Customised quality improvers

Cement additives continue to play an important role in reducing the carbon footprint of cement production. Identifying the proper additive chemistry is crucial to the reduction in clinker and CO_2 emissions while maintaining a substantial increase in cement performance. GCP Applied Technologies explains how a suitable customised quality improver can enable sustainable and profitable cement production.

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A customised cement additive or quality improver (QI) solution takes advantage of the synergy between the various additives and cements, helping to achieve technical and economical targets and reduce the carbon footprint of cement production

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Climate change poses an imminent challenge to the global community. In 2015 the nations of the world banded together and collectively reached the UNFCCC Paris Agreement. It aims to reduce the threat of climate change by keeping the global temperature rise this century well below 2˚C above pre-industrial levels.

This goal is ambitious but achievable. Concrete, the most commonly-used material in the world, will need to play a role. Fortunately, concrete has many environmentally-friendly attributes. Few other construction materials are able to offer the same durability, ease of production and low production costs, but, more significantly, concrete has the lowest embodied energy and CO_2 (see Figure 1, Chatham House Report 2018).

Yet, cement, the binder that holds the concrete together, accounts for around eight per cent of global CO_2 emissions (Chatham House Report 2018). The cement industry has, through the years, deployed different methods to reduce CO_2 emissions. One method is to produce blended cements with large quantities of supplementary cementitious materials (SCMs). As illustrated in Figure 1, a substitution of 60-80 per cent clinker can reduce the carbon and energy footprint of ordinary Portland cement (OPC) by more than 50 per cent.

The 2DS (2˚C Scenario) and the B2DS (Beyond 2˚C Scenario) published by the International Energy Agency (IEA) and Cement Sustainability Initiatives (CSI) in the 2018 Technology Roadmap presented four key levers to reduce carbon emissions for the cement industry (see Figure 2):

1. improving energy efficiency
2. switching to alternative fuels
3. reducing clinker-to-cement ratio
4. using emerging and innovative technologies (eg carbon capture storage and utilisation).

Based on 2DS, the 2018 Technology

Figure 1: a substitution of 60-80 per cent clinker can reduce the carbon and energy footprint of OPC by more than 50 per cent

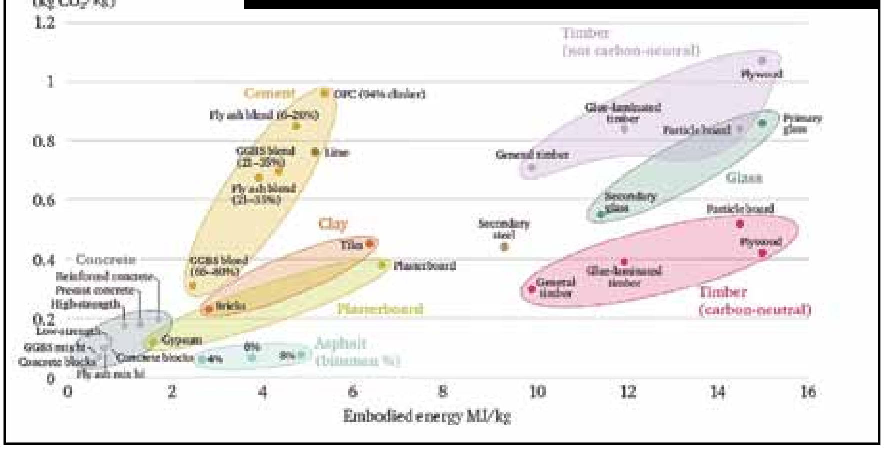
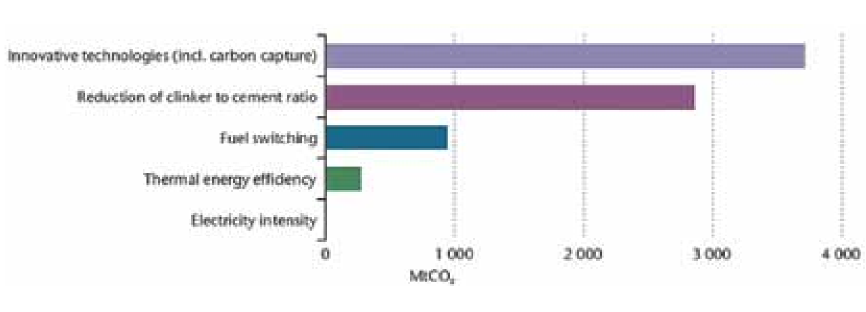


