The Right Reaction

Luca Pagani, Keith Marsay and Alessandro Schibuola, GCP Applied Technologies, show how high-performance chemical additives can facilitate reductions in the clinker-to-cement ratio and help contribute towards carbon neutrality in the European cement industry.

COURTESY of gcp

Climate change is a challenge for the whole world, requiring substantial social, political, and cultural shifts. Amid the many challenges of the COVID-19 lockdowns, one bright spot emerged – seeing images of clear skies over many of the most polluted cities showed that there are opportunities to drastically reduce emissions and improve human health.

Some steps have been taken in recent years, though there is much more work still to be done. In the 1990s, the European Union (EU) became the first to launch a scheme to monitor and control CO_2 emissions in its area of influence. The European Union Emissions Trading Scheme (EU-ETS) was a direct result of the 1997 Kyoto Protocol, which set absolute targets for quantitative emissions for industrial countries.

The key features of the EU-ETS are a maximum emissions limit, or cap, and the allocation of emissions allowances (EUA) to key industries and installations within the zone. If an installation does not use all of its allowance, it would then be able to sell, or trade this allowance to industries struggling to meet their allowance, such that the total emissions in the zone remain within the cap. This is what is known as a cap and trade system.

The first phase of the EU-ETS was to measure emissions and establish the EUAs, with each country having its own National Allocation Plan. Subsequent phases progressively reduced the absolute value of the cap. Phase 4 begins in 2021 and promises an ongoing 2.2% per year reduction in emissions allowances.

The result of the progressive reduction in the emissions cap is an increase in the trading price for CO_2 allowances, from a low of €3/t in April 2013 to a high of €28/t in late 2019. According to the authors' estimates, EUAs are likely to remain in excess of €25/t and increase further. This will be a significant ongoing operational cost for cement plants, and is expected to provide a driver for further CO_2 reductions in cement production.

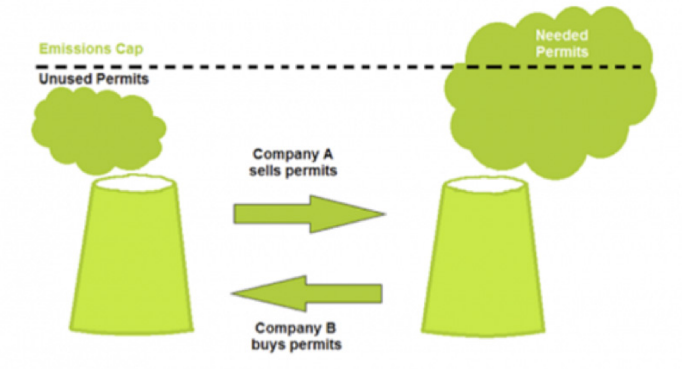

Figure 1. If companies emit less than the cap, they are permitted to sell the excess carbon permits to companies that are emitting more. The company emitting less will profit from this transaction. (Figure adapted from Energy Royd, 2013).

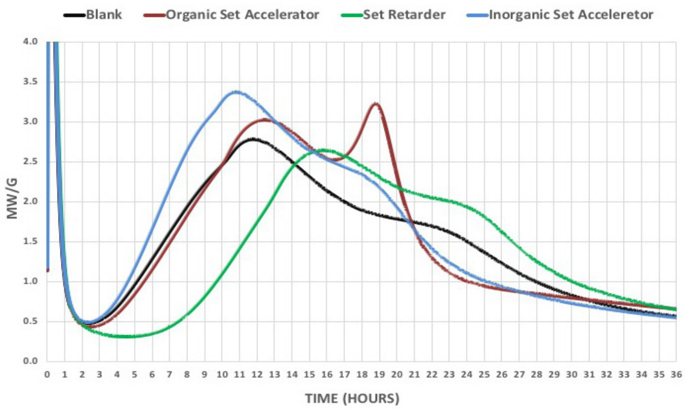

Figure 2. Isothermal calorimetry plots of different chemistries.

