New superplasticizer based on the Intelligent Cluster System (ICS) Technology

Gaetano Guarino, Customer Segment Manager Precast and MCP Europe, Master Builders Solutions Italia Spa
Ida Ros, Admixtures Development Precast and MCP Manager, Master Builders Solutions Italia Spa
Sandro Moro, Concrete Technology and Materials Innovation Manager, Master Builders Solutions Italia Spa

With a global consumption of approximately 14 billion m3, concrete is by far the most widely used man-made material. It accounts for about 8% of CO_2 emissions worldwide, 90% of which can be attributed to cement clinker production. Substituting clinker in cement, and ultimately in concrete, with alternative materials can save considerable amounts of carbon emissions. The construction industry is actively called upon to contribute to achieving the ambitious CO_2 reduction targets by taking clear action in a period of profound transformation. The introduction of the newly released cement standard (EN 197-5 2021) and the wide availability of cements with reduced clinker amount in the European market are just a couple of examples of this transformation. In this new environment, the precast segment, where a high dosage of CEM I is commonly used (clinker content ≥ 95%), is challenged to reduce CO_2 emissions by clinker content reduction.

Lowering the percentage of clinker in concrete is a crucial goal to make construction more sustainable in the future and this can be achieved mainly in three ways:

- Using already clinker-reduced cement types
- Further reducing the content of conventional cement
- Replacing a significant portion of cement with supplementary cementitious materials (SCMs)

Although alternative mixes with reduced amounts of clinker offer significant improvements in reducing the embodied carbon of precast concrete elements, they lead to various performance issues: loss of workability, deterioration of rheology, and slower strength development. The production of low-clinker concrete requires a proportional reduction in water content to ensure the desired mechanical properties, especially in the early ages, which is often not possible due to a worsening of the rheology and concrete aspect.

As a leading supplier of concrete admixtures, Master Builders Solutions aims to enable the construction industry to meet current sustainability challenges and simplify the production of low-clinker concrete without compromising on quality and efficiency. The newly developed MasterCO$_2$re superplasticizer range effectively counteracts these limitations and supports the achievement of challenging environmental targets by closing the performance gaps of low-clinker concretes compared to standard concrete mixes. Because of its unique Intelligent Cluster System (ICS) technology, MasterCO$_2$re ensures prolonged workability retention, advanced rheology, excellent strength properties, and high robustness even in concrete mixes with reduced clinker amount.

Additionally, in precast concrete mixes where the amount of clinker is significantly reduced (above 15%), MasterCO$_2$re can be used in combination with Master X-Seed®. The synergistic effect of the two admixtures allows a further boost to the early strength development required for fast demoulding of the elements to achieve the desired production output.

Intelligent mechanism of action

All concrete mixes must meet both workability and strength criteria. MasterCO$_2$re is an innovative technology that significantly improves low-clinker content performances thanks to the Intelligent Cluster System (ICS). ICS technology smartly creates clusters of finely tuned chemical structures, thus ensuring the release of the chemicals as required in the system.

Once MasterCO$_2$re, with its clusters, is added to concrete, a portion of the polymers is freely available and provides initial water reduction. Meanwhile, the variation of pH and the dissolution of ionic species in the pore solutions triggers a controlled release of molecules from the cluster, which intelligently releases the molecules as long as the dissolution of cement progresses, ensuring prolonged workability retention. In addition, the ICS technology ensures that the same amount of polymers unwrap their chains and distribute themselves in the cluster matrix, occupying a total volume about ten times bigger than the polymeric distribution. The dimension and

■ Gaetano Guarino has a master's degree in chemistry and 11 years of experience in the construction chemicals business. After covering different positions at the European Development Centre in Treviso, he is now responsible for the precast and manufactured concrete products (MCP) markets in Europe in his current role as Customer Segment Manager at Master Builders Solutions.
gaetano.guarino@masterbuilders.com

■ Ida Ros received her PhD in Science and Engineering of Materials from the University of Padua in 2010. She is currently Admixture Development Precast and MCP Team Leader and DFSS Black Belt at Master Builders Solutions. Her research interests include basic interaction of the properties of cement with chemical admixtures, data analysis and new concrete technologies for sustainability.

