Cement Additives Division

"GREEN GRINDING: ENVIRONMENTAL PROTECTION AND COSTS SAVINGS THROUGH THE USE OF GRINDING AIDS IN THE CEMENT INDUSTRY"

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Introduction

Portland cement clinker is basically made by heating limestone and clays to a 1450°C in a kiln. During clinker manufacturing, a fixed quantity of carbon dioxide (CO_2) is released in the atmosphere according to the decarbonation reaction of limestone:

$$CaCO_3 = CaO + CO_2$$

Apart from this unavoidable release, there are further direct emissions of greenhouse gases (CO_2, but also nitrogen and sulphur oxides NO_x and SO_x) associated with the burning of kiln fuels and indirect emissions linked to the energy consumption, especially for grinding operations. Globally, for each ton of clinker coming out of the kiln, approximately 800 kg of greenhouse gases are produced [1].
Due to the more stringent regulation on CO_2 release and to the general needs of more efficient and economical processes, the main issue that the worldwide cement industry will have to face in the next years will be the reduction of such emissions.
Since the improvement of the efficiency of kilns has probably reached the maximum (from the '70s up to now, the energy required to produce clinker has fallen by about 30% in Europe [2]), the strategies that can be used to reach this target are the following:

1. the use of secondary fuels;
2. the production of cements with reduced clinker content.

The use of mineral additions such as limestone, fly ash, slag, pozzolan in cement production is increasing year by year. On the other hand, it is well known that if the clinker content is reduced, cement performances can be affected, in terms of lower compressive strengths and workability. There is the need of technologies that allows higher amounts of secondary materials to be used, minimising the negative effect on cement quality. In this paper we describe in details the advantages that can be obtained by the use of cement additives in blended cements production, in terms of clinker reduction and energy savings.

Blended cements

Mineral additions to Portland cements can be divided in two types:

1. active additions, such as slag, fly ash and hydraulic materials. This type of additions give a contribution on cement strengths thanks to their hydraulic behaviour.

2. Inert additions (usually referred as fillers), such as limestone. This additions are considered having no effect on strengths, even though this is not always true.

The use of pozzolanic materials as mineral additions to cements is based on their latent hydraulic properties. When mixed with clinker, the calcium hydroxide supplied from alite and belite hydration is used by silica and alumina contained in slag, fly ash, pozzolan and others hydraulic materials to form calcium silicate and calcium aluminate hydrates, thus contributing to strengths development. The principal hydration products and the microstructure are essentially similar to those given by pure Portland cements, but the

quantity of portlandite (calcium hydroxide) found in the hydrated pastes is lower, since this has been consumed [3]. A general discussion about the characteristics of blast furnace slag cements and the use of grinding aids has already been presented elsewhere [4].
The pozzolanic reaction can be represented as follows:

- hydration of tricalcium silicate, with formation of calcium silicate hydrate (C-S-H) and calcium hydroxide (CH):

$$C_3S/C_2S + H_2O = \text{C-S-H} + CH$$

- reaction of calcium hydroxide with silicon and aluminium supplied from mineral addition, with formation of further C-S-H and C-A-H (calcium aluminates hydrates):

$$CH + SiO_2 + Al_2O_3 + H_2O = \text{C-S-H} + \text{C-A-H}$$

Cement additives can accelerate the hydration rate of alite and belite, thus allowing higher amounts of calcium hydroxide to be available for pozzolanic reaction. This increases the hydration products, giving higher compressive strengths.
The use of limestone is very common in Europe, especially in Spain and Italy, where limestone cements (with limestone content up to 35%) accounts for about 65% of total production. Limestone can be considered as a inert, but it is well known that the addition of 2-4% limestone to OPC allows to maintain the same (or even better) compressive strengths of the same cements made only with clinker and gypsum [5].
Limestone can fill the voids between cement grains, leading to a more compact microstructure of mortars and concrete. Moreover, it has recently been discovered that limestone is not only an inert filler, but it can participate to cement hydration. The strength contribution given by limestone can be explained considering that as CO_3^{2-} increases, the monosulphate become less stable toward monocarboaluminate and hemicarboaluminate. This conversion leads to the formation of ettringite, and the final effect is the increase in the “solid mass” of the system, leading to a more compact micro structure and higher mechanical performances [6].
Cement additives are active accelerating the conversion between ettringite and monosulphate and monocarbonate, and their effect can be interesting also in limestone cements.

