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The challenge of low clinker cements

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Abstract

In the last years, the Cement Industry has been forced to a change that never happened before in all its long history. Words like green economy, CO2 reduction, digitalization, zero emission, carbon-neutral etc., before applied to other sectors of industry, now are the core strategy of any cement producer. In addition to this scenario, the recent Covid pandemic and crisis of the raw materials/logistics has pointed out the fragility of the traditional cement industry, particularly exposed to all the before mentioned factors. To mitigate the effect of these situations, manufacturers are taking steps to reduce the clinker content in cements. This reduction can be achieved to a limited extent within the composition ranges established for common cements. More importantly, it can be achieved by shifting the production of CEM I and CEM II towards types of cement with higher substitution, such as CEM IV, or by adopting the new compositions defined in the new EN 197-5. In the next few years, we will also see new opportunities thanks to the introduction of new constituents in the composition of cements, such as recycled concrete fines which will be foreseen by EN 197-6. All these new types of "low clinker" cements (limestone cements, pozzolanic cements, calcined clay cements) are perfectly fulfilling the current cement standards in mortar (strengths, setting times, water demand) 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. In this article we want 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).

Keywords

Cement, Clinker, Additives, CO2 reduction, Workability

1 Introduction

In recent years, the cement industry has been facing new challenges related above all to the need to reduce CO2 emissions to achieve carbon neutrality.

In fact, the production of cement is one of the main sources of CO2 emissions and it is estimated that it contributes to 8% of global emissions. It is produced in part by the decarbonation of calcareous minerals used to produce clinker and in part by the large quantities of fuels necessary to reach high temperatures. Overall, it is estimated that for each ton of clinker, approximately 0,85 tons of CO2 are produced and emitted into the atmosphere.

To achieve the carbon neutrality goal by 2050, the cement industry is implementing various actions. These include, for example, increase of use of alternative fuels, reduction of clinker to cement ratio, use of natural gas and hydrogen, use of alternative raw materials, carbon capture, usage and storage, renewable energy and efficiency, local supplying and green transports.

Among these possible actions, the most rapid one is the reduction of the clinker content of the cements. Currently, in Europe the average clinker/cement ratio is around 0,75 and to achieve neutrality it is estimated that it will have to be reduced to 0.65.

Within certain limits, a reduction in clinker/cement can be achieved within the types of cement classified in EN 197-1. Thanks to the optimization of the chemical-physical characteristics of the cements and thanks above all to the use of specific additives, it is often possible to obtain significant reductions of 3-4% of clinker while maintaining the performance of the cement. However, if we consider the cements most used to produce concrete (CEM I and CEM II / A-L) it is not possible to further lower the clinker/cement ratio.

A more important step, however allowed by EN 197-1, is for example that of making greater use of composite cements in the production of concrete as it is possible to strongly reduce the clinker/cement. In particular, pozzolanic cements with natural pozzolan (P) are an alternative that can be exploited in various parts of the world by taking advantage of the pozzolanic activity of sands of volcanic origin.

Alongside the environmental and economic benefits associated with lower clinker/cement, concretes produced with pozzolanic cements also have some improvement properties such as greater resistance to external attacks and consequently greater durability. Unfortunately, the use of this type of cements frequently presents critical aspects related above all to the high specific surface and the high adsorbing capacity of the pozzolans. These characteristics can lead to a greater demand for water, a loss of workability of the fresh concrete and a loss of the effectiveness of the superplasticizing additives used in the concrete production.

An even greater step in this approach took place with the publication of the EN 197-5 standard in which new composite and ternary cements with very low clinker content are classified. The use of these cements would make it easier to achieve the objectives of carbon neutrality. For example, the compositions of limestone-calcined clay cements fall within this standard. However, with their use the criticalities related to concrete performance are even greater.

To meet these new requirements, Mapei has developed a new range of grinding additives called MA.P.E./C-C (from Cement to Concrete). These additives have the peculiarity of, beside the improvement of grindability and mechanical performance of cement, lead to an enhancement of the workability both in mortar and concrete application.