Figure 2: four key levers to reduce carbon emissions for the cement industry



Roadmap estimated that more than one-third (or 2.9GtCO_2) of targeted reduction of the global cumulative CO_2 emissions can be realised by decreasing the clinker-to-cement ratio from 0.65 to 0.60 in the next 30 years. This is a challenging objective and, under the coordination of the Global Cement and Concrete Association (GCCA), the cement industry has redoubled its efforts to meet this challenge. Notably, cement producers need to overcome the limitations to clinker substitution levels coming from standards and regulations, required cement performance and limited availability of reactive SCMs.

Cement additives technology and blended cements

Cement additives have and will continue to play an important role in reducing the carbon footprint of cement production. These chemicals act by increasing grinding efficiency even while improving the quality, performance and handling properties of the finished cement. As a result they enable the production of cements with a low clinker factor.

Three of the most significant additive technologies designed to influence the reaction and hydration kinetics in cement have been introduced by GCP Applied Technologies in the last eight decades. They are triethanolamine (TEA), tri-isopropanolamine (TIPA) and diethanol-isopropanolamine (DEIPA). These technologies continue to play a key role in the production of low-clinker cement.

TIPA, a technology patented by GCP in 1990, accelerates the hydration of carboaluminates in cements containing limestone to provide increased seven and 28-days strengths (Gartner, 1991 and Gartner, 1998). DEIPA, patented by GCP in 1998, catalyses the hydration of cement with calcium-aluminate-containing SCMs. The degree of slag hydration enhancement of a 30 per cent slag cement for the first 10 days is illustrated in Figure 3 (Riding, 2010).

Identifying the proper additive chemistry is crucial to the reduction in clinker and CO_2 emissions while maintaining a substantial increase in cement performance. The customised cement additive or quality improver (QI) solution takes advantage of the synergy between the various additives and cements. Some of the characteristics of the cement additives and the cement are summarised in Figure 4.

"Notably, cement producers need to overcome the limitations to clinker substitution levels coming from standards and regulations, required cement performance and limited availability of reactive SCMs."

In the example shown in Figure 5, a customised QI is used to make a new composite cement containing more than 40 per cent of slag and limestone. In this specific case, two customised QIs provided more than 20 per cent strength increase over the blank cement. This level

Figure 3: DEIPA, patented by GCP in 1998, catalyses the hydration of cement with calcium-aluminate-containing SCMs