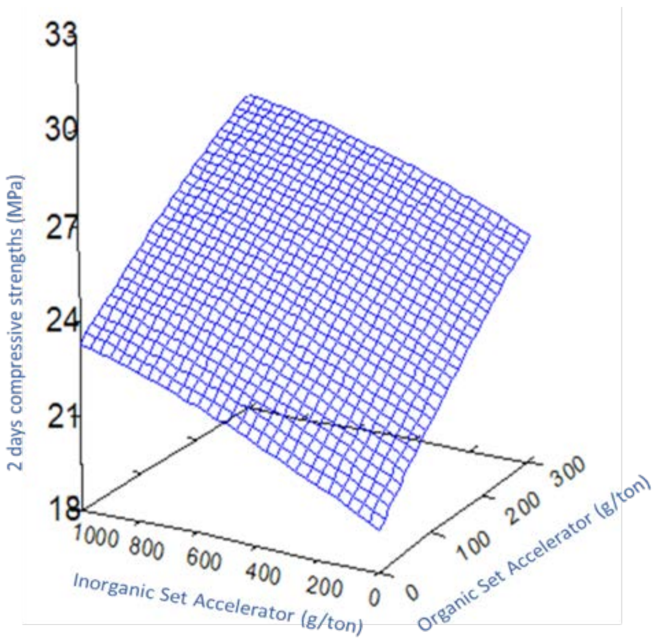

Figure 3. Two set accelerating chemicals achieved maximum 25.5 MPa at two days when tested separately. The positive interaction between these two chemicals together increased two day strengths to more than 29 MPa.

Direct CO_2 emissions in cement manufacture are the result of burning fuels to manufacture clinker, and of the decarbonation process when the limestone used to make clinker is calcined in the kiln. CO_2 from fuels can be reduced significantly by using carbon-neutral alternative fuels, such as domestic refuse (RDF, SRF) and organic sources such as wood pulp and animal meal. CO_2 from calcination can be reduced by producing alternative low-carbon binders.

EU cement industry 2030 goals and roadmap to 2050

The European cement industry's efforts in reducing its carbon footprint resulted in a 15% emissions reduction based on 1990 levels in 2017 (Roadmap to 2050, Cembureau, 2020). The roadmap to 2050 carbon neutrality set by the European cement industry highlights an ambitious target of reducing its gross CO_2 emissions 30% by 2030 for cement and 40% down the value chain. Cembureau (The European Cement Association) roadmap 5C Approach considers clinker, cement, concrete, construction, and (de)carbonation, setting targets for each of the value chain steps expressed as carbon emission reductions. A significant role is played by cement itself, which accounts for 18% of the total 2030 target. 70% of this cement portion will be achieved by lowering the cement clinker factor, and 30% will be achieved by energy efficiency increases and the use of renewable or carbon-neutral energy sources.

Lowering the clinker-to-cement ratio is a critical lever for the European cement industry in its path towards carbon neutrality. Cembureau is targeting a significant reduction in cement clinker ratio: from 77% to 74% by 2030, and to 65% by 2050.

Cement manufacturers need to control all the resultant effects of the required reduction in clinker-to-cement ratio. Challenges to be considered include a potential negative impact on cement performance, the availability of suitable supplementary cementitious materials (SCMs), limitations from standards and acceptance in the market. Chemical additives to cement have been used for over 80 years to improve the comminution process and finished cement performance. The ambitious targets set by the cement industry with regard to CO_2 have promoted the research and development of further high-performance chemical additives to facilitate additional reductions in clinker-to-cement ratios.

GCP Applied Technologies has launched a new additive line, OPTEVA® CO_2ST® Reducers, specifically developed to allow a significant reduction in clinker factor and an increase in SCM level, while mitigating any detrimental effects on finished cement performance. The line involves the use of new chemicals, a new combination of components and a new proprietary design process. During this process, the laboratory stage is critical to first test several chemistries and identify the most reactive chemistries with the specific cement system. This assessment is made based on a deep understanding of the influence on cement performance and hydration kinetics. One of GCP's recent designs was tested on a CEM II/B-LL 42.5R type cement to maximise limestone substitution. Figure 2 displays the influence on cement hydration coming from different chemistries tested with isothermal calorimetry, organic and inorganic set accelerators and a set retarder.

When the most promising chemicals are identified, the evaluation of synergies and interactions are then measured. Figure 3 illustrates an interaction between an inorganic and an organic chemical on early strengths. In this example, the two chemicals show a good additive interaction. All this specific information on cement-chemical systems is then used to design the most suitable formulation.

Figure 4 shows the outcome of the laboratory validation of three additive formulas with the studied CEM II/B-LL 42.5R, demonstrating an increase of 9 – 10 MPa at 2 days and 6 – 7 MPa at 28 days strengths in comparison to a blank cement, or a gain of 5 – 6 MPa at all ages, when compared to cement made with the reference additive. This special laboratory project outlined different formulations that enabled high compressive strength gain, especially in the early stages.

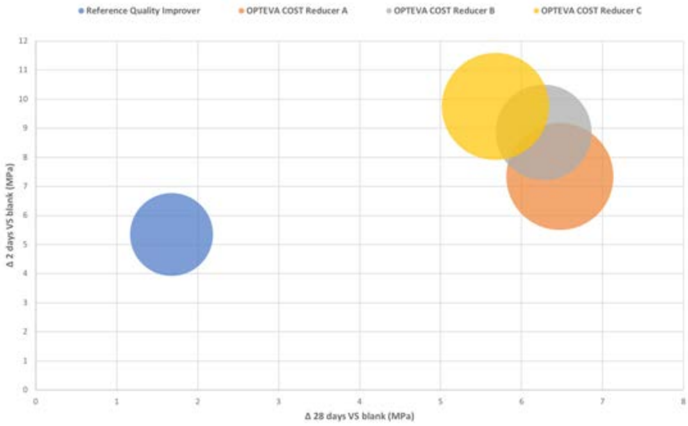

Figure 4. Laboratory validation of three OPTEVA CO_2ST Reducers formulas. Bubble size represents the expected throughput impact.

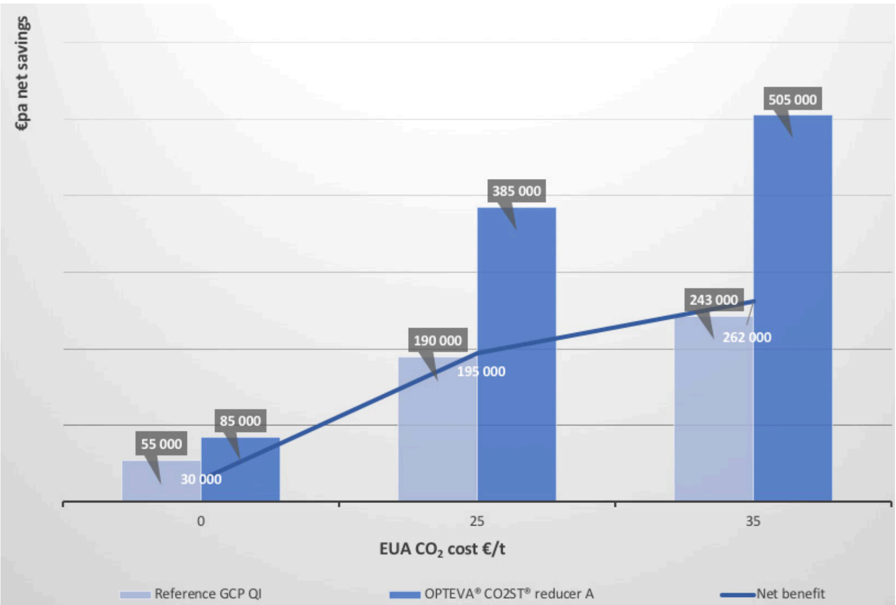

Figure 5. Field Case Study 1 – Cement manufacturer net savings at increasing EUA CO_2 cost per ton: the advantages provided by GCP technology increases with EUA CO_2 cost.

Table 1. Case study 1 – field trial results.

Additive	Dosage	Blaine	Alpine 45μm	Output	2d	7d	28d
	g/t	cm²/g		tph	MPa	MPa	MPa
Untreated cement (3% more clinker)	-	5500	1.1%	85	20	-	51
Reference GCP QI	500	5300	1.6%	93	20.3	33.7	51.6
OPTEVA® CO_2ST® Reducer A	2000	5100	1.5%	97	23.1	36.3	55.7
OPTEVA® CO_2ST® Reducer A (4% less clinker)	2000	5300	1.8%	99	20.8	33.5	51.8

Field case study 1

A customer in eastern Europe requested a grinding additive to facilitate a further 4% clinker replacement for a CEM II/B-M 42,5N cement type, over and above the 3% reduction that a traditional GCP quality improver was already delivering. GCP designed a new product, which was tested on site, producing the same cement at the same fineness.

The resultant cement strengths were increased

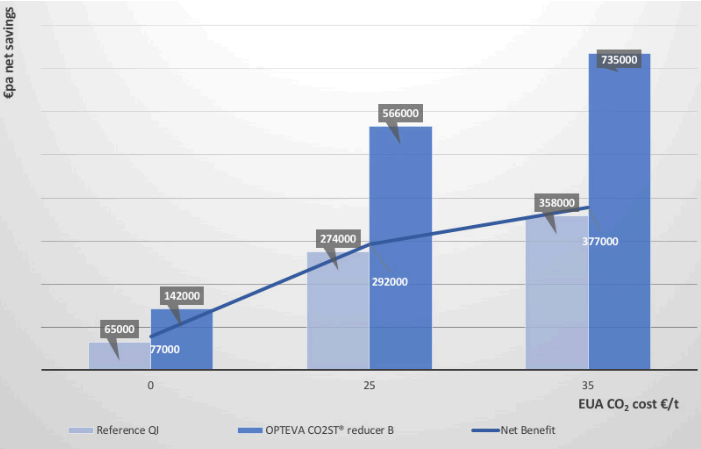

Figure 6. Field case study 2 – Cement manufacturer net savings at increasing EUA CO_2 cost per ton: the advantages provided by the GCP's technology increase along with the EUA CO_2 cost.

in the order of 10% at all ages, in addition to an increase in mill output of just over 4%. This enabled the plant to reduce clinker factor by the desired 4% by increasing limestone content, and still maintaining the same target strengths. The plant also saw a further 6.5% gain in productivity. Considering a 2018 CO_2 emission factor of 815 kg/t of clinker produced (GCCA, 2018) and a CO_2 emission factor of 0.5 kg of CO_2/kWh (IEA Statistics, 2018) consumed for grinding, the additive helped achieve a CO_2 emission reduction of over 10%, from 596 kg for the untreated cement down to 536 kg/t for the cement treated with OPTEVA CO_2ST Reducer A, or a reduction of 6%, from 569 kg for the current additive. The detailed data is presented in Tables 1 and 2.

If CO_2 related costs were not considered, the difference between the compositional and energy savings provided by the product and by the reference QI would be €30 000/y. When CO_2 emissions related costs are considered, the advantages provided by the implementation of OPTEVA CO_2ST Reducer A increase. In the current scenario, with EUA at €25/t, the net benefit would result in further savings of €195 000/y. In a scenario with EUA at €35/t, the net benefit provided by GCP's additive would increase to €262 000/y (Table 2 and Figure 5).

Table 2. Field Case Study 1 - EUA CO_2 related costs analysis *Assumes 815 CO_2 kg/ton of clinker. **Assumes 0.5 kg/CO_2 per kWh.

		No additive	Reference GCP QI	OPTEVA CO_2ST Reducer A
Additive	Dosage (g/cem t)	-	500	2000
	Use cost (€/cem t)	0	0.6	1.4
Cement composition and cost	Clinker (%)	70.5	67.5	63.5
	Gypsum (%)	4.5	4.5	4.5
	Fly ash (%)	12	12	12
	Limestone (%)	13	16	20
	Composition cost (€/cem t)	18.7	18.1	17.4
	CO_2 from CLK* (CO_2 kg/cem t)	575	550	518
Grinding	Mill output (cem t/h)	85	93	99
	Specific energy (kWh/t)	42.4	38.7	36.4
	Specific energy cost (kWh/t cost)	3.18	2.90	2.73
	CO_2 from grinding** (CO_2 kg/cem t)	21	19	18
CO_2 related costs	CO_2 cement factor (CO_2 kg/cem t)	596	569	536
	If ETS carbon cost (€/CO_2 t) = 0	0	0	0
	If ETS carbon cost (€/CO_2 t) = 25	14.9	14.2	13.4
	If ETS carbon cost (€/CO_2 t) = 35	20.9	19.9	18.8
Savings at ETS carbon cost € 0/CO_2 t	Net savings (€/cem t)	-	0.28	0.42
	Annual € savings (0.2 Mta)	-	55 000	85 000
Savings at ETS carbon cost € 25/CO_2 t	Net savings (€/cem t)	-	0.95	1.92
	Annual € savings (0.2 Mta)	-	190 000	385 000
Savings at ETS carbon cost € 35/CO_2 t	Net savings (€/cem t)	-	1.22	2.52
	Annual € savings (0.2 Mta)	-	243 000	505 000

Field case study 2

A GCP OPTEVA CO_2ST Reducer was tailor-made for a customer in southern Europe, with the target of allowing a minimum 3% clinker replacement with limestone in a CEM II/A-LL 42.5 R, currently produced in 250 000 tpy and treated with a mid-range quality improver, dosed at 1000 g/t. Based on the information available before the trial, the reference additive allowed 4% clinker replacement with respect to the untreated cement produced at the same fineness, and with a limited output increase.

During the field trial, the untreated cement and cement treated with the reference quality improver, and the new GCP

Table 3. Field Case Study 2 trial results.

