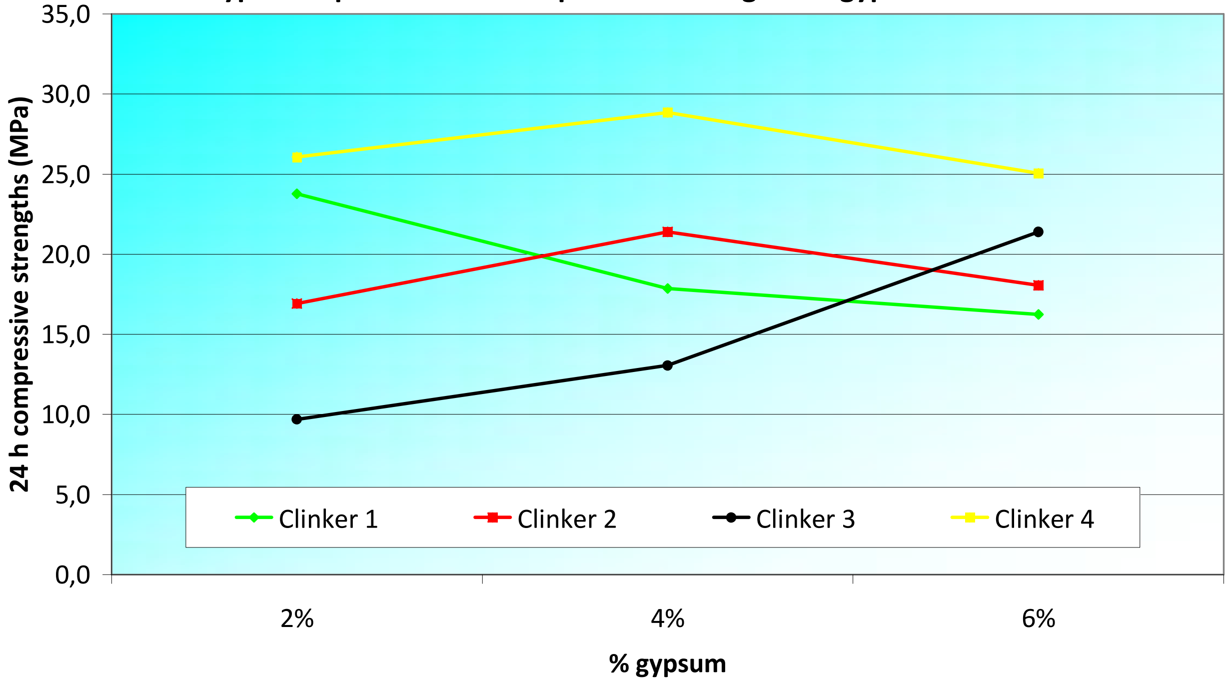
Sulphate optimisation

It is known that gypsum in cement affects not only setting time, but also strengths development. For each clinker, depending on its chemical and mineralogical composition there is a SO_3 content that maximize compressive strengths.

After grinding the clinkers were mixed with different amounts of ground gypsum in order to reproduce samples of CEM I. Compressive strengths in mortar were tested according to European standard EN 196-1. Results are summarized in Graph 2.