The use of grinding aids in cement industry: pure grinding aids and performance enhancers
Cement grinding aids are process additives used during finish grinding in order to reduce cement pack set inside the mill and to increase production. Grinding aids act by coating the particles which cause agglomeration with a mono-molecular film which neutralizes the surface electrical charges. This reduces significantly the energy needed to grind, allowing interesting reduction of the specific consumption (in terms of kWh/t) [7].
In the last years, cement grinding aids have faced an evolution, and nowadays we usually consider the use of performance enhancers: these can be viewed as products not only reducing the energy needed for cement grinding, but also improving the performances of cements, in terms of compressive strengths and workability. These products allow the cement producer to reduce the amount of clinker in the cement recipe, thus minimizing the environmental impact as well as saving energy and fuel. The use of performance enhancers is a simple and direct way to protect the environment.
In this paper, we present some examples of the use of performance enhancers in blended cements optimization. The main target is the reduction of clinker content, maintaining the

performances of cement unaffected. This is the best way to significantly reduce the contribution of cement industry to greenhouse gases generation.

Case of slag cement

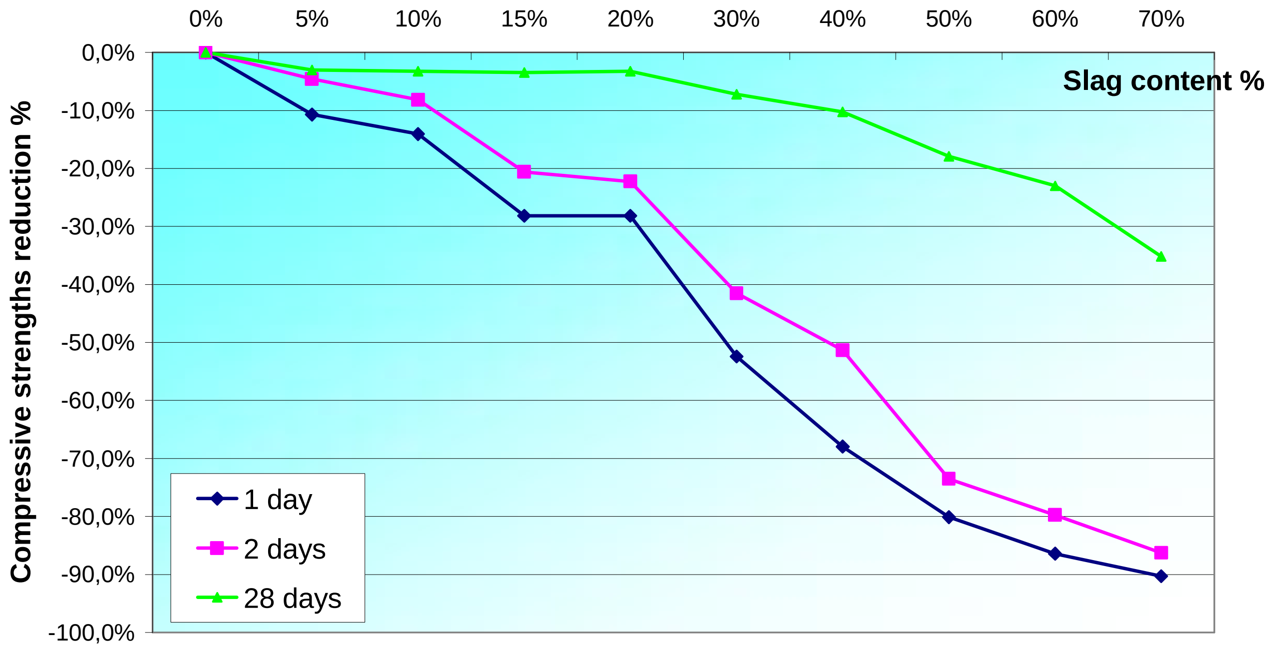
The use of blast furnace slag in cement production is very common. European standard allows the use of cements containing in some cases up to 70% slag and in some European countries slag cements account for more than 50% of total production.

As described, slag gives a contribution on strengths at late ages, thanks to the pozzolanic reaction with calcium hydroxide produced during clinker hydration. In spite of the good performances at 28 days, the substitution of clinker with slag leads to a sensitive reduction of early strengths.

Effect of slag addition on strengths

In the graph the results of a study showing the effect of slag increase on compressive strengths are reported [8].

Compressive strengths reduction vs slag content



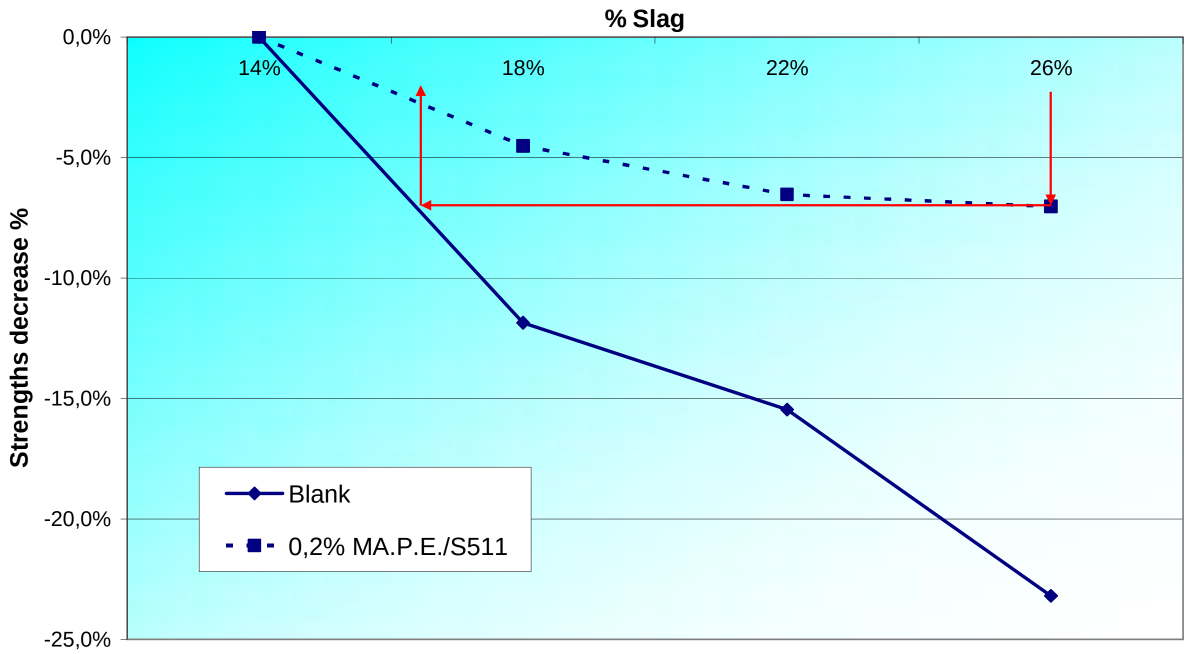
Late strengths are not affected up to 20% slag, while early strengths start decreasing immediately.