■ Sandro Moro has the role of Concrete Technology and Materials Innovation Manager in the European Development Team of Master Builders Solutions Italy. He is working in the field of admixtures for concrete, collecting experiences in new technologies for cementitious-based materials. Part of various RILEM committees, he received his MS from Venice University, Venice, Italy, in 1999.

steric hindrance of the clusters provide an additional boost in terms of rheological properties: the clusters provide a kind of tribological/lubrication effect between the concrete components and, especially at low water-to-cement ratios, can reduce friction, consequently ensuring better rheology of concrete. Therefore, the viscosity of concrete is lower at time zero and remains lower over time, since some clusters are continuously present to lubricate it, even if the friction among concrete particles increases as the hydration of the cement progresses and the crystals grow.

The hydration process is not slowed down by the controlled release, allowing excellent early strength development. It also provides more orderly growth of hydration crystals and reduced porosity, resulting in excellent long-term strength development. Studies using various analytical techniques such as physisorption/BET on hydrated pastes, thermogravimetric analysis, scanning electron microscope, and X-Ray Diffraction confirm an enhanced degree of hydration and a more compact structure.

The high-class workability retention, advanced rheology, and excellent strength properties of MasterCO$_2$re help decrease the environmental footprint of construction materials.

Section 1 – Lowering carbon footprint through cement content reduction

As already mentioned, one possible approach for reducing CO_2 emissions in concrete is to decrease the dosage of conventional cement per unit volume. Depending on the amount of cement removed, CO_2 emission reduction is directly proportional. The limit of this approach is dictated by the norms and exposure limits. For example, according to EN 206-1, the cement content for the exposure class XC4 cannot be lower than 340 kg/m³. This means that if the reference mix contains 360 kg/m³, the cement content reduction cannot be higher than 20 kg/m³, resulting in a maximum of 6% CO_2 reduction. Depending on the countries and the local implementation of the European Standard, the minimum amount of cement per m³ of concrete for each exposure class may vary slightly. France represents a special case where the new document FD P18-480 released in October 2022 permits to use the performance approach of EN 206. The minimum amount of binder required is ≥ 260 kg/m³ or ≥ 300kg/m³ depending to the exposure class of the concrete and the minimum clinker content in the total binder must be at least 15%. This performance approach allows pushing clinker content reduction to the limit.

In terms of performance, the reduction of cement content negatively impacts both the fresh and hardened properties of concrete. Due to the lower paste content, concrete appears stickier and flows more slowly. Moreover, compressive strengths would be lower, especially at early ages and in cold conditions due to the reduction of clinker content, causing delays in demolding. If the water-to-cement ratio is further reduced to overcome the strength issue, concrete rheology would be even more negatively impacted when using conventional superplasticizers.

The newly launched MasterCO_2re product range is a unique technology for redesigning concrete mixes, allowing the sustainable reduction of cement content. Concrete produced with MasterCO_2re has a lower viscosity than conventional superplasticizers. For this reason, the cement and water content can be easily reduced from the original concrete recipe without affecting the rheological properties and while promoting strength development.

Furthermore, MasterCO_2re can be used in addition to Master X-Seed in concrete mixes where the amount of clinker is significantly reduced, further boosting the early strength development required to guarantee a fast turnover of the molds. Two cases are described below where the use of MasterCO_2re technology successfully contributed to reducing the cement content without any negative impact on the fresh and hardened properties of low-clinker concrete mixes.

Case 1 – Roof panels, CEM I 52,5 R reduction

In this example, CEM I 52,5 R is used by the precast producer. The high amount of cement in the reference mix (465 kg/m³) is due to the special roof panel design with a very thin shape and the need to demold the elements in 12 hours. The results of introducing MasterCO_2re are underlined in Table 1, where a reduction of 50 kg/m³ of cement (low-clinker mix) is possible compared to the reference mix, contributing to a 10% reduction in CO_2 emission.

