The additive approach

Riccardo Stoppa and Richard Sibbick, GCP Applied Technologies, outline a method to mitigate the effects of alternative fuels on cement quality.

It is inevitable that more fossil fuels will have to be replaced with alternative fuels (AFs) in the coming years. If cement or concrete quality is a concern, chemical cement additives can help, delivering kinetic and morphological improvements to cement products.

Fossil fuels

The combustion of fuels accounts for over 30% of the CO_2 emissions of a cement plant primarily using fossil sources,[1] and, according to GCP estimates, for about one fourth of the cradle-to-grave embodied carbon in concrete. It is not surprising therefore to observe the efforts the cement industry is presently making to replace fossil sources with alternative, environmentally friendly fuel sources.

Through a combination of innovation and emerging technologies, cement plants are becoming remarkably effective at replacing fossil fuels.

As an example, the cement plants covered by the 'Getting the Numbers Right' Project increased their use of AFs from less than 3 million t in 1990 to over 20 million t in 2019, demonstrating a Compound Annual Growth Rate of 1.7%.[2] Replacement rates of more than 80% are already regularly achieved in some plants.[1]

Moreover, the industry is committed to continuing, and even accelerating their switch to AFs. For example, Cembureau estimates that an average of 60% kiln energy produced by AFs may be achieved by 2050.[3] Another 1 – 2% (or higher) replacement of fossil fuels is due this year, and cement additives are there to further help mitigate some of the more painful, and negative impacts on finished clinker and cement quality.

Figure 1. When things go seriously wrong: a lump of clinker with a piece of RDF embedded.

Alternative fuels

Selecting alternative fuels requires careful consideration of the potential impact on environmental emissions, process operation, cement health and safety, cement performance and overall economics, as well as compliance to relevant legislation. Fuels that are commonly used as an alternative to fossil fuels include: waste plastics, rubber, tyres, wood, paper, textiles, processed refuse-derived fractions, municipal sewage and industrial sludge, animal meal, agricultural waste, paints, oils and solvents.

Table 1 summarises GCP's experience with some of the downsides of the most common AFs, relative to the addition of minor elements in clinker, as well as other issues relating to AF calorific value, steadiness, sourcing, financials, regulations, CAPEX, storage, preparation and use. Figure 1 is an extreme example in which residual RDF material is actually found within a clinker nodule.

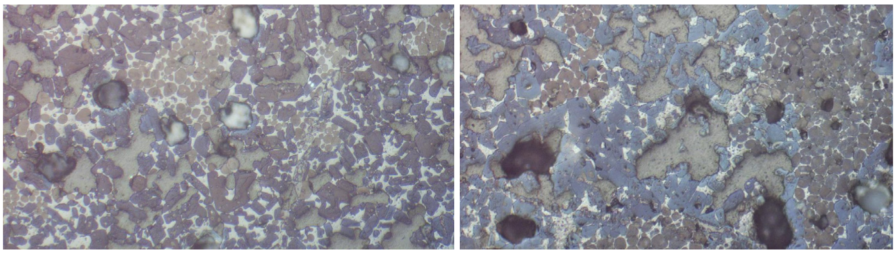

Figure 2a. Left – Clinker photomicrograph from original fuel mix showing a reasonably homogeneous moderate hard to light burnt area of clinker with estimate average alite size (EAAS) of 30 microns (blue etched prismatic crystals) and a moderate amount of small brown belite clusters (100 – 500 microns). Figure 2b. Right – Clinker photomicrograph from 85% petcoke and 15% RDF mix showing a moderate hard burnt clinker with a high alite content (blue etched prismatic crystal) with an EAAS of 30 microns, exhibiting some inter-crystal growth and a reasonably high abundance of large randomly shaped large clusters of belite (brown, rounded crystals) and free lime (buff, rounded crystals).

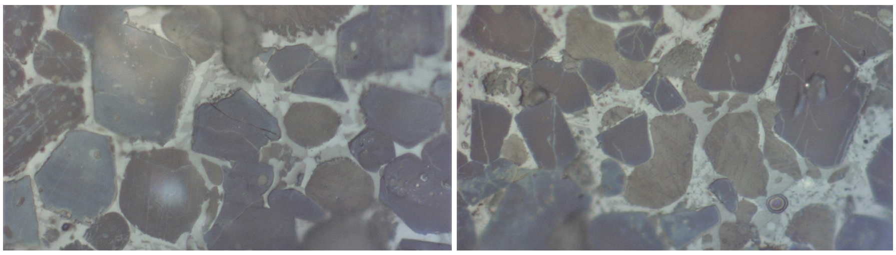

Figure 3a. Left – Clinker Photomicrograph from original fuel mix showing a low amount of moderate to well crystalline flux material consisting primarily of ferrite (white) with a lesser amount of aluminate (grey) being present, indicating a moderate to slow rate of cooling. The alite (blue) and belite (brown) phase crystals appear largely stable. Figure 3b. Right – Clinker photomicrograph from 85% petcoke and 15% RDF mix showing an area of moderate to slow cooled flux dominated by well-formed crystals of ferrite (white etch) along with lesser amounts of small elongate needle crystals of aluminate (grey etch).

Minor elements

The introduction of minor chemical components via AFs is one of the main concerns relating to clinker and cement quality. Minor elements may influence the properties of clinker phases, eventually causing changes in phase reactivity, crystal size, morphology or structural perfection, and can also modify the microstructure of the clinker as a whole.[4]

Effects on crystals due to minor elements can include: inhibiting or enhancing growth, altering the crystal morphology, the melt phase viscosity and decomposing crystals altogether.

The role of many minor elements has been studied sufficiently to predict certain potential effects, for example concerning setting time (shorter/longer) and compressive strengths (early/late). Table 2 summarises some of the most relevant downsides of these minor elements.

Chemical cement additives

An increased use of AFs can sometimes lead to a loss of clinker and cement quality. Particularly when AFs are first tried, a significant loss of strength and setting time can be observed. Once an impact on quality has been identified, it is possible that the appropriate use of a cement additive can mitigate the effects of quality loss, thereby facilitating the use of the AF.

Cement additives are aqueous chemical formulations that are incorporated into the cement. They are either added on to the mill feed belt or injected directly into the mill through a lance. Depending on the desired performance characteristics, a cement additive may contain anywhere from 3 – 8 chemical components.[5] Dosages vary widely but are generally low, ranging from about 300 – 3000 ppm of finished cement. Cement additives help the cement hydration process by improving the degree of hydration of the cement minerals, the morphology of the hydration products, and the pore size distribution of the resulting cement paste, such that when mortar or concrete are subsequently mixed the cement hydration is enhanced at all ages.[6] Table 3 summarises the typical performance benefits provided by a modern cement additive such as OPTEVA® Quality Improvers or CO_2ST® Reducers.

Case study

A cement plant in Europe was aiming to switch from the current fuel mix composed of pet coke powder (50%) and fuel oil of fossil origin (50%) to a mix with petcoke (85%) and refuse-derived fuel (RDF, 15%). In doing so, the plant experienced a loss of strength at all ages (measured at 1-2-28 days) of between 2 and 3 MPa in their high performance CEM I 52.5R cement.

Investigations carried out at the GCP Analytical Laboratories showed that the clinker from the new fuel mix demonstrated the presence of strong reducing kiln conditions that were not present in the clinker from the original fuel mix.

The presence of such reducing kiln conditions would likely explain the observed strength differences.

The clