# *Quality improvers for optimization of blended cements performances*

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**Abstract**
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 and carbon dioxide emissions reduction and energy savings.

## Introduction

In 2011 global cement production worldwide has been reported to be close to 3.6 billion tons, with China accounting for about 57% of the total. Asia and Africa and Middle East cement production growth rate, although lower than expected, has been showing positive increase, while Europe and North America suffered due to the economic downturn [1]. Among this general figures, a closer glance to the type and characteristics of cement produced shows important differences.

Cement production is reported to contribute about 5% to global anthropogenic carbon dioxide emissions [2], mainly related to clinker production (due to decarbonation of limestone and the use of fossil fuels in order to reach the elevated temperatures needed for clinkerisation process). Blended cements, in which part of the clinker is replaced by industrial or natural by-products, such as blast furnace slag, coal fly ash, natural volcanic pozzolan, limestone, play a key role in reduction of greenhouse gases emissions, but their use dates back to the origin of building materials, a long time before concerns for climate change started.

The production and use of blended cements is strongly related to cultural and local availability of secondary cementitious materials. For example, European standards allow the addition of limestone up to 35% in cement composition, while in several countries (such as USA or Australia) the maximum content allowed is limited to 5-7%. In USA only a few percent of secondary mineral additions are used in cement production, leaving to concrete mix design the reduction of cement content. In Europe blended cements are widely used. In Italy, for example, limestone and pozzolan blended cements production accounts for more than 90% of the total, with 30% being cements with clinker content lower than 80% [3]. In Eastern Europe, due to the presence of developed steel industry, blast furnace slag cements are common. In the so-called fast growing economies the use of blended cements is mandatory, in order to sustain the growth of the building industry and limiting the environmental impact. For example, in India during the last ten years the cement production has been doubled, but the amount of OPC has not changed significantly: the increase is mainly due to new production of blended cements that now accounts for more than 60% of the total [4].

These trends reflect the general tendency of the cement industry to limit clinker production many years before the relative recent concerns about greenhouse gases emissions and climate change.

## Characteristics and performances of blended cements

A blended cement is composed of Portland cement and one or more inorganic materials (so-called mineral additions or secondary cementitious products) that take part in the hydration reactions and give a substantial contribution to the hydration products. The definition includes materials with very different composition, chemical characteristics and effects on cement performances. A very general classification can be made by dividing in three categories [5]:

- Pozzolanic materials, such as pozzolan and fly ash: rich in $SiO_2$ and low in CaO, when mixed with stoichiometric amounts of CaO (supplied in form of calcium hydroxide by clinker hydration) they develop C-S-H (calcium silicate hydrates). Secondary C-S-H gives a significant contribution of mechanical properties.
- Latent hydraulic cements, such as blast furnace slag: their composition approaches Portland clinker (broadly is intermediate between OPC and

pozzolanic materials) and they act as hydraulic cements when activated, for example by calcium hydroxide and alkalis produced by clinker hydration. Also in this case, the secondary C-S-H originated by silicon and lime contained in the addition allow increases in the hydrated cement paste and gives a contribution to mechanical performances.

- Fillers, such as limestone: they do not contain (or contain only a little) silicon, but their addition to Portland cement gives a contribution on early strengths thanks to a partly physical and partly chemical effect. Finely ground limestone act as a filler between clinker grains, and chemically it reacts with the aluminate phases and aluminium-containing hydration products giving a contribution to strengths [6].

Regardless of the secondary mineral addition, when clinker content is reduced, generally speaking a decrease in cement performances can be noticed. Figure 1 show the effect on compressive mechanical strengths when clinker content is substituted with slag [7]. Data are referred to a lab testing with the following procedure:

- Reproduction of an OPC by grinding in lab ball mill (95% clinker with 5% gypsum, Blaine specific surface 4700 $cm^2/g$).
- Grinding of slag at 10±1% residual material through a 32 µm air jet sieve.
- Blending of OPC and slag in different proportions.
- Determination of compressive strengths according to European standard EN 196-1.

In the graph, the strengths percent decrease with reference to the initial OPC (0% slag content) is reported in function of slag content.

