Promoting performance in low clinker cement

Emanuele Gotti and Davide Padovani, Mapei SpA., review a new series of additives designed to enhance the performance of low clinker cements.

In recent years, the cement industry has been forced into a change unlike any before in its long history. Phrases like 'green economy', 'CO_2 reduction', 'digitalisation', 'zero emissions', 'carbon neutral', etc., that once applied to other sectors of industry are now core components of any cement producer's strategy.

In fact, the production of cement is one of the most significant sources of CO_2 emissions, and is estimated to contribute 8% of global emissions. These emissions are produced in part by the decarbonisation of calcareous minerals used for the production of clinker, but also by the large quantities of fuel necessary to reach high temperatures. Overall, it is estimated that for each ton of clinker, approximately 0.84±0.10 t of CO_2 is produced and emitted into the atmosphere.[1]

Figure 1. Laboratory ball mill for the reproduction of cements.

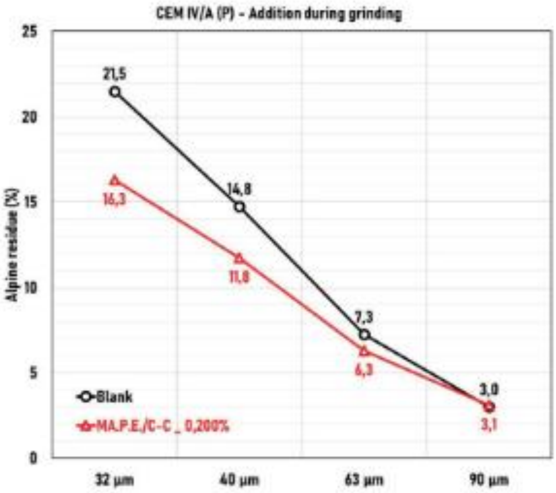


Figure 2. Alpine granulometry of the laboratory cement reproduced with and without MA.P.E./C-C.

Figure 3. Flow table disc to assess workability of cements.

To achieve the goal of carbon neutrality by 2050, the cement industry is implementing a range of measuress.[2] These include, for example:

- Increasing the use of alternative fuels.
- Reducing the clinker-to-cement ratio.
- Using natural gas and hydrogen fuel.
- Using alternative raw materials.
- Implementing carbon capture technology.
- Using renewable energy sources.
- Improving energy efficiency.
- Sourcing local supplies.
- Using green methods of transportation.

In addition to this scenario, the Covid pandemic and the ongoing crisis in raw materials/logistics has pointed out the fragility of the traditional cement industry.

When considering the effects of this challenge on the main product of the cement industry – the cement itself – the following steps can be distinguished:

- 1. A moderate clinker reduction (3 – 5%) in traditional cement types, by using high quality cement additives to boost strengths.[3,4] In this area, even in the best cases, there is still a further 2 – 3% clinker to be reduced according to current standards. This is a short-term approach, mainly based on immediate savings.
- 2. The switch from the traditional CEM I and CEM II (limestone) cements to the more sustainable CEM IV pozzolanic cements, ideally with natural pozzolan. In addition to the environmental and economic benefits associated with lower clinker/cement concretes produced with pozzolanic cements, these cements also display enhanced properties such as greater resistance to external attacks and greater durability.[5] But can CEM IV fit with all the uses in concrete? A key limiting factor is that natural pozzolan is only available in a few countries and it is now clear that alternatives are not easily available: good quality fly ash and slag are expensive and not going to be available in sufficient quantities in the near future.
- 3. The cement industry, in response to points 1 & 2, has introduced completely new types of cement containing significantly less clinker than before (on average 50% of clinker compared to the current 65 – 70%), together with new standards (e.g. EN 197-5) to regulate these new cements. Examples include limestone-calcined clay cements and all the cements based on a similar chemistry (the activated pozzolanic reaction) containing 'recycled' materials.

All these new types of 'low clinker' cements are able to fulfil the current cement standards (mortar strengths, paste setting times), but very often are difficult to use in concrete, where water demand, slump retention and other characteristics are often inferior to those of the traditional cements.