The total global warming potential (GWP tot) is estimated based on Ecoinvent 3.8 world datasets and industry average EPDs, taking into account the raw material supply (A1), transport (A2), and manufacturing (A3) for these calculations: 46 kg CO_2 eq/m³ savings are possible with the low-clinker mix (about 10% CO_2 reduction).

Table 1: Mix design and CO_2 emissions for 1 m³ of concrete

Materials type	u.m.	Reference mix	Low clinker mix
Sand	kg/m³	1022	1070
Gravel 7/10	kg/m³	649	708
CEM I 52,5 R	kg/m³	465	415
Water	kg/m³	205	180
W/C	kg/m³	0.44	0.43
Conventional superplasticizer	kg/m³	6	
MasterCO_2re™	kg/m³		6
GWP tot	kg CO_2eq/m³	478	432

Table 2 summarizes the fresh state properties of the reference mix and low-clinker mix: self-compacting concrete (SCC) is the focus and can be achieved because one of the sands used contains 10% of fines below 0.125mm. The slump flow, t_{500}, and the plastic viscosity have been measured through "4C rheometer" equipment (Figure 1), which, thanks to dedicated software, can calculate the rheological properties by analyzing the flow time recorded by a camera placed above the flow area. Both concretes reach 760 mm flow (SF3 class) with a similar speed (t_{500}) and consequently a similar plastic viscosity.

Figure 1: 4C Rheometer

Table 2: Fresh state properties of concrete

Property	u.m.	Reference mix	Low-clinker mix
Initial slump flow	mm	760	760
Plastic viscosity	Pa·s	29	39
t_{500}	s	1.6	2.4

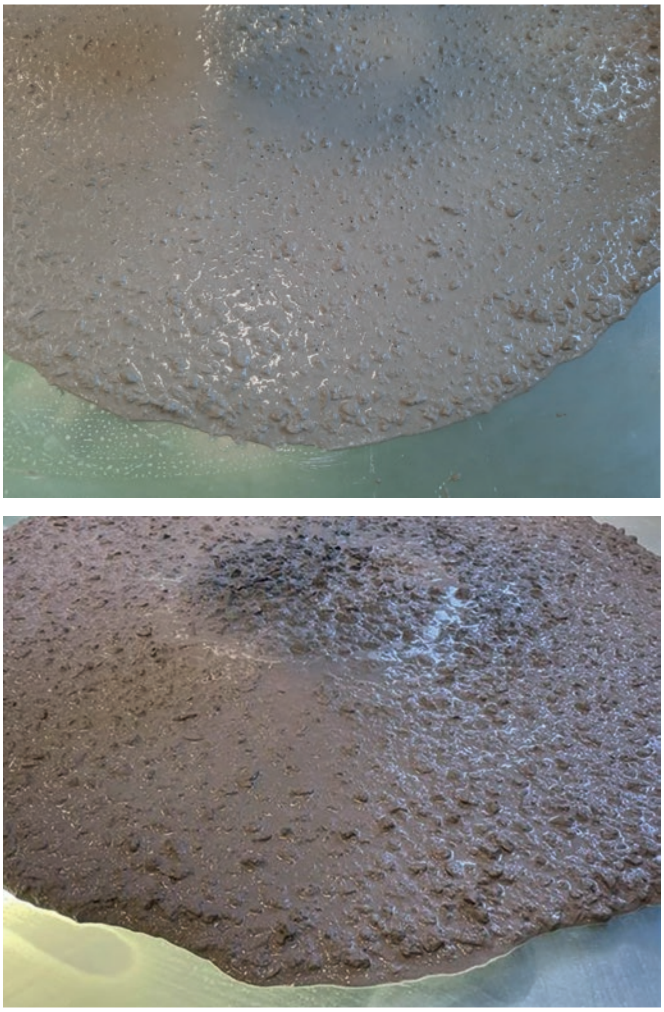

Fig. 2: On the top reference mix (465 kg/m³ of cement), on the bottom low clinker mix (415 kg/m³ of cement)

Figure 2 compares the concrete aspects and despite the lower paste content in the low-clinker mix, no bleeding or segregation is visible and the low-clinker mix appears equivalent to the reference one.

Both concretes have been prepared by mixing the raw materials in a planetary mixer capable of adjusting the concrete temperature within a range of 10°C to 40°C (Figure 3): these mixes have been cast at a concrete temperature of 15°C and using raw materials formerly conditioned at 10°C to simulate winter conditions.

Fig. 3: Planetary mixer with temperature range setting

The reduction of the cement content in the low-clinker concrete mix does not affect the compressive strength measured on 15x15x15cm concrete cubes according to EN 12390-3 (Figure 4): the values of the low-clinker concrete mix are similar to those of the reference mix, even when stressing the system at early ages and at 10°C. The similarity of the compressive strength at 28 days is also ensured.

Table 3: Mix design and CO_2 emissions for 1 m³ of concrete

Materials type	u.m.	Reference mix	Low-clinker mix
Sand	kg/m³	940	1000
Gravel 12/19	kg/m³	940	980
CEM II/A-LL 52,5 R	kg/m³	450	400
Limestone filler	kg/m³	50	100
Water	kg/m³	189	168
W/C	kg/m³	0.42	0.42
Conventional superplasticizer	kg/m³	3.15	
MasterCO$_2$re™	kg/m³		3.20
GWP tot	kg CO$_2$eq/m³	379	342

Case 2 – Beams, CEM II/A-LL 52,5 R reduction

In this example, the precast producer was forced to switch from CEM I 52,5 R to CEM II/A-LL 52,5 R as CEM I was no longer available in the market. In order to keep the same early strength development and the desired production output, the cement content was increased by the concrete producer from 400 kg/m³ CEM I in the original mix design to 450 kg/m³ CEM II/A-LL in the adjusted recipe. The increase of 50 kg/m³ of cement provides no advantage in terms of CO_2 reduction per m³ of concrete.

MasterCO$_2$re was proposed as a solution to reduce the amount of CEM II/A-LL 52,5 R from 450 kg/m³ to 400 kg/m³, thus returning to the original dosage of CEM I 52,5 R. Table 3 indicates the compositions of the self-compacting concrete: commonly used limestone filler was also added to achieve a total powder content of 520 kg/m³, with almost 20 kg/m³ of

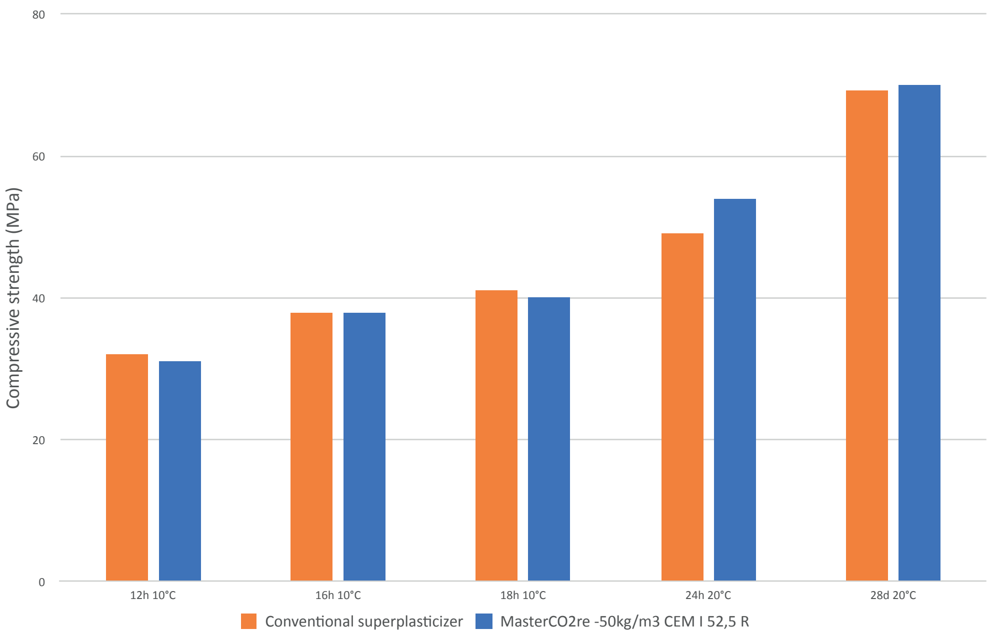

Fig. 4: Compressive strength of the reference mix containing conventional superplasticizer and of the low-clinker mix containing Master-CO$_2$re with 50 kg/m³ less cement.

Table 4: Fresh state properties of concrete

Property	u.m.	Reference mix	Low-clinker mix
Initial slump flow	mm	710	690
Plastic viscosity	Pa·s	65	79
t_{500}	s	2.9	3.9

this coming from the sand. The new low-clinker mix guarantees a 10% reduction in CO_2 emissions based on the same calculation approach as in case 1.

Based on the same "4C Rheometer", Table 4 summarizes the fresh state properties of the reference mix and low-clinker mix. As with case 1 at similar slump flow, both plastic viscosity and t_{500} are almost similar among the two concretes. From Figure 5, concrete produced with the advanced MasterCO_2re technology has similar aspects to the reference mix.

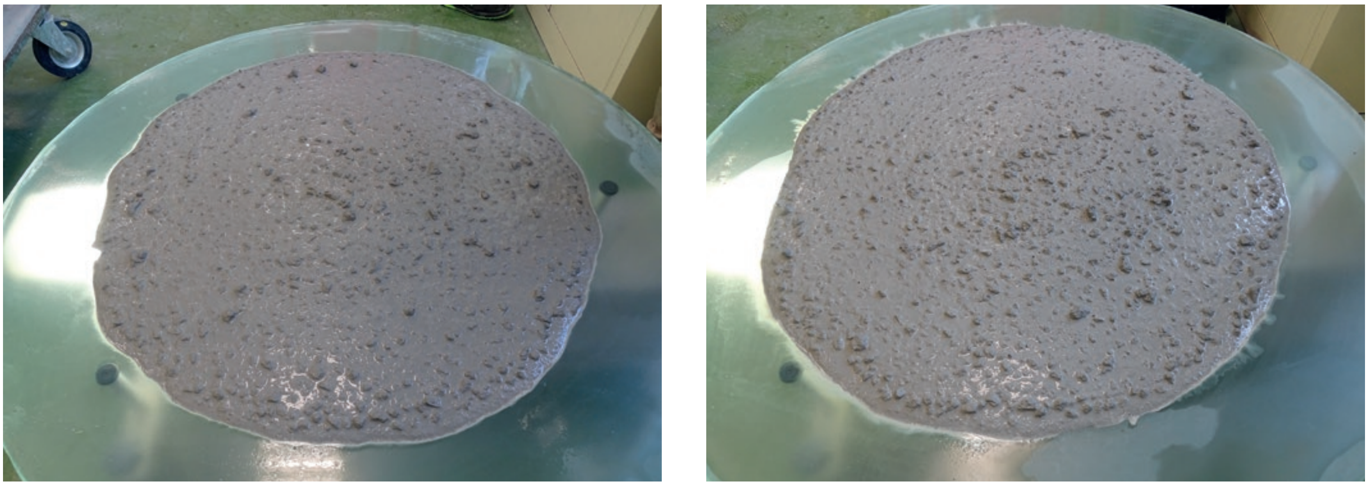

Fig. 5: On the left reference mix (450 kg/m³ of cement), on the right low clinker mix (400 kg/m³ of cement)