Effect of additives on strengths

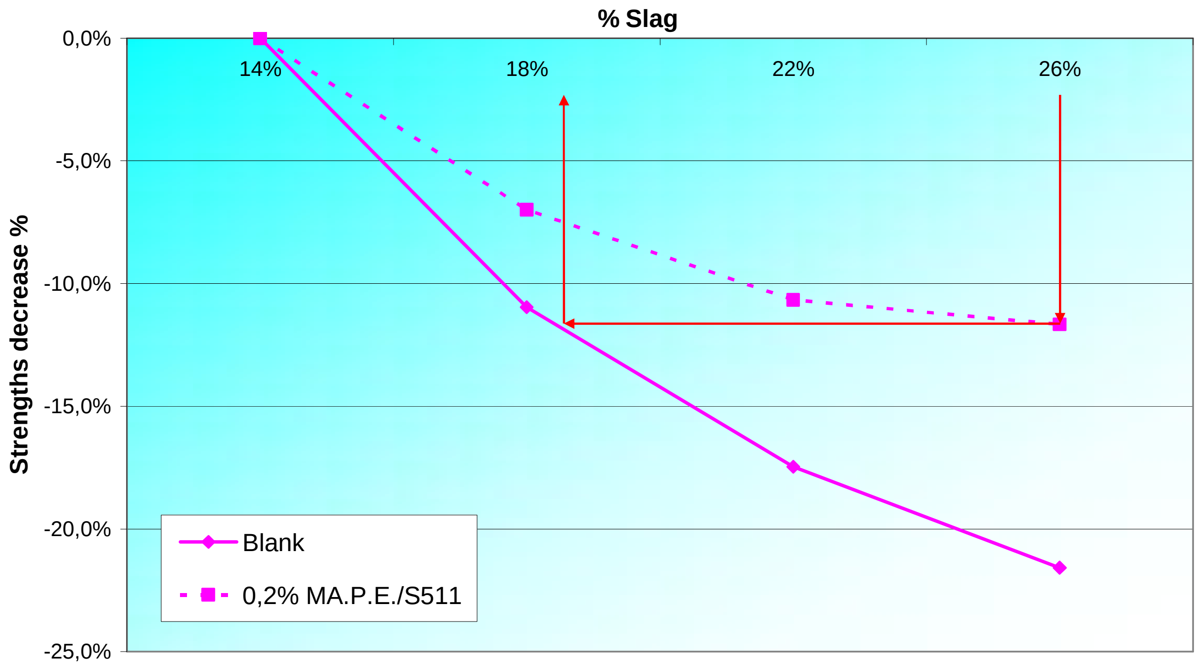
Clinker reduction on slag cements without adverse effect on strengths can be obtained with the use of suitable performance enhancers. As example, we present the results of a lab test: several cements (with slag contents between 14% and 26%) were reproduced in a mill and hydrated with and without a suitable performance enhancer (MA.P.E./S511, dosed at 0,2%). Cements composition are reported in the table, while percent compressive strengths decrease (referred to the cement with 14% slag) are summarized in the graphs.

Cement	Clinker	Limestone	Gypsum	Slag
1	78%	4%	4%	14%
2	74%	4%	4%	18%
3	70%	4%	4%	22%
4	66%	4%	4%	26%

1 day strengths decrease vs slag content



2 days strengths decrease vs slag content



The results show the following:

- the use of MA.P.E./S511 reduces the compressive strengths decrease, allowing the use of higher slag contents. As showed with the red arrow in the graphs, a cement with 26% slag hydrated in presence of MA.P.E./S511 has 1 day compressive strengths similar to a cement with 16% slag, and 2 days strengths similar to a cement with 18% slag.

- As the slag content increases, the effect of cement additive becomes more evident: the percent decrease is lower at higher slag content.

- Using a suitable performance enhancer, there is the possibility to reduce about 8-10% clinker in cement composition.

Case of limestone/fly ash cement

We performed a lab study on clinker reduction in a limestone/fly ash cement. The target was to increase the total amount of mineral additions from 20% to 30% (corresponding to a 10% clinker reduction), keeping the same fineness and compressive strengths at early ages. We studied in details the best balance between limestone and fly ash, and the effect of a performance enhancer on cement hydration.

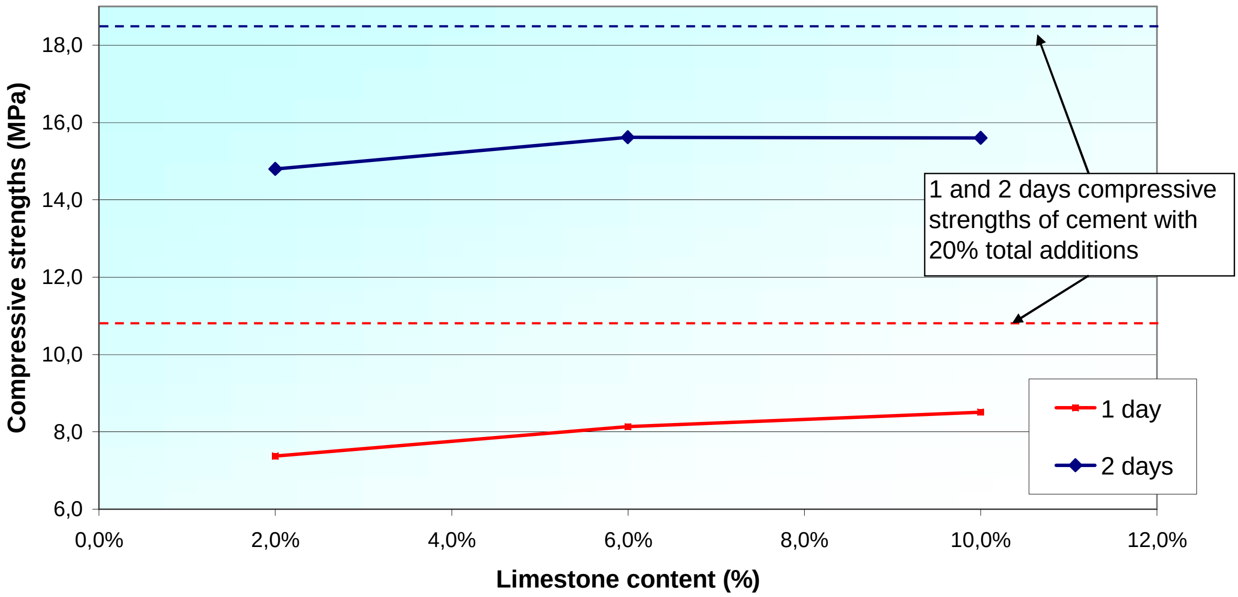
Optimisation of cement composition

A samples of OPC (95% clinker + 5% gypsum) was reproduced in lab mill and mixed with different amounts of ground limestone and fly ash, in order to reproduce different blended cements with 20% and 30% total additives (with different amounts of limestone/fly ash). For each cement, compressive strengths at early ages were tested. The compositions of all the cements reproduced are summarized in the table, while compressive strengths versus limestone content are represented in the graph.

Cement	OPC	Limestone	Fly ash
20% addition	80%	5%	15%
30% addition	70%	2%	28%
30% addition	70%	6%	24%
30% addition	70%	10%	20%

After reduction of 10% clinker, there is a sensitive decrease of early strengths, as expected. It is interesting to note that for cements with 30% total additions, as the limestone content increases, a general increase in early strengths can be noticed. On the other hand, compressive strengths at 28 days were similar, since the amount of fly ash is still quite high.

Limestone/Fly ash blended cement, 30% additives
Early strengths vs limestone content



Effect of GA at different limestone addition

The same cement compositions were hydrated by adding in mixing water a performance enhancer (MA.P.E./S828) dosed at 0,20%. In the graphs below are summarized:

- The compressive strengths at 1 and 2 days of cement with 20% additions (reference), and cements with 30% additions (different limestone/fly ash content) hydrated in presence of MA.P.E./S828.

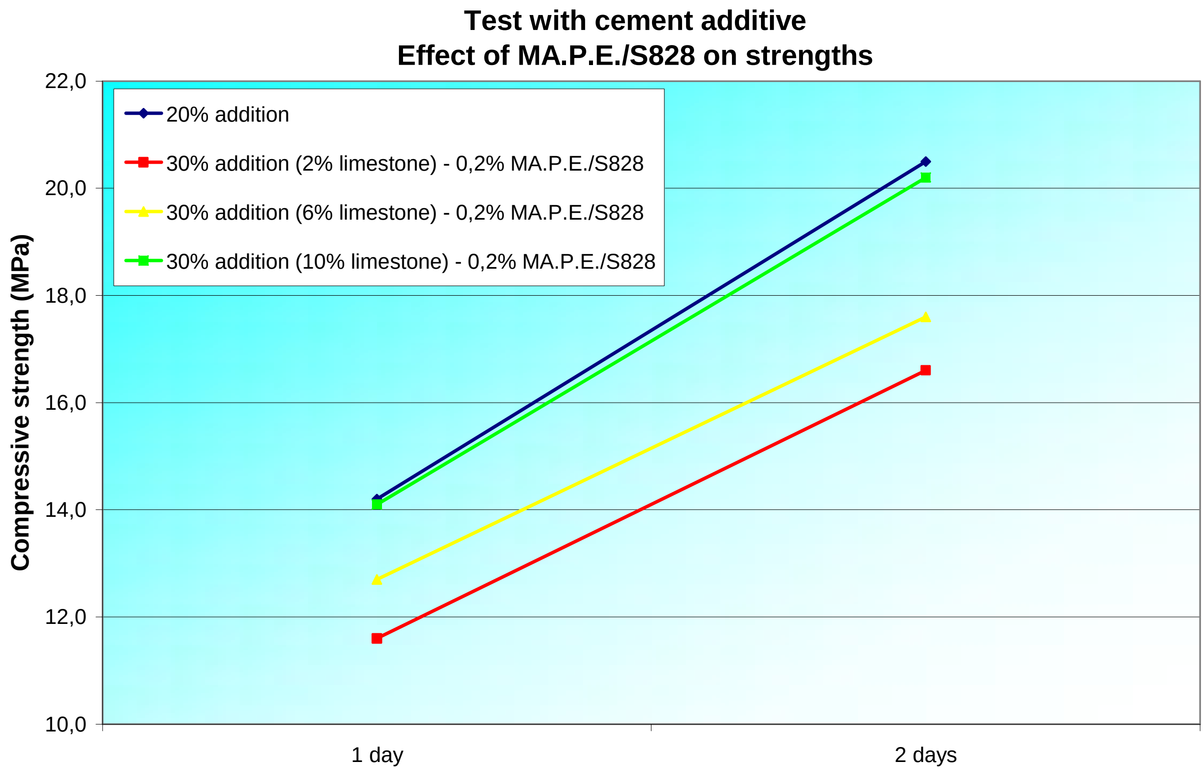
- The % increase at early strengths obtained by the use of MA.P.E./S828.