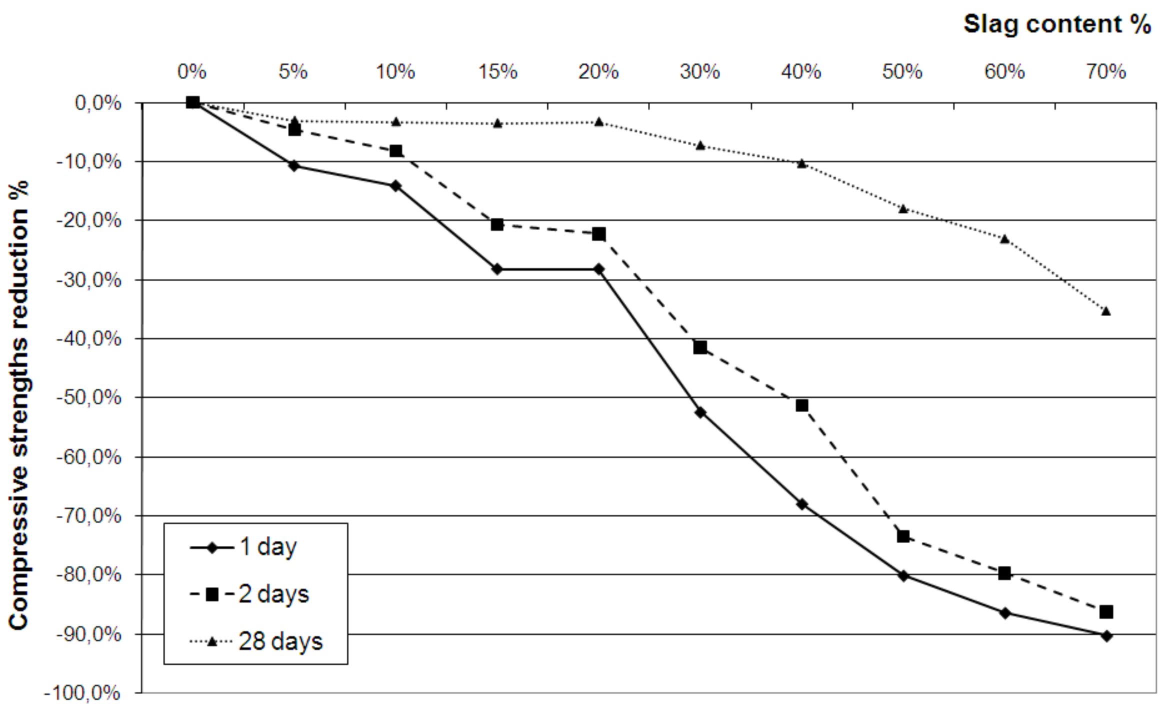


Figure 1: effect of clinker reduction and slag addition on compressive strengths

Results clearly show that the early strengths rapidly decrease even at low slag content, while at later ages higher substitutions (up to 20%) are possible without any particular difference. This is due to hydraulic properties of slag, that develop on the long run secondary C-S-H that substitute the clinker hydration products.
When limestone is used as substitution of clinker, a strong reduction can be noticed on late strengths, not supported anymore by secondary C-S-H. Early strengths with limestone addition below 5% remain similar to OPC or are in some cases positively affected. This can be seen in Figure 2, that summarises lab data collected with the same procedure of slag cements, but using ground limestone.

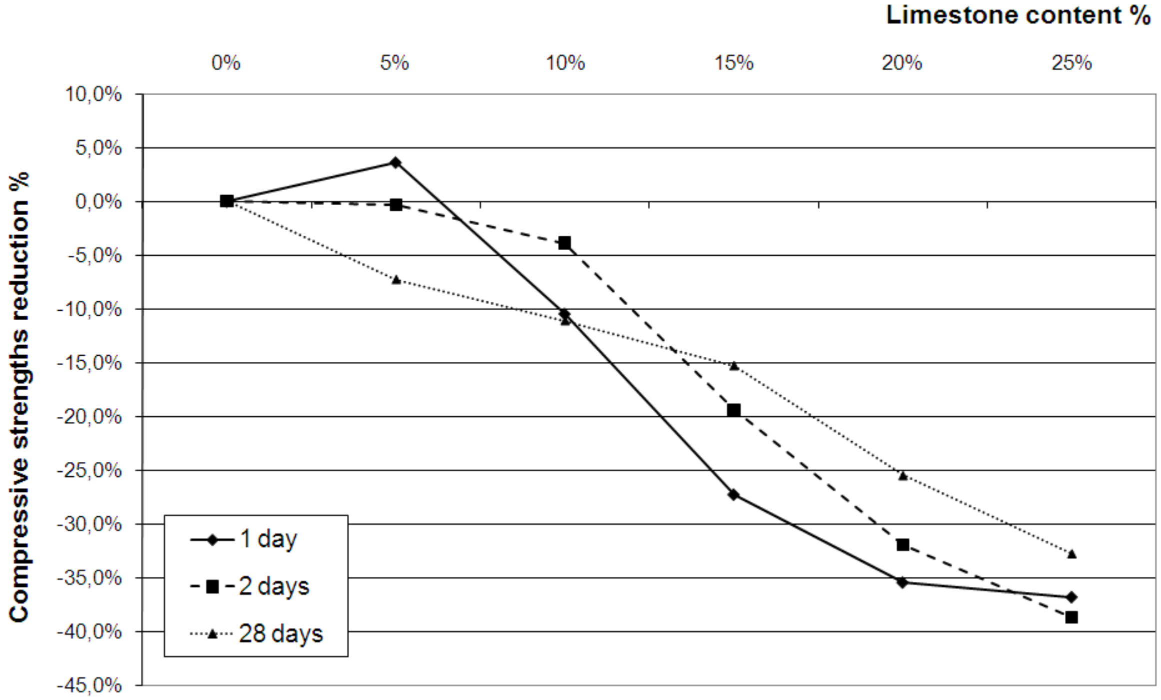


Figure 2: effect of clinker reduction and limestone addition on compressive strengths

**Improvement of blended cements performances**

Considering the effect of mineral addition increase on cement performances, it follows that the possibility of higher clinker substitution is directly related to the possibility of maintaining acceptable strengths values. One of the most promising technologies for blended cements production is related to the use of grinding aids.
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 layer 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) [8]. 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.

Considering that different secondary mineral additions have different properties and effect during cement hydration, the problem of increasing their reactivity should be approached considering both cement and clinker chemistry, together with nature and amount of additions.
Generally speaking, the main parameters that affect reactivity of mineral additions are the following:

- Rate of calcium hydroxide (portlandite) production during tricalcium silicate hydration. This is particularly true with pozzolanic materials (fly ash, pozzolan, microsilica), that, having low amount of lime, relying on CaO supplied by Portland clinker. Latent hydraulic cements (such as slag) receive benefits from increased portlandite production, since this promotes formation of secondary C-S-H with silicon.
- Rate of dissolution of mineral addition: the faster the secondary material supplies silicon or calcium to the pore water, the faster is the formation of secondary C-S-H. Dissolution rate is related to the pH of pore water, to the particle size distribution of addition and to the presence of chemicals that can promote the dissolution.

A grinding aid intended to be used for improvement of blended cements performances should be designed and formulated in order to be active as accelerator of clinker hydration, allowing higher amounts of calcium hydroxide to be available for secondary materials activation. In addition, thanks to the reduction of cement pack-set during grinding and consequently to the reduction of energy required, higher fineness and better particle size distributions are possible, thus improving the dissolution rate of mineral additions. The following examples clarify the benefits given by grinding aids.

**Increasing calcium hydroxide production rate**
Several fly ash cements have been reproduced in lab ball mill by grinding the same composition (65% clinker, 5% gypsum, 30% fly ash) without any grinding aid (blank) and with different grinding aids.

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | Free CaO | $SO_3$ | Eq. $Na_2O$ |
|---|---|---|---|---|---|---|---|---|
| Clinker | 20.90 | 5.20 | 3.02 | 65.22 | 1.36 | 0.75 | 0,73 | 0,85 |
| Fly ash | 54.62 | 28.41 | 3.54 | 8.52 | 1.40 | - | 0.52 | 0.98 |

Table 1: Clinker and fly ash composition (% mass, expressed as oxides of main elements)

| C3S | C2S | C3A | C4AF | CaO |
|---|---|---|---|---|
| 63.2 | 12.3 | 8.5 | 9.7 | 0.6 |

Table 2: Clinker mineralogical composition (% mass of main mineralogical phases)