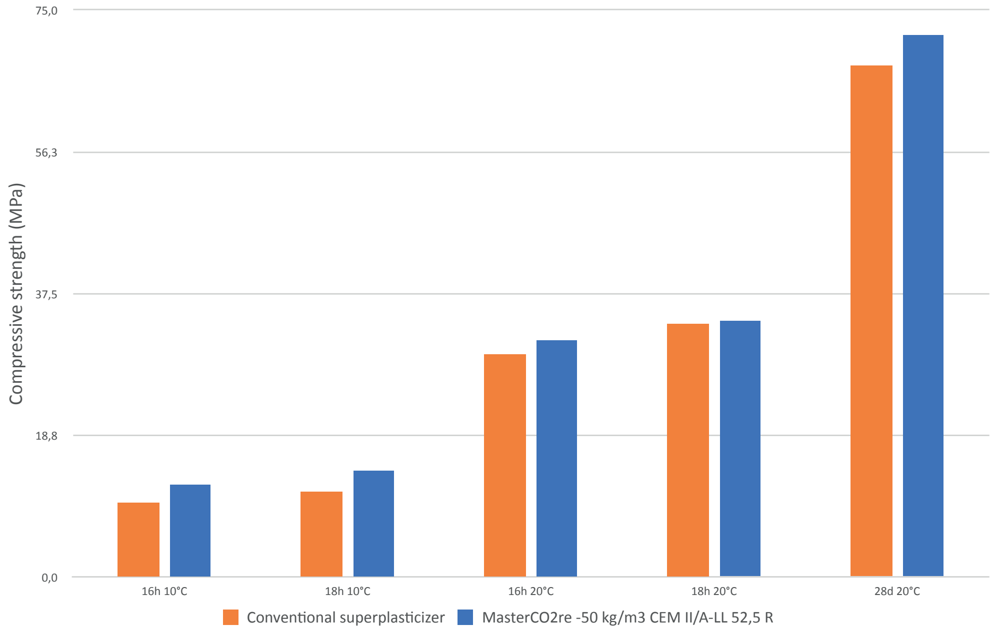

Fig. 6. Compressive strength of the reference mix containing conventional superplasticizer and of the low-clinker mix containing Master-CO_2re with 50 kg/m³ less cement.

The compressive strengths of the low-clinker concrete mix are comparable to the ones of the reference mix (Figure 6), confirming the possibility of reducing the cement content by 11%, also with a CEM II/A-LL 52,5 R cement.

Section 2 – Substitution of CEM I 52,5 R with CEM II/A-LL 52,5 R combined with cement reduction

As mentioned in Section 1, reducing the carbon emission according to the decrease of the cement content of the mix design is an approach limited by the minimum amount of cement declared in the norms. Until the performance approach of EN 206 is generalized to all of Europe, the way to further lower the CO_2 emissions beyond cement reduction is to combine it with the switch to a lower clinker cement type.

Therefore, in precast, for a considerable saving in the amount of carbon emissions, it is crucial not only to reduce cement content, but to substitute CEM I 52,5 R with more sustainable cements. In the case presented, a limestone blended cement is proposed to substitute CEM I 52,5 R.

In recent years, several cement producers have replaced the traditional Portland CEM I 52,5 R with the new CEM II/A-LL 52,5 R to reduce the carbon footprint of their product portfolio. The new cements have been specifically formulated and produced in accordance with the European standard EN197-1 to achieve the same performance as their CEM I predecessors, while simultaneously meeting the need for a more sustainable product. CEM II/A-LL 52,5 R contains between 6-20% of limestone and usually has a higher Blaine respect to a CEM I 52,5 R. For this reason, the achievement of targeted fresh properties can be challenging with conventional superplasticizers.

Table 5 reports the self-compacting concrete mix design of the reference formulation and low-clinker mix: in the low-clinker mix, CEM I 52.5 R is substituted with CEM II/A-LL 52.5 R and the cement dosage is lowered by 30 kg/m³. The CO_2 reduction with respect to the reference mix is about 19%. In this case, the GWP evaluation was conducted considering the specific EPDs of the two cements in scope.