Graph 2

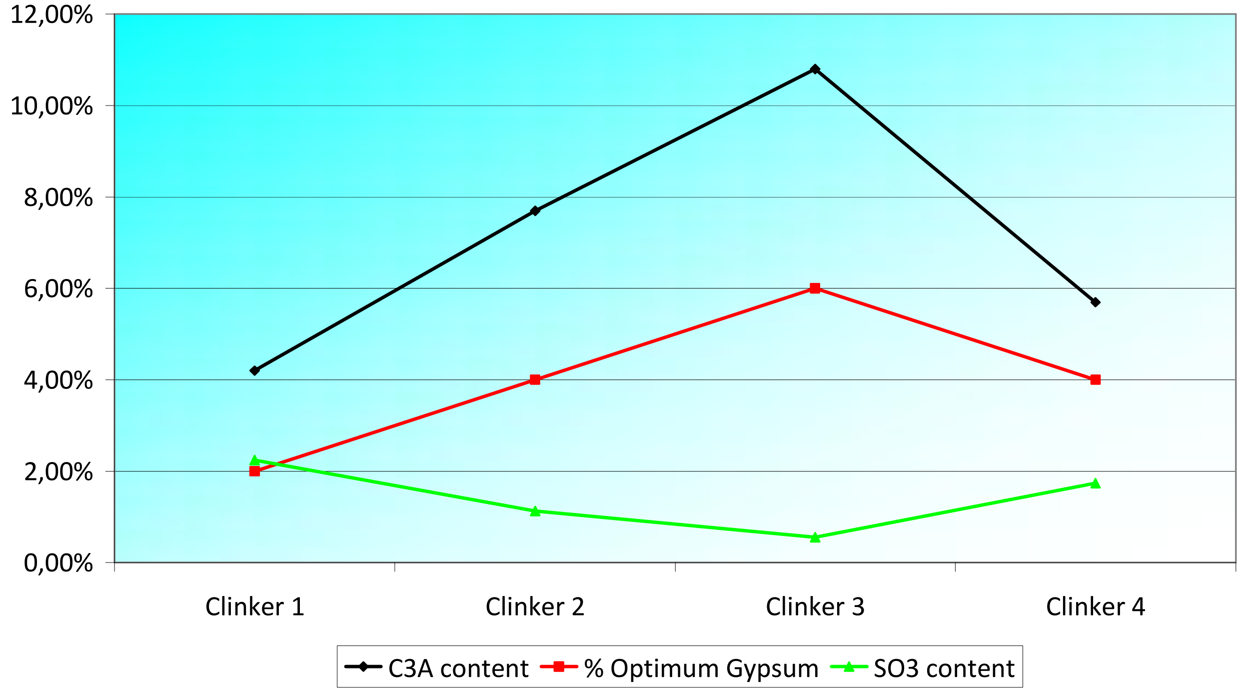
Gypsum optimisation: compressive strengths vs gypsum content



Optimum gypsum was close to 4% for clinker 2 and 4, while for clinkers 1 and 3 was close to 2% and 6% respectively. There was a quite evident correlation between optimum gypsum, tricalcium aluminate and SO_3 content of clinkers (graph 3): as C_3A increases and SO_3 decreases, the clinker needs more gypsum for better hydration and strengths development.

Graph 3

Comparison of optimum gypsum and C_3A/SO_3 content of clinker



In table 3 the compressive strengths of cements at optimum gypsum content are summarized and compared to alite content and fineness. As expected, clinker 4 (characterized by the highest C_3S content and best grindability) developed maximum strength levels. Clinker 2, due to the lowest C_3S content, reached poor strengths despite the good grindability. Clinker 3 presented the opposite situation: high level of C_3S, but lower strength due to difficult in grinding. On the basis of the data collected, the most promising cement was identified as made with clinker 4 with the addition of 4% gypsum, ground at the highest fineness possible with acceptable mill output and water demand.

	24 h strength at optimum gypsum	**C_3S content**	**Residual 40 µm**	**Blaine (m^2/kg)**
Clinker 1	23,8 MPa	67,9 %	8,8 %	394
Clinker 2	21,4 MPa	61,1 %	5,5 %	440
Clinker 3	21,4 MPa	70,9 %	9,2 %	376
Clinker 4	28,8 MPa	73,4 %	4,2 %	436