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

2 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 defect of absorbing a lot of water due to its high specific surface. This feature causes a high demand for water and poor workability in concrete applications, which make it extremely difficult to use.

For this type of cement, the MA.P.E./C-C additives were evaluated in different ways: on industrial cements adding them in the mixing water and on cements reproduced adding the additives in 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 3mm. 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 important proportions of materials with different hardness, and to reconstruct the final cements by mixing on the base 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 of preparation.

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 have made it possible to significantly improve, at a same grinding time, the fineness of the cement thanks to the inclusion of specific high-adjuvant components in their formulation. MA.P.E./C-C is then able to reduce the energy required to produce cement or to increase the production for a same energy consumption.

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

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

Workability of cements has been 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 during time.

As shown in Figure 4, MA.P.E./C-C has allowed to greatly increase the initial workability on the industrial cement. Moreover, it has maintained the workability over time with a flow value that, after 90 minutes, is 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 due to the different particle sizes.

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

It is well known that sometimes performance on concrete is different from those obtain on 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 deduced 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 can increase workability both in mortar and concrete application.

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 allowed to enhance the performance in every mortar condition and for every curing time. This characteristic will reasonably permit to improve the production process of the pozzolanic cement by reducing ulteriorly the clinker/cement ratio or reducing the fineness.

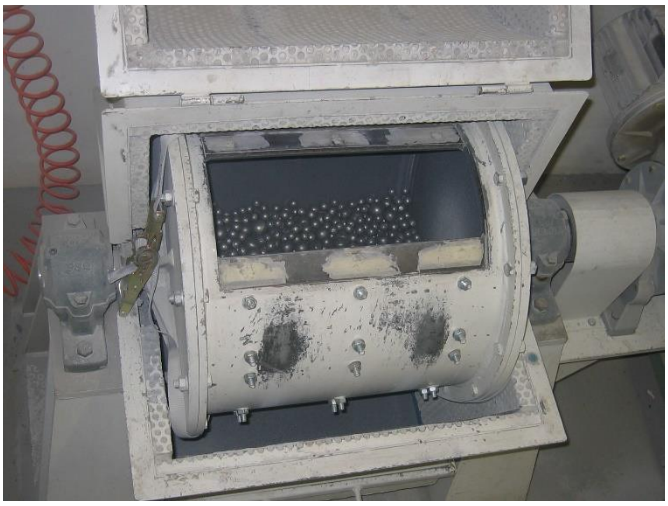

Figure 1: Laboratory ball mill for the reproduction of cements.

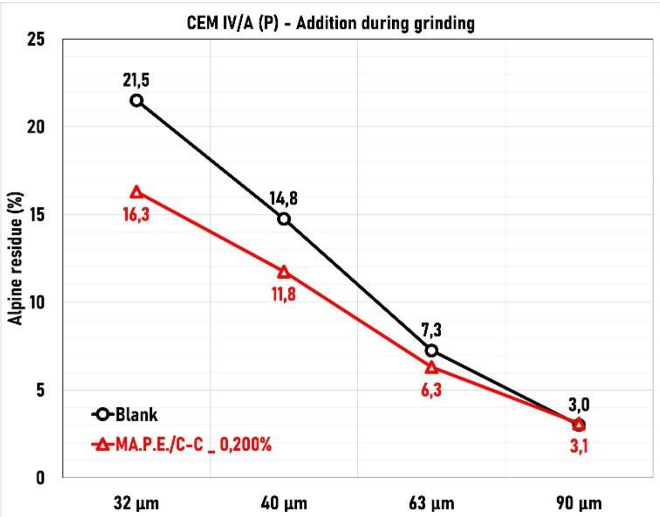

Figure 2: Alpine granulometry of the laboratory cement reproduced with and without MA.P.E./C-C.

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

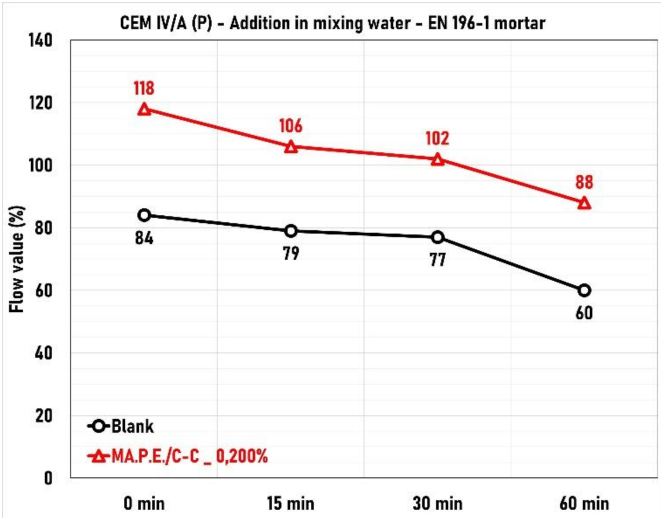

Figure 4: Flow values of standard mortars with and without addition of MA.P.E./C-C in the mixing water.

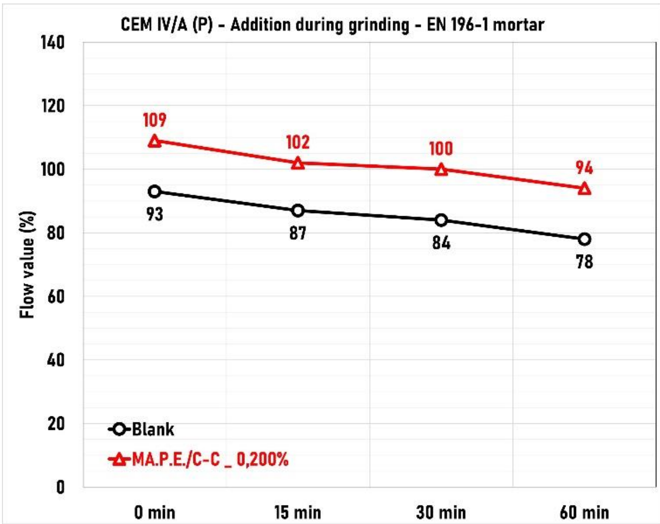

Figure 5: Flow values of standard mortars with and without addition of MA.P.E./C-C during laboratory grinding of cements.

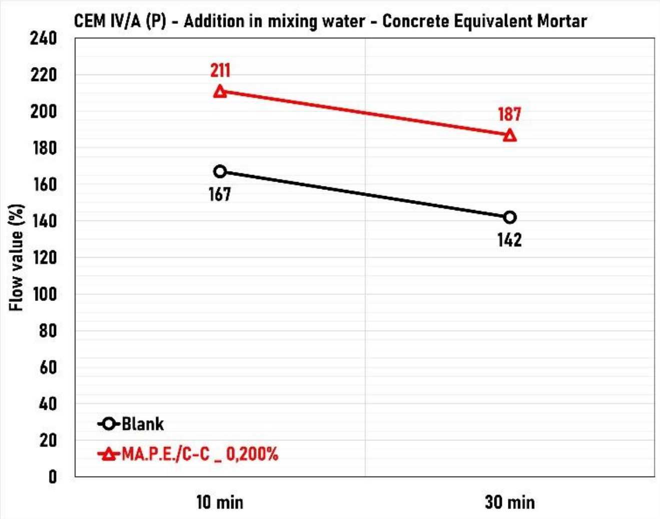

Figure 6: Flow values of C.E.M. mortars with and without addition of MA.P.E./C-C in the mixing water.

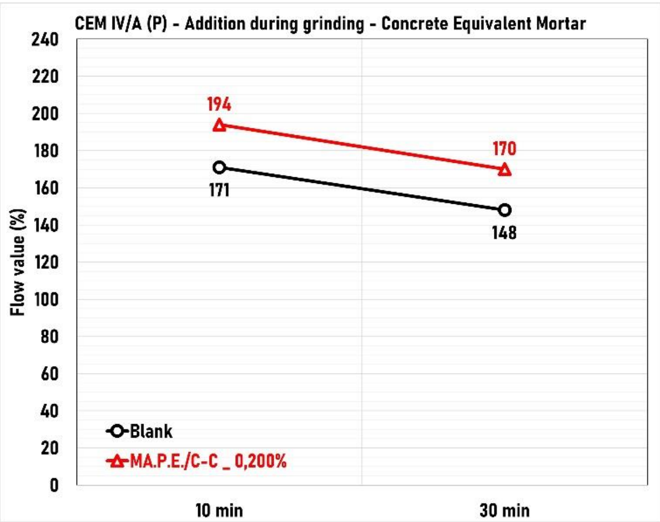

Figure 7: Flow values of C.E.M. mortars with and without addition of MA.P.E./C-C during laboratory grinding of cements.

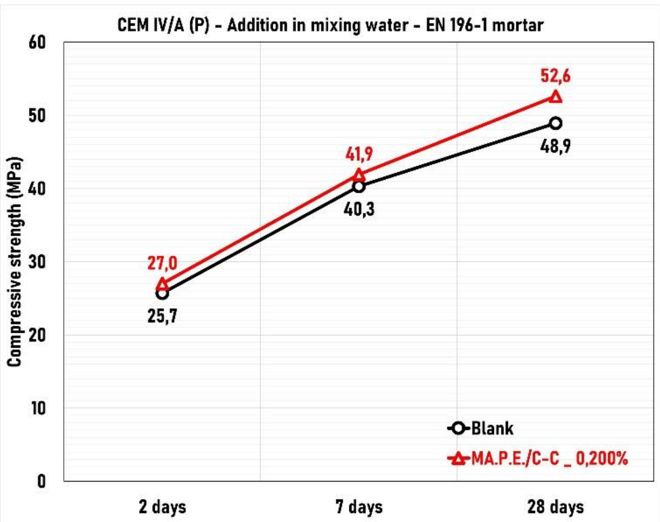

Figure 8: Mechanical strength of standard mortars with and without addition of MA.P.E./C-C in the mixing water.

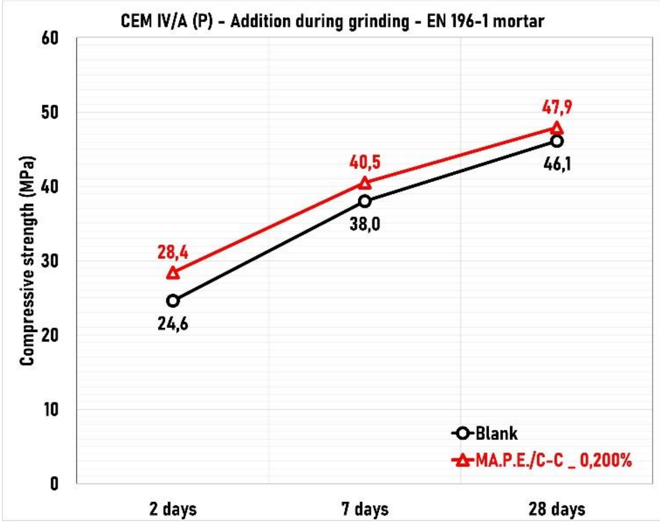

Figure 9: Mechanical strength of standard mortars with and without addition of MA.P.E./C-C during laboratory grinding of cements.

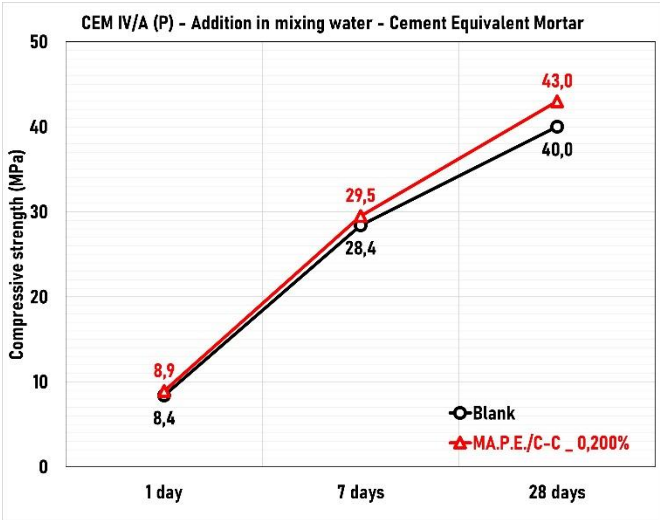

Figure 10: Mechanical strength of C.E.M. mortars with and without addition of MA.P.E./C-C in the mixing water.

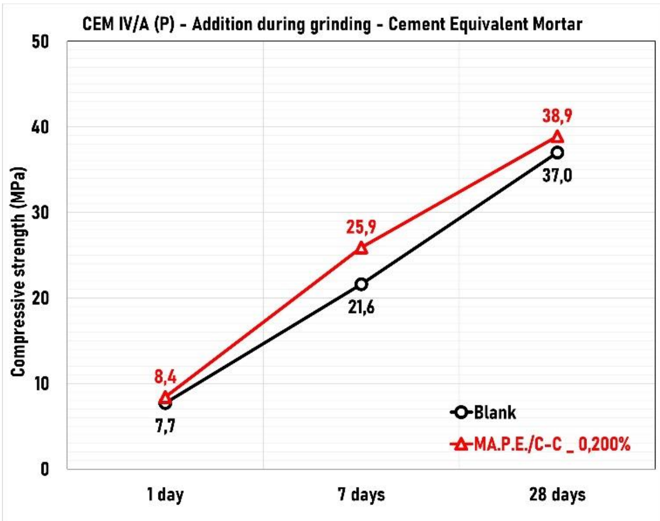

Figure 11: Mechanical strength of C.E.M. mortars with and without addition of MA.P.E./C-C during laboratory grinding of cements.

3 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 CO2.

The secondary raw material used for this cement is a blend of calcined clay and recycled inert minerals characterized by a high porosity/adsorption that leads to a high request of water. Consequently, the cement shows a noticeable loss of workability and 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 allowed to greatly increase the initial workability on the industrial cement and maintain it 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 has been estimated by a rheometer equipped by the so-called "ball measuring system"6 (Figure 13) at a shear rate of $1s^{-1}$. The evolution of viscosity has been monitored for 90 minutes 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 maintain a low viscosity of the fresh mortar over the time, with viscosity at 90 minutes from the mix lesser than the initial viscosity of the blank sample.

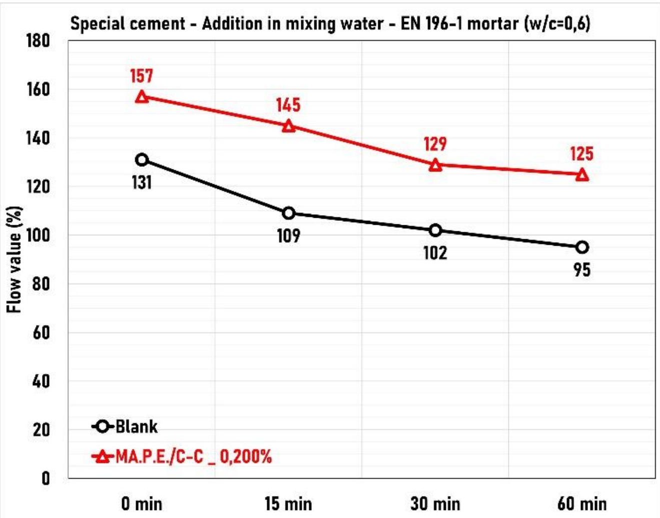

Figure 12: Flow values of standard mortars with and without addition of MA.P.E./C-C in the mixing water.

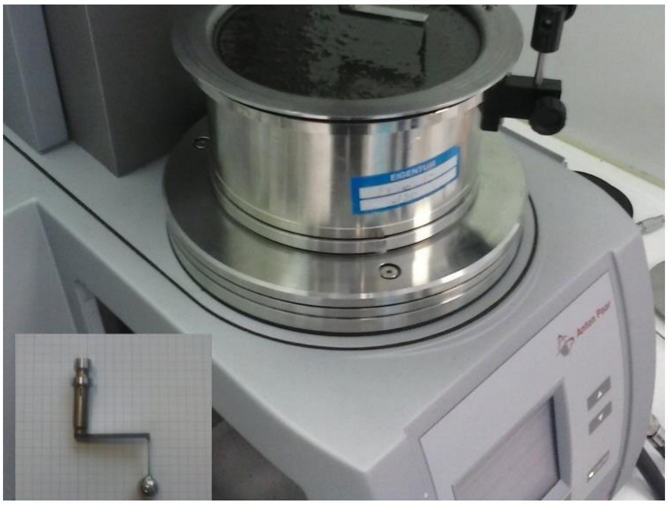

Figure 13: Rheometer equipped with a ball measuring system.

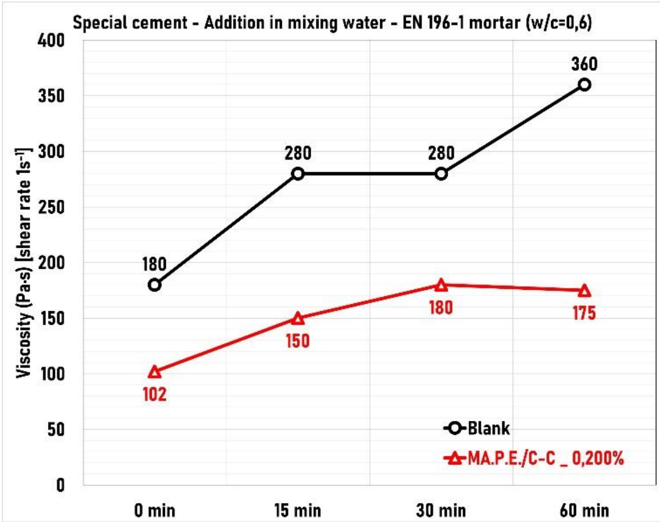

Figure 14: Viscosity of standard mortars with and without addition of MA.P.E./C-C in the mixing water.

4 Conclusion

MA.P.E./C-C, the new range of additives developed by Mapei, can help cement producers and users in the most difficult cases, thanks to the combination of numerous benefits: increased grinding efficiency, improved workability in mortar and in concrete, increase in 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 cements, 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 coming decades.

These additives can make it possible to produce cements with a lower clinker content, lower production costs, lower CO2 emissions and with a higher quality, the effect of which will be noticed in applications in mortar and concrete.

References

[1] World Business Council for Sustainable Development (WBCSD) (2016) *Cement industry energy and CO2 perfor-mance: getting the numbers (GNR)*, Available online: https://www.wbcsd.org/contentwbc/download/6001/84250/1, December 2016.

[2] Cembureau (2020) *2050 Carbon neutrality roadmap*, Available online: https://cembureau.eu/media/kuxd32gi/cembureau-2050-roadmap_final-version_web.pdf.

[3] Magistri, M.; D'Arcangelo, P. (2009) *Clinker savings using additives*, International Cement Review.

[4] Bogerd, J., Forni, P. (2012) *The activation of pozzolanic materials with specific Cement Additives*, World Cement.

[5] Massazza, F. (1993) *Pozzolanic cements*, Cement and Concrete Composites, 1993.

[6] Schatzmann, M., Bezzola, G.R., Minor, H.E., Windhab, E.-J., Fisher, P. (2009) *Rheometry for large-particulated fluids: analysis of the ball measuring system and comparison to debris flow rheometry*, Rheol Acta.