Table 5: Mix design and CO_2 emissions for 1 m³ of concrete

Materials type	u.m.	Reference mix	Low-clinker mix
Sand	kg/m³	914	954
Gravel 8/19	kg/m³	747	773
Limestone filler	kg/m³	100	130
CEM I 52,5 R	kg/m³	400	-
CEM II/A-LL 52,5 R	kg/m³	-	370
Water	kg/m³	190	175
W/C	kg/m³	0.48	0.47
Conventional superplasticizer	kg/m³	3.2	
MasterCO_2re™	kg/m³		2.6
Master X-Seed	kg/m³		3.7
GWP tot	kg CO_2eq/m³	388	315

Table 6 summarizes the fresh state properties of the reference mix and the low clinker mix, while Figure 7 shows the images of the reference and low-clinker mixes. This new experiment reconfirms the conclusions of case 1 and case 2 - similar consistency and rheology. Indeed, the V-Funnel time again measured the equivalence between the two concretes.

Table 6: Fresh state properties of concrete

Property	u.m.	Reference mix	Low-clinker mix
Initial slump flow	mm	700	680
Plastic viscosity	Pa·s	37	49
Initial V-funnel	s	9	11

However, the substitution of CEM I with CEM II/A-LL presents a challenge in terms of strength development and this becomes even greater when the limestone-based cement is reduced by 30 kg/m^3.
The additional usage of the hardened accelerator Master X-Seed synergistically helps MasterCO$_2$re completely recover the early strength of the reference mix at 10°C and to reach the minimum strength required for prestressed elements at 20°C (> 35MPa), as described in Figure 8.

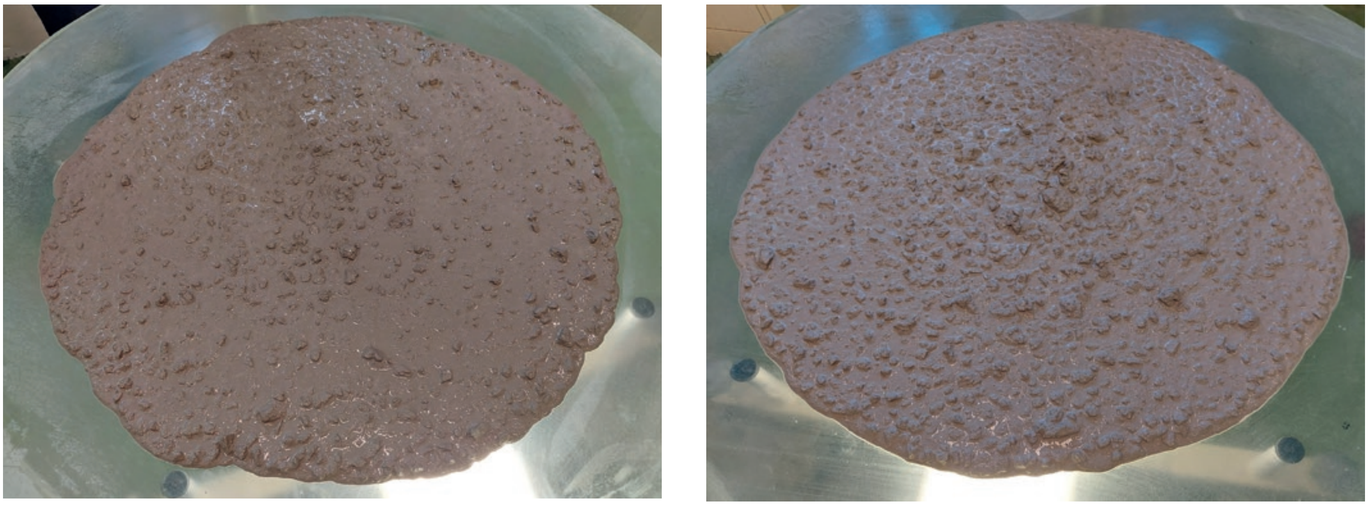

Fig. 7: On the left reference mix (400 kg/m^3 of CEM I 52,5 R), on the right low clinker mix (370 kg/m^3 of CEM II/A-LL 52,5 R)