The aim of this article is to move the focus from 'how to produce low clinker cements' to 'how to make the low clinker cements work' with the use of the new family of products MA.P.E./C-C (from Cement to Concrete).

These additives have the unique characteristic of being able to increase workability both in mortar and concrete applications (in addition to improving the grindability and mechanical performance of cement).

In this article, some significant examples are shown that prove their effectiveness.

Pozzolanic cement

The first example presented relates to a pozzolanic cement, CEM IV/A (P) according to EN 197-1. The pozzolan available in the production plant is highly active but has the drawback of absorbing a large amount of water due to its high specific surface. This results in a high demand for water and poor workability in concrete applications, thus making it extremely difficult to use.

For this type of cement, the MA.P.E./C-C additives were evaluated two different ways:

- In industrial cements and added in the mixing water.
- In cements with the additives introduced via a laboratory ball mill (Figure 1).

With the first modality it was possible to evaluate the 'chemical' activation effect of the additive, while with the second modality it was possible to evaluate the adjuvant properties and the stability of the additive during grinding.

For the preparation of the laboratory cements, all the materials were initially crushed to reduce them to a particle size of less than 3 mm. In the subsequent preparation phase, it was decided to grind the clinker/gypsum mixture and the pozzolan separately to avoid the packing problems that can occur when grinding large proportions of materials with varying hardness, and to reconstruct the final cements by mixing them according to the proportions of the industrial cement recipe (69% clinker, 4% gypsum, 27% pozzolan).

To evaluate the effect of the additives, they were added in predetermined quantities both in the grinding of the clinker/gypsum mixture and in the grinding of the pozzolan. Furthermore, the grinding times were kept fixed for each batch.

The fineness of the laboratory cements has been estimated by the air-jet sieving method (EN 196-6) and results are shown in Figure 2. MA.P.E./C-C made it possible to significantly improve, in the same grinding time, the fineness of the cement due to the inclusion of specific high-adjuvant components. MA.P.E./C-C is, therefore, able to reduce the energy required to produce cement (or to increase production for the same energy consumption).

As reported above, the main problem of the cement is its poor workability, mainly related to its high level of water adsorption.

The effects of MA.P.E./C-C have been evaluated in different ways:

- For industrial cement, MA.P.E./C-C has been added to the mixing water to obtain information purely on the chemical effect.
- In parallel, laboratory cements were also tested to evaluate the overall effect of additives during grinding.

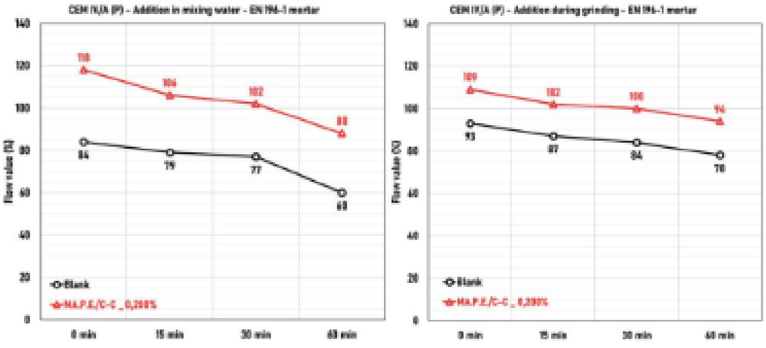
The workability of cement was assessed on standard mortar according to EN 1015-3. The flow value is determined by the diameter of a test sample of a fresh mortar which has been placed on a flow table disc by means of a mould and a given number of vertical impacts by raising the flow table and allowing it to fall freely through a given height (Figure 3). The test has been repeated after fixed time from the mixing to also assess the loss of workability over time.

As shown in Figure 4, MA.P.E./C-C greatly increased the initial workability of the industrial cement. Moreover, it maintained the workability over time with a flow value that, after 90 min., was still higher than the initial flow value of the blank sample. The workability of the laboratory cement (Figure 5) is slightly higher than the industrial cement, due to the different particle sizes.

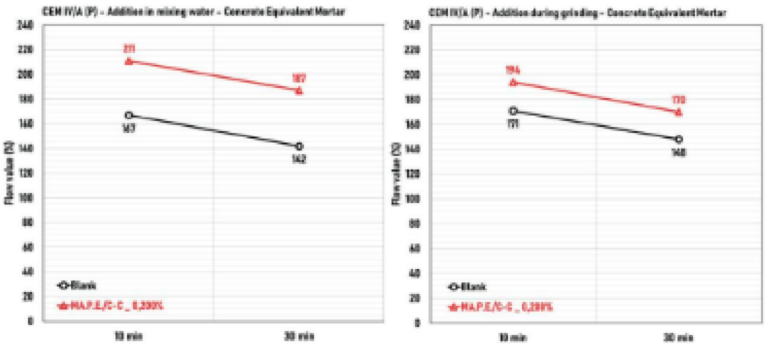
MA.P.E./C-C confirmed its ability to increase initial workability and to maintain it over time. Even in this case, the flow value after 90 min. is higher than the initial flow value of the blank sample. These results indicate that MA.P.E./C-C has good stability during grinding.

It is well known that sometimes performance on concrete is different from those obtained in mortar. For this reason, to simulate the effect in concrete application, the same tests have been performed on Cement Equivalent Mortars (C.E.M.). In fact, these mortars, whose composition is derived from that of concrete, have rheological properties related to those of concrete.

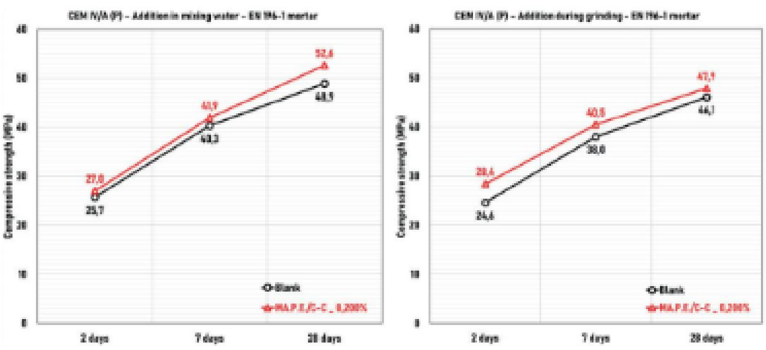
To prepare C.E.M. without supplementary use of concrete additives, it was decided to work with a high amount of water (w/c = 0.61) to simulate semi-fluid concretes. The results, shown in Figures 6 – 7 have confirmed those obtained on standard mortars for both industrial and laboratory cements: an increase in the initial flow value and its maintenance over time. These are clear indications that MA.P.E./C-C



Figures 4 & 5. (Left) Flow values of standard mortars with and without addition of MA.P.E./C-C in the mixing water. (Right) Flow values of standard mortars with and without addition of MA.P.E./C-C during laboratory grinding of cements.



Figures 6 & 7. (Left) Flow values of C.E.M. mortars with and without addition of MA.P.E./C-C in the mixing water. (Right) Flow values of C.E.M. mortars with and without addition of MA.P.E./C-C during laboratory grinding of cements.



Figures 8 & 9. (Left) Mechanical strength of standard mortars with and without addition of MA.P.E./C-C in the mixing water. (Right) Mechanical strength of standard mortars with and without addition of MA.P.E./C-C during laboratory grinding of cements.

can increase workability both in mortar and concrete applications.

Figures 8 – 11 show the effect of MA.P.E./C-C on the development of mechanical strength for the same mortars described above. The addition of MA.P.E./C-C has enhanced the performance in every mortar condition and for every curing time. This characteristic will allow for improvements to the production process of the pozzolanic cement by reducing the clinker/cement ratio or reducing the fineness.

Special cement with alternative raw materials

The second example relates to a special cement produced by replacement of around 50% of clinker with a secondary raw material in the view of a considerable reduction of the specific emission of CO_2. The secondary raw material used for this cement is a blend of calcined clay and recycled inert minerals characterised by a high porosity/adsorption that leads to a high request of water. Consequently, the cement shows a noticeable loss of workability and an increase of viscosity of the fresh concrete which make it difficult the use in concrete applications.

For this type of cement, the MA.P.E./C-C additives were evaluated on an industrial cement by adding them in the mixing water of standard mortars with an increased water/cement ratio (w/c = 0.6).