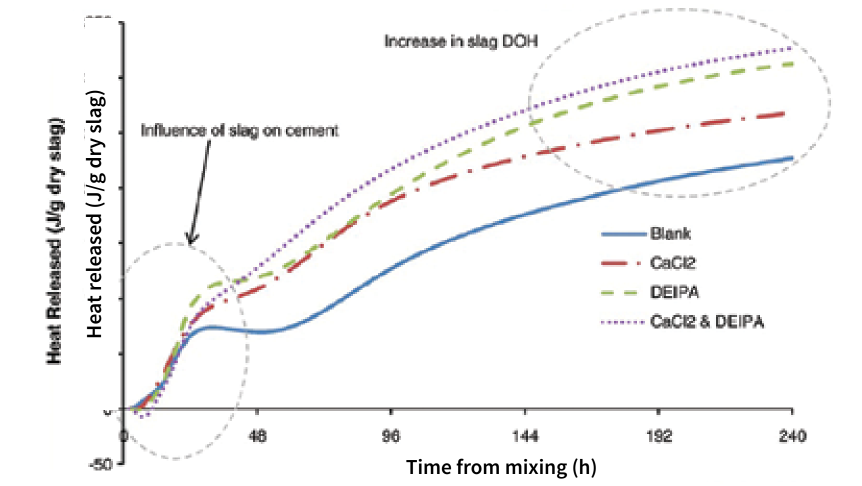


Figure 4: characteristics of cement additives and cement

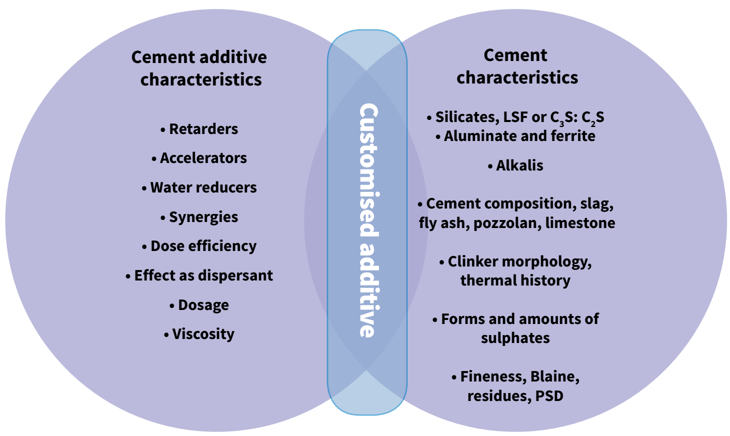


Figure 5: customised QI used to make a new composite cement containing more than 40 per cent of slag and limestone

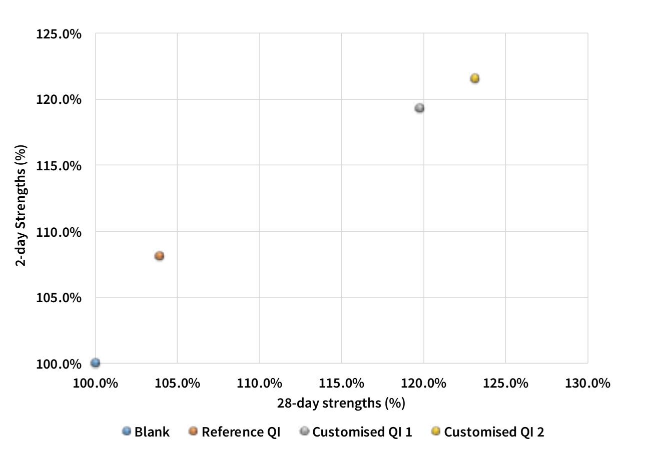
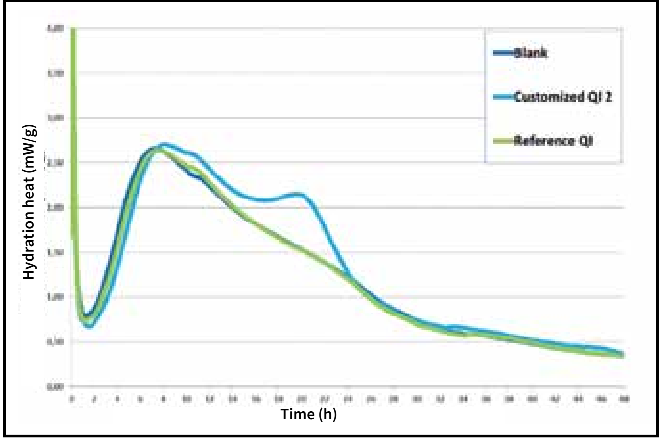


Figure 6: the customised QI 2 delivered a high performance by improving the kinetics of hydration of the silicate and, especially, of the aluminate phases



of strength increase allows five per cent or more additional SCMs to be used. This is similar to the target of the 2DS, bringing the clinker-to-cement ratio from 0.65 to 0.60. The customised QI 2 delivers high performance by improving the kinetics of hydration of the silicate and, especially, of the aluminate phases, as indicated by the exothermic peaks shown in Figure 6.

Economics and CO_2

The increase of CO_2 prices in the European Trading Scheme (ETS) cost over the last two years (Figure 7) had a significant impact on CO_2 emission costs. This impact is clearly visible in the case study reported in Table 1, which discusses the application of a customised QI of the "CO_2ST Reducers" series, in a CEM II/A-LL 42.5R.