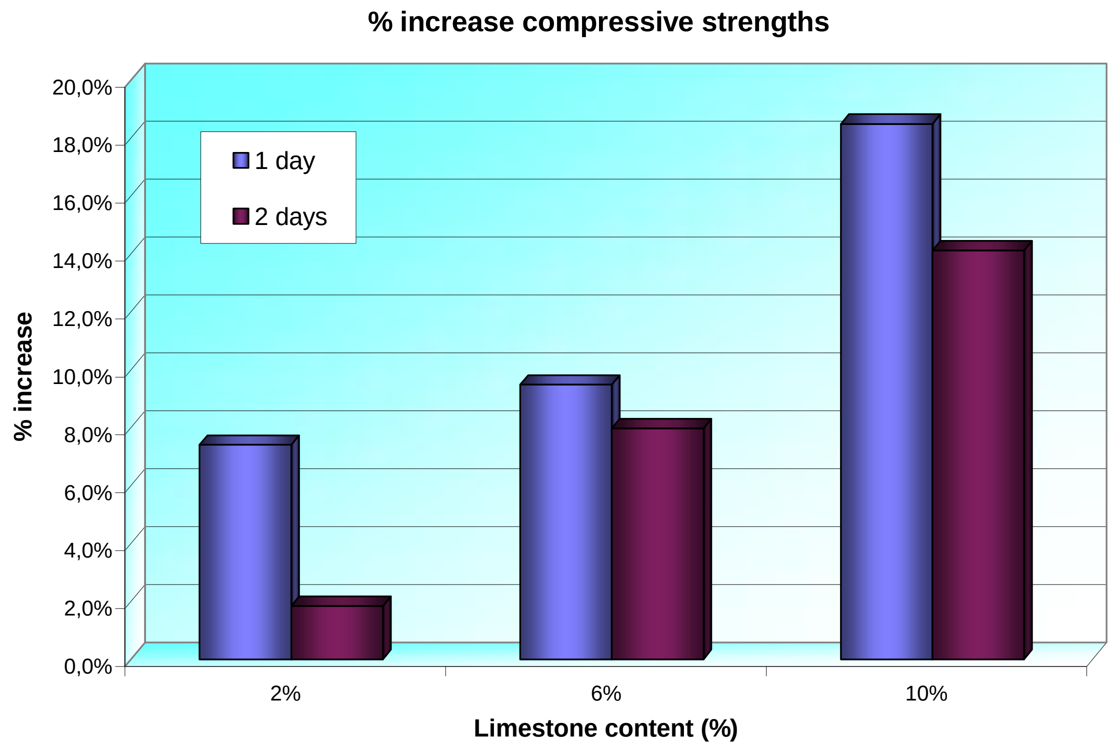
The following comments can be made:

- At the highest limestone content (10%) the early strengths of cement with 30% addition are similar to cement with 20% addition.

- The effect on strengths seems to be related to the limestone content. As explained before, according to our experience cement additives accelerate the conversion of monosulphate to monocarboaluminate, and we can make the hypothesis that the effect of MA.P.E./S828 is more evident as the amount of limestone increases.

- The use of MA.P.E./S828 allows the reduction of 10% clinker, with similar results in terms of early compressive strengths. Considering a production of 1 million t/year cement, this means a reduction of 100.000 t/y clinker produced.





Conclusions

The reduction of carbon dioxide release associated with the decarbonation of limestone and with the use of fossil fuels is probably the main issue that the worldwide cement industry will have to face in the next years. The production of blended cements with reduced clinker content plays a key role in reaching this target.

The use of cement additives as performance enhancers can be considered as a “green grinding”: while reducing the energy cost for cement grinding, these products allow the reduction of clinker in the cement recipe, thus minimizing the environmental impact as well as saving energy and fuel, while maintaining similar performances in terms of compressive strengths.

Bibliography

[1] N. Mahasenan; S. Smith, K. Humphreys: "The Cement Industry and Global Climate Change: Current and Potential Future Cement Industry CO_2 Emissions". Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies, October 2002, Kyoto, Japan

[2] “Climate Change, Cement and the EU” - Cembureau publication, available on line: http://www.cembureau.be/Documents/Publications/Climate_Change_Cement_and_the_EU_Contribution_to_CO2_reduction_CEMBUREAU_Brochure_EN.pdf

[3] H.F.W.Taylor: “Cement Chemistry”, Academic Press, London, 1990.

[4] L.Sottili, D.Padovani: “Improved performances of Granulated Blastfurnace Slag (GBS) cements with cements additives” - Cemtech Conference, Istambul, Turkey, 26-29 September 2004.

[5] M.A.Caldarone: “The Use Of Limestone On Various Properties Of Portland Cement” - Portland Cement Association R&D serial n°2891.

[6] T.Matschei, R.Skapa, B.Lothembach, F.P.Glasser: “The Distribution of Sulphate in Hydrated Portland Cement Paste” - 11th International Congress on the Chemistry of Cement, Montreal, Canada.

[7] L.Sottili, D.Padovani: “Effect of grinding aids in the cement industry” - Petrocem, St.Petersburg, April 2002.

[8] M.Magistri, P.D’Arcangelo: “Clinker savings using additives” - International Cement Review, February 2009 issue.