Additive	Dosage	Blaine	Alpine 45µm	Output	2d	7d	28d
	g/t	cm²/g		tph	MPa	MPa	MPa
Blank		4000	3.1%	94	20.9	33.7	45.2
Reference QI	1000	3800	2.5%	97	22.7	34.8	48.1
OPTEVA CO_2ST Reducer B	1800	3700	2.6%	104	25.9	38.8	53.9

additive, were produced. The tests were carried out with the same composition in order to evaluate and compare the impact on the grinding system output and the potential for clinker replacement. The reference QI confirmed the ability to replace 4% clinker with limestone in normal customer operating conditions. The OPTEVA CO_2ST Reducer B allowed for a 10.6% output increase, +5 MPa above the blank at 2d and +8,7 MPa at 28d (Table 3). These results made the 4% clinker replacement with limestone possible. More importantly, an annual saving of €77 000/y was made possible, as well as a reduction in CO_2 emissions of 68 kg/t produced (Table 4 and Figure 6).

Considering the CO_2 emissions per t of clinker produced and the grinding-energy-related CO_2 emissions, the reference blank cement would have a CO_2 cement factor of 706 kg/t. The cement produced with the reference QI would show a 5% CO_2 cement factor reduction, while GCP's product would be expected to provide a CO_2 cement factor reduction of 10%.

With the current CO_2 allowances at €25/t, the net benefit would raise up to €292 000/y. In a scenario with CO_2 allowances at €35/t of CO_2 the benefit would widen to €377 000/y (Table 4 and Figure 6).

Table 4. Field Case Study 2 EUA CO_2 related costs analysis. Figures based on same finished cement performance. *Assumes 815 CO_2 kg/t of clinker produced. **Assumes 0.5 kg/CO_2 per kWh.

		No additive	Reference GCP QI	OPTEVA® CO_2ST® reducer B
Additive	Dosage (g/cem t)	-	1 000	1800
	Use cost (€/cem t)	0	0.7	1.5
Cement composition and cost	Clinker (%)	84.5	80.5	76.5
	Gypsum (%)	4.5	4.5	4.5
	Limestone (%)	11	15	19
	Composition cost (€/cem t)	24.7	23.8	22.9
	CO_2 from CLK* (CO_2 kg/cem t)	689	656	623
Grinding	Mill output (cem t/h)	94	97	105
	Specific energy (kWh/t)	34.0	33.0	30.5
	Specific energy cost (kWh/t cost)	2.55	2.47	2.29
	CO_2 from grinding** (CO_2 kg/cem t)	17	16	15
CO_2 related costs	CO_2 cement factor (CO2 kg/cem t)	706	672	638
	If ETS carbon cost (€/CO_2 t) = 0	0	0	0
	If ETS carbon cost (€/CO_2 t) = 25	17.65	16.81	15.96
	If ETS carbon cost (€/CO_2 t) = 35	24.71	23.54	22.34
Savings at ETS carbon cost €0/CO_2 t	Net savings (€/cem t)	-	0.26	0.57
	Annual € savings (0.2 Mta)	-	65 000	142 000
Savings at ETS carbon cost €25/CO_2 t	Net savings (€/cem t)	-	1.10	2.26
	Annual € savings (0.2 Mta)	-	274 000	566 000
Savings at ETS carbon cost €35/CO_2 t	Net savings (€/cem t)	-	1.43	2.94
	Annual € savings (0.2 Mta)	-	358 000	735 000

Conclusions

GCP's new technology has been seen to provide an important sustainability advantage to cement producers. The specific CO_2 emissions are reduced by means of clinker replacement and improvement in grinding efficiency. In the case studies described, the technology has been proven to reduce CO_2 cement factors up to 10% compared with untreated cement, resulting in around 15 000 tpy of CO_2 being saved.

As demonstrated by the 4% clinker replacement that was made possible, the adoption of GCP's new quality improver contributes to cement producers' abilities to match 2030 targets of clinker reduction and to reach 2050 EU targets of carbon neutrality, as well as the ability to enhance the economics of cement production in the presence of increasing EUA CO_2 prices. ■

References

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About the authors

Luca Pagani is a Cement Additives Technologist and holds a Master's degree in Physics. Since the beginning of his career, he has worked in the construction industry. Luca joined GCP in 2010 where he has covered different roles both in the concrete and cement additives businesses. He is currently working as formulator in the EMEA R&D team.

Alessandro Schibuola is R&D Manager at GCP EMEA. He graduated with a degree in Chemistry in 2009 and has more than 10 years of experience in the field of R&D and Technical Service in cement additives. He is fully dedicated to developing innovative solutions that enable the manufacture of advanced cements with lower carbon footprint, higher quality and lower cost.

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