In this case, the customised formulation of the "CO_2ST Reducers" series allowed a replacement of four per cent clinker by limestone, while providing a cement with 2-5 per cent higher two-day and 28-day compressive strengths and a six per cent increase in mill production. Table 1 shows how the customised QI impacts the economics and carbon footprint of cement. First of all, although the cost of the customised additive is approximately four times higher (€0.24/t to €0.99/t of treated cement) than the reference additive, this customised QI solution provides significantly higher cost savings (from €170,000 to €360,000 a year assuming cement production of 300,000tpa) whilst enabling a significant reduction in CO_2 emissions (34.8kg CO_2/t of cement or 10,500t of CO_2/yr). This saving is realised by the following factors:

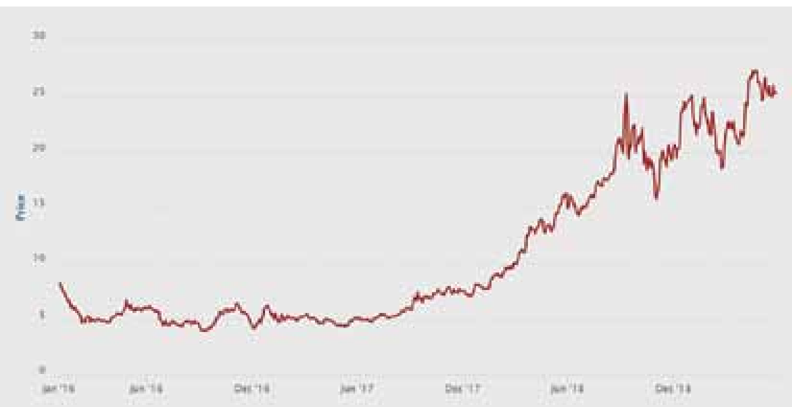
- cement composition: the reduction of clinker-to-cement ratio allows a decrease of €1/t in compositional cost and a reduction of 34.8kg CO_2/t of cement
- cement grinding: reduction in power consumption allows a decrease of €0.13/t in cement grinding cost and ≈1kg CO_2/t of cement
- CO_2 reduction value: reduction of 34.8kg CO_2/t of cement corresponds to CO_2 virtual ETS sales €0.82/t, which is four times higher than the €0.15/t value with CO_2 market prices of 2016.

The increase in CO_2 costs significantly changes the net value of the application of a premium customised quality improver. This is illustrated in Figure 8, where the CO_2 savings increased from 14 per cent to 40 per cent of the total savings, or an increase from €0.19/t to €0.82/t, an addition of €0.67/t of cement produced. This represented a doubling in net savings from €170k/annum to €360k/annum with an estimated production of 0.3Mta of cement.

Conclusions

Currently available chemical technologies can offer a substantial decrease in clinker-to-cement ratio. When chemical technologies are customised effectively with a target cement composition, production of low clinker cement with a target ratio of clinker-to-cement ratio of 0.60 can be realised. The examples presented in this article show that both the technical and economical target can

Figure 7: the increase of prices of CO_2 in the European Trading Scheme (ETS) cost in Europe over the last two years had a significant impact on CO_2 emission costs



https://www.eex.com/en/market-data/environmental-markets/spot-market/european-emission-allowances#!/2019/05/29

"... two customised QIs provided more than 20 per cent strength increase over the blank cement. This level of strength increase allows five per cent or more additional SCM to be used."

Table 1: the impacts of a customised QI solution on the economics and carbon footprint in a CEM II/A-LL 42.5R