A glycol based grinding aid has been used to check the effect of fineness increase, so the same grinding time - this means same energy consumption - has been maintained. Alkanolamine-based grinding aids and blends of alkanolamines/inorganic accelerator have been used in grinding with reduced grinding time - this means lower energy consumption - in order to have similar fineness and check the chemical effect on cement hydration.
Details of clinker and fly ash used are reported in table 1 (chemical composition of slag and clinker according to X-Ray Fluorescence) and table 2 (clinker X-Ray Diffraction analysis with Rietveld refinement), while details on grinding aids used and fineness reached are reported in table 3.

| Cement | Grinding aid | Grinding time (min) | 32 µm air jet residual |
|---|---|---|---|
| FA CEM | No GA (blank) | 45 | 12.3 % |
| FA CEM - 1 | 400 g/t glycol based grinding aid | 45 | 7.4 % |
| FA CEM - 2 | 400 g/t alkanolamines based grinding aid | 36 | 11.7 % |
| FA CEM - 3 | 2000 g/t alkanolamines/inorganic accelerator based grinding aid | 34 | 12.1 % |

Table 3: Fly ash cement activation

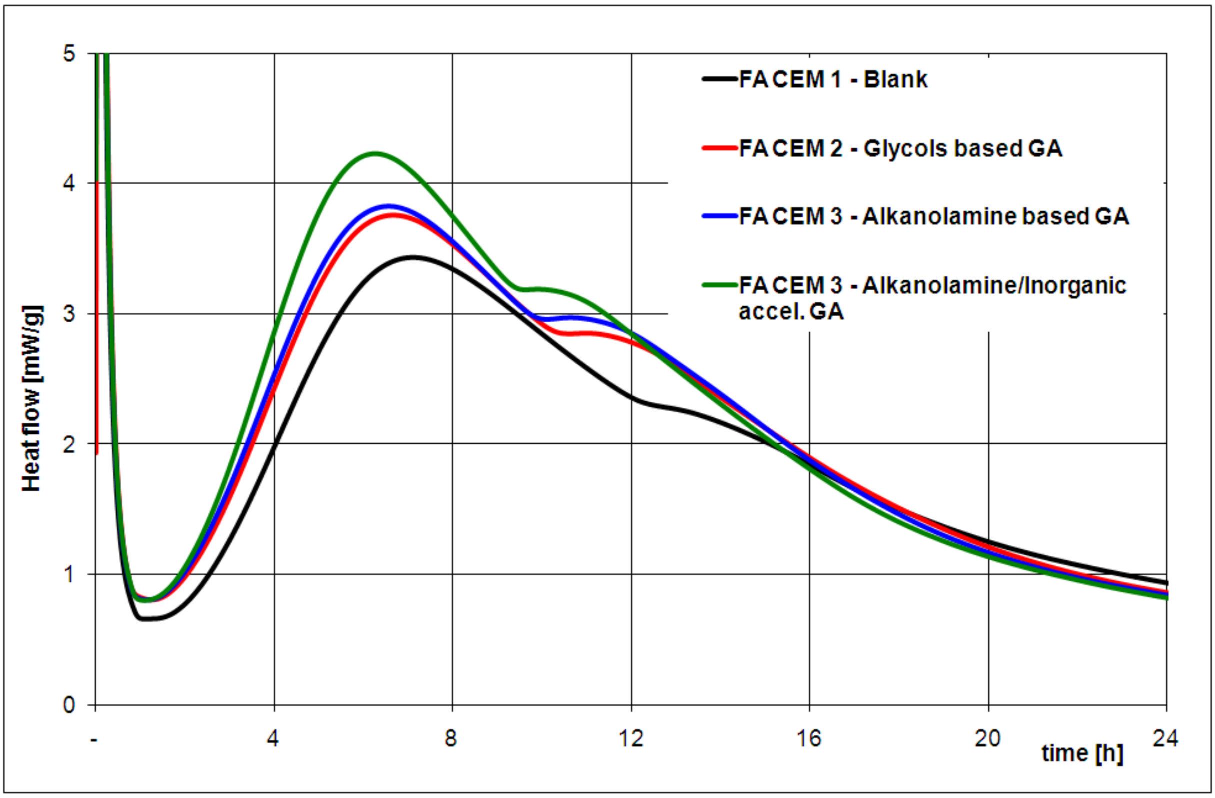


Figure 3: Heat of hydration of fly ash cement ground with grinding aids

The effect of grinding aids on cement hydration can be clearly evidenced by isothermal Calorimetry (TAM-Air Calorimetry, cement pastes w/c = 0.5, temperature