As shown in Figure 12, MA.P.E./C-C has provided a significant increase to the initial workability of the industrial cement and maintains this over time with a flow value that, after 90 minutes, is still higher than the initial flow value of the blank sample.

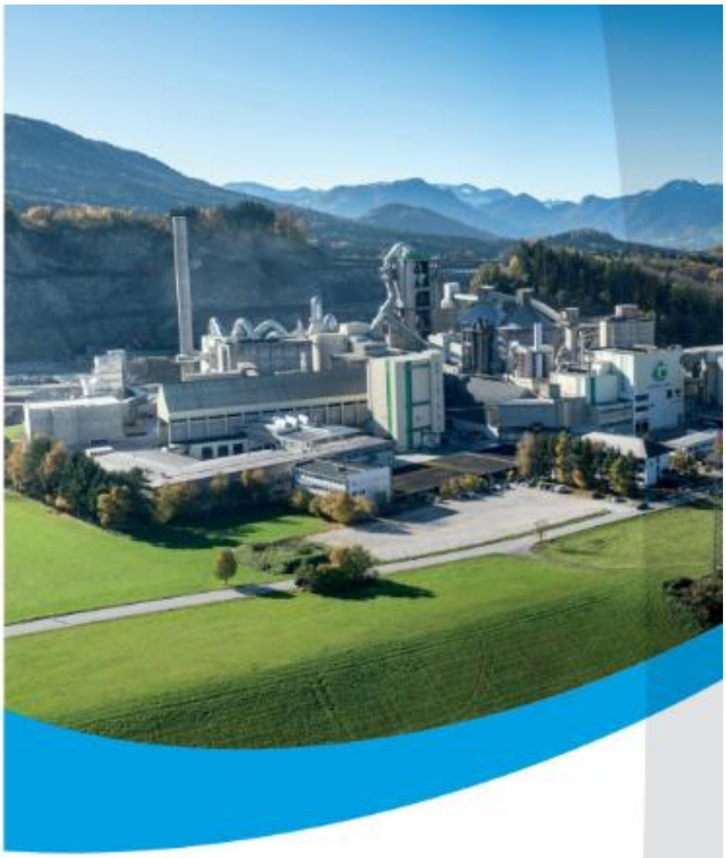
The viscosity of the mortars was estimated using a rheometer equipped with a 'ball measuring system'[6] (Figure 13) at a shear rate of $1 s^{-1}$. The evolution of viscosity was monitored for 90 min. from the mixing of the mortars. The results, shown in Figure 14, have confirmed the increased fluidity of the mortar with MA.P.E./C-C added. Moreover, MA.P.E./C-C allows the fresh mortar to maintain a low viscosity over time, with viscosity at 90 min. from the mix recorded as lower than the initial viscosity of the blank sample.