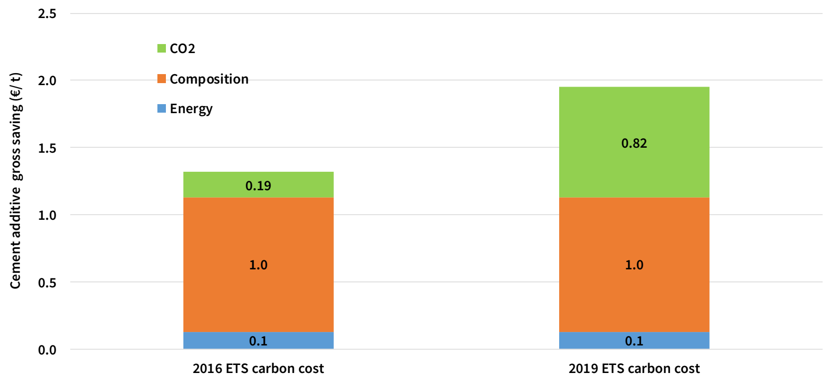
Category	Parameter	Reference	Test	Test
Cement additive	Cement additive	Reference QI	Customised CO_2ST reducer	Customised CO_2ST reducer
	Use cost (€/cem t)	0.24	0.99	0.99
Cement composition and cost	Clinker (%)	79.5	75.5	75.5
	Gypsum (%)	4.5	4.5	4.5
	Limestone (%)	16.0	20.0	20.0
	Blaine SSA (m^2/kg)	371	392	392
	Residue @ 45µm (%)	5.8	6.7	6.7
	Strengths @ 2-days (MPa)	27.6	29.0	29.0
	Strengths @ 28-days (MPa)	50.1	51.6	51.6
	Composition cost (€/cem t)	24.5	23.5	23.5
	CO_2 from clinker* (kg/cem t)	685	651	651
Cement grinding	Mill output (tph)	142	150	150
	Specific energy consumption (kWh/t)	30.3	28.7	28.7
	Specific energy cost (kWh/t cost)	2.42	2.29	2.29
	CO_2 from grinding** (kg/cem t)	15.1	14.3	14.3
Total costs and CO_2	CO_2 emissions (kg/cem t)	700.1	665.3	665.3
	ETS carbon cost (€/CO_2t)	–	≈5.5 (2016)	≈23.5 (2019)
	CO_2 cost / virtual ETS sales (€/cem t)	0	-0.19	-0.82
	Total costs (€/cem t)	27.2	26.6	26.0
	Gross savings (€/cem t)	–	1.3	2.0
	Net savings (€/cem t)	–	0.6	1.2
	Annual € savings (0.3Mta)	–	€170,000	€360,000

** assumes 0.50kg CO_2/kWh   ** assumes 862kg CO_2/t of clinker*

be achieved with the use of a suitable customised QI of the "CO_2ST Reducers" series. Figure 8 shows that the net savings grew by ~50 per cent (from €1.29 to €1.92) and the portion of savings from carbon has grown from 15 per cent to 43 per cent from 2016 to 2019.

Research focus is now on the development of additive technologies to deliver higher clinker substitution rates and on the conversion of inactive SCMs to active ones. Cement additives will continue to play a critical role to attain the objectives set by the Paris Agreement to keep the global temperature rise well below 2˚C above pre-industrial levels. ■

Figure 8: net savings achieved with the use of a suitable customised QI of the "CO_2ST Reducers" series



REFERENCES

[1] INTERNATIONAL ENERGY AGENCY AND CEMENT SUSTAINABILITY INITIATIVE (2018), *Technology Roadmap: Low-Carbon Transition in the Cement Industry.* https://www.wbcsd.org/Sector-Projects/Cement-Sustainability-Initiative/Resources/Technology-Roadmap-Low-Carbon-Transition-in-the-Cement-Industry [Accessed on 22 July 2019]

[2] LEHNE, J AND PRESTON, F (2018) *Making Concrete Change Innovation in Low-carbon Cement and Concrete (Chatham House Report)*, London, UK: The Royal Institute of International Affairs, 138p.

[3] SCRIVENER, KL (2014) 'Options for the future of cement' in *The Indian Concrete Journal*, 88 (7), p11-21.

[4] GARTNER, E, MYERS, D AND GAIDIS, J (INVENTORS) AND WR GRACE & CO-CONN (ASSIGNEE) (1991) *Processing additives for blended cements. United States patent US 5,017,234.* 21 May.

[5] GARTNER, E, HU, R, CHEUNG, JH (1998) 'Influence of tertiary alkanolamines on rates of reaction of C_3A and C_4AF with calcite under conditions typical of Portland cement hydration in concrete' in: WC, 29, p74–90.

[6] SUMNER, M, MARSAY, K, STOPPA, R AND CHEUNG, J (2015) 'Reducing CO_2 emissions through cement grinding optimisation' in: *The Cement Plant Environmental Handbook 2nd Edition*. Dorking, UK: Tradeship Publications Ltd, p152-155.

[7] RIDING, K, SILVA, D AND SCRIVENER, K (2010) 'Early age strength enhancement of blended cement systems by $CaCl_2$ and diethanol-isopropanolamine' in: *Cement and Concrete Research,* 40, p935-946.