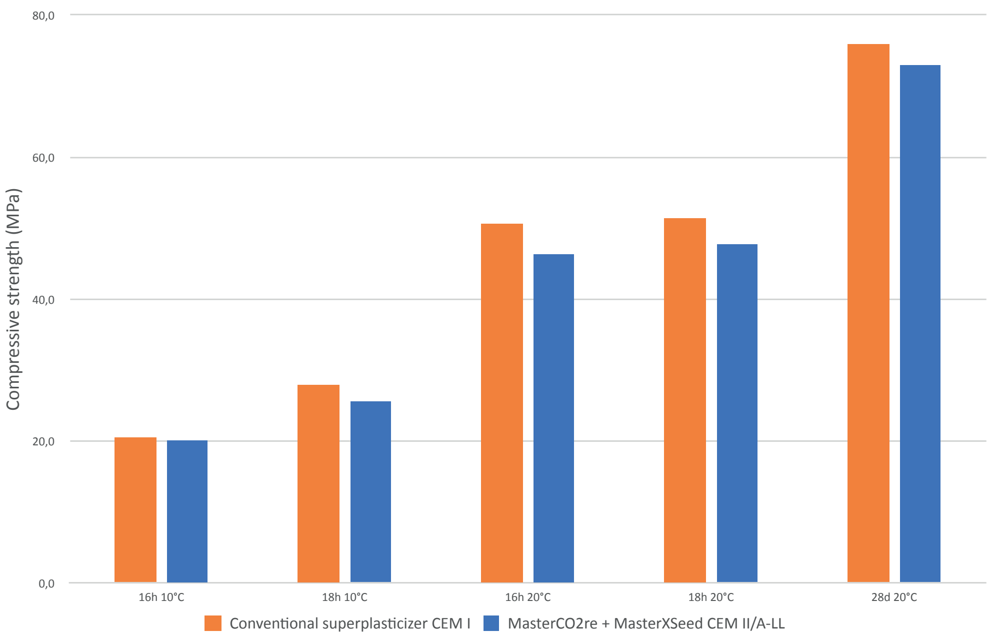

Fig. 8: compressive strength of the reference mix containing conventional superplasticizer and of the low-clinker mix containing MasterCO_2re and Master X-Seed based on CEM II/A-LL

Conclusion

MasterCO_2re is an innovative superplasticizer based on the Intelligent Cluster System (ICS) technology developed in the R&D laboratories of Master Builders Solutions. MasterCO_2re combines the performances of fluidification, extended workability retention, high early and ultimate strength with excellent rheology in one single solution. This advanced technology provides a perfect choice for stable and robust concrete performance in challenging low-clinker applications, paving the way for a more responsible future in the construction industry.

MasterCO_2re offers the following main benefits to precast producers:

- Extended workability retention: MasterCO_2re releases the polymer over time, ensuring consistent workability of concrete.
- Advanced rheology: concrete containing MasterCO_2re has a very low viscosity. This allows good workability and flowability during casting even with concrete using a difficult cement such as low clinker cement or concrete formulated with high SCM content for instance.
- Strength properties: Thanks to the very good rheology provided by ICS technology of MasterCO_2re, the content of water in the concrete recipe can be further reduced. This allows the achievement of the early strengths needed to meet the production requirements even in concrete mixes with reduced clinker amount. MasterCO_2re promotes the formation of a denser and more homogeneous structure of cement hydrates, which is reflected in optimal strengths development.
- Superb robustness: with rapidly changing cement types and binder compositions, the stability and quality consistency of concrete is a challenge in precast plants' daily operations. MasterCO_2re successfully counteracts the potential of high-water absorption and other undesirable effects caused by the variation in the chemical and mineralogical composition of the binders.

The synergic combination of MasterCO_2re and Master X-Seed pushes the limits of low-clinker concrete by enabling the easy usage of high volumes of clinker substitutes while safeguarding substantial performance characteristics. ■

FURTHER INFORMATION

Master Builders Solutions Deutschland GmbH
Glücksteinallee 43-45,
68163 Mannheim, Germany
https://info.master-builders-solutions.com/en/masterco2re
www.master-builders-soulutions.com