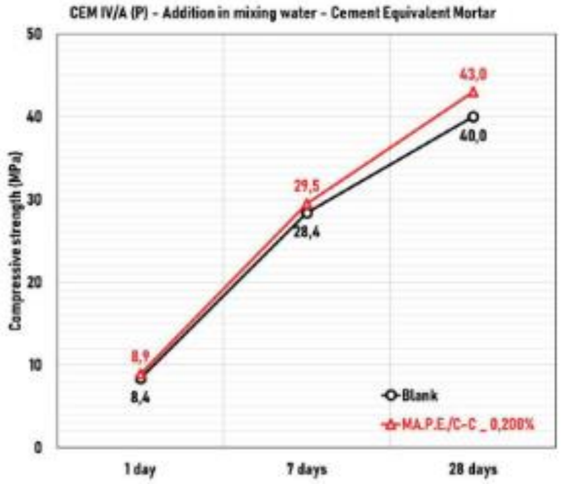
Conclusion

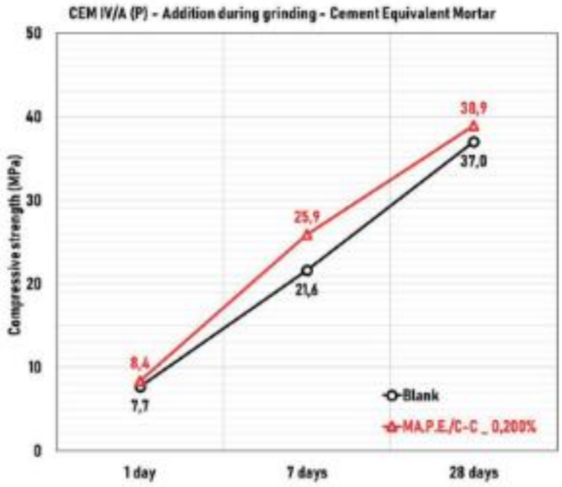
This new range of additives can help cement producers and users in the most difficult cases through a combination of benefits, including: increased grinding efficiency, improved workability in mortar and in concrete, increased mechanical strength.

The examples shown demonstrate the versatility of these new additives used in cases of a high substitution rate of clinker with materials that, under normal conditions, would lower the quality of the cement, making it very difficult to use.

MA.P.E./C-C makes it possible to solve these problems and represents an answer to the challenge that the cement industry will have to face in the







Figures 10 & 11. (Top) Mechanical strength of C.E.M. mortars with and without addition of MA.P.E./C-C in the mixing water. (Bottom) Mechanical strength of C.E.M. mortars with and without addition of MA.P.E./C-C during laboratory grinding of cements.

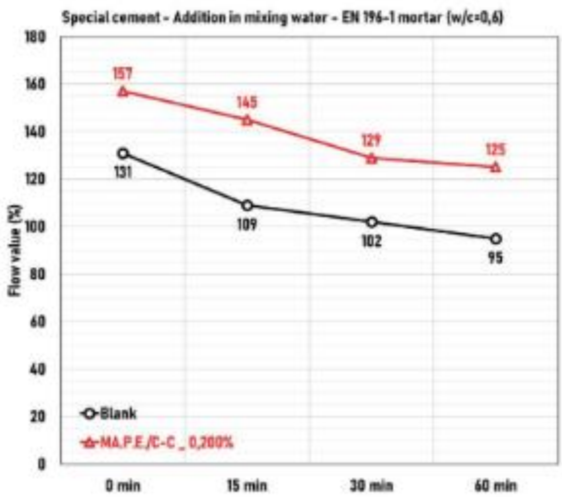


Figure 12. Flow values of standard mortars with and without addition of MA.P.E./C-C in the mixing water.

coming decades. These additives can make it possible to produce cements with a lower clinker content, lower production costs, lower CO_2 emissions and with a higher quality, the effect of which will be noticed in applications in mortar and concrete. ■

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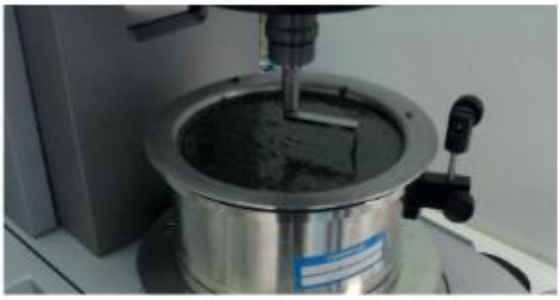

Figure 13. Rheometer equipped with a ball measuring system.

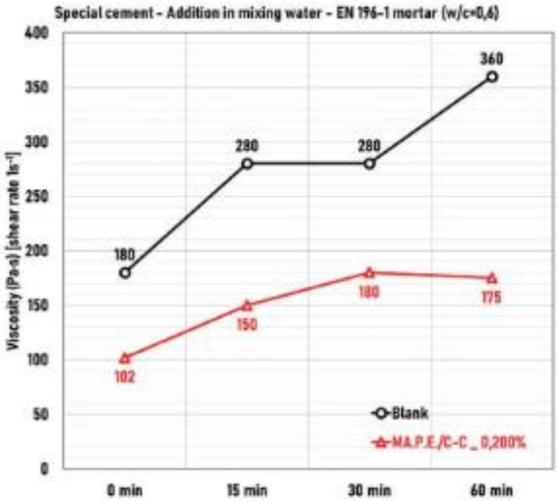

Figure 14. Viscosity of standard mortars with and without addition of MA.P.E./C-C in the mixing water.