23°C) as reported in Figure 3. In comparison to blank cement, the use of grinding aids strongly increases the second peak of heat release, usually associated to hydration of tricalcium silicate. The higher calcium hydroxide released allows a better activation of fly ash, with consequent benefits in terms of compressive strengths that resulted proportional to total heat released (see figure 4). Higher compressive strengths allow the increase of secondary mineral addition in cement, thus reducing clinker content.

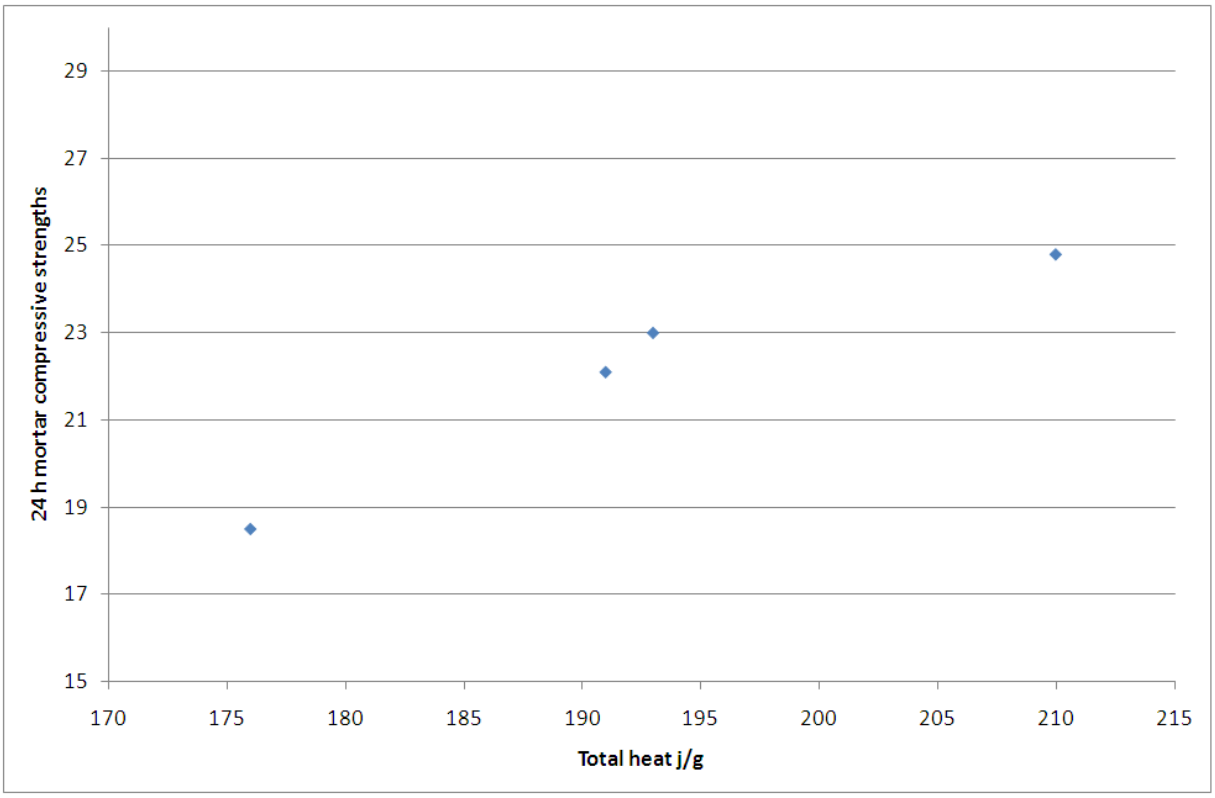


Figure 4: 24 h compressive strengths of FA cements versus total heat release

## Conclusions

The use of grinding aids in blended cements production represents probably the easiest way to improve the performances of blended cements. The effect of grinding aids is related to amelioration of fineness and particle size distribution and to the accelerated clinker hydration, allowing higher amounts of calcium hydroxide to be available for activation of mineral additions and consequently for higher mechanical properties.

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