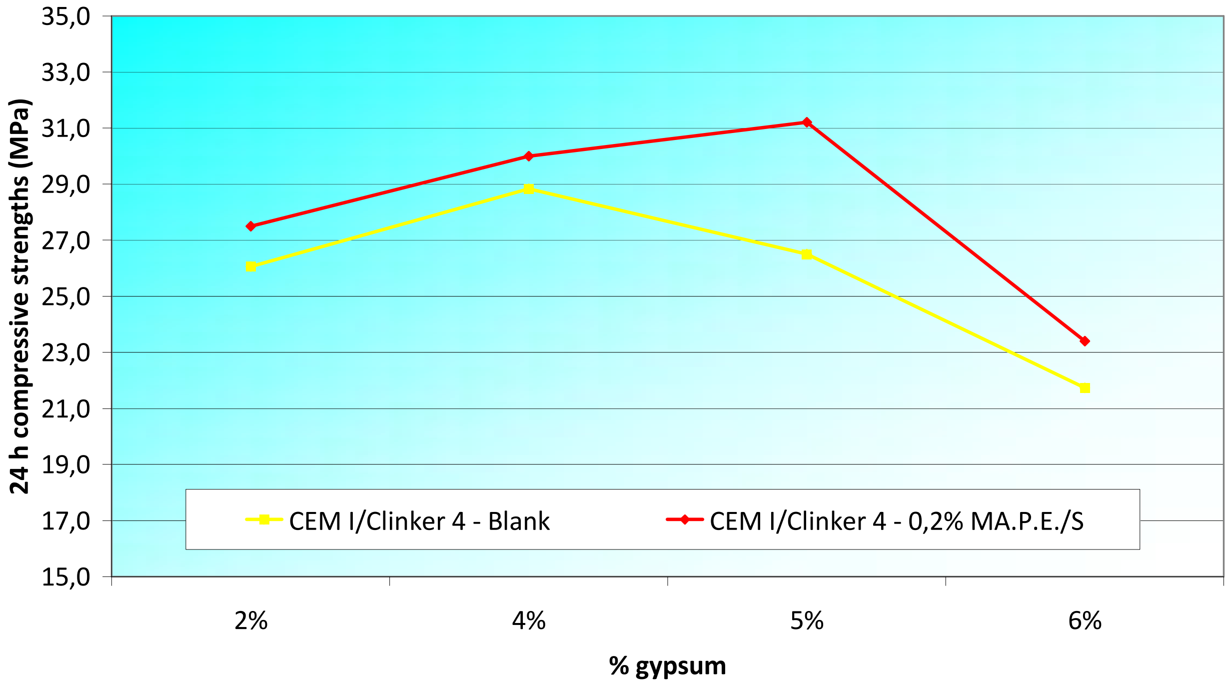
Table 3: compressive strengths at optimum gypsum, fineness and C_3S content

Choice of cement additive

The fineness levels needed for early strength increase can be reached at a reasonable cost only through the use of a specific grinding aid. In addition, a suitable formulated product able to accelerate the clinker hydration can contribute to strength development allowing to boost cement performances. We tested in lab some formulations by concentrating on the chemical effect on hydration and we identified the most promising as a performance enhancer belonging to the MA.P.E./S series.

The final step of this work was the optimization of sulphate content in presence of chemical additive. According to our experience, the optimum gypsum can be very different if a grinding aid is used during cement production [5]. The reason of this lies in the fact that hydration of cement is modified by the presence of chemical addition.

Graph 4
Gypsum optimisation with cement additive



Several cements have been reproduced by mixing ground clinker 4 with different amounts of gypsum. All cement samples were hydrated without any cement additive (blank test) and with the addition of 0,2% MA.P.E./S. The results (reported in graph 4) showed a slight shift of optimum gypsum towards higher values. This is quite coherent with the fact that some grinding aids accelerate the hydration of aluminate phases, thus requiring the supply of higher amount of sulphates [6].

Industrial test

The data collected during this complete lab investigation were used during industrial trial in the grinding plant. The results confirmed what expected and it was possible to produce a CEM I with high early strengths (higher than 30 MPa at 24 h) at a reasonable cost and with interesting mill output.

Conclusions

The use of grinding aids is of extreme importance during production of high performance cements needed for top quality concrete. Beside the positive effects on reduction of agglomeration and improvement of mill efficiency, grinding aids have a strong chemical effect on cement hydration.
In order to optimize cement performances, several parameters should be taken into account. Chemical and mineralogical composition, grindability of clinker, amount of gypsum and cement fineness are probably the most important.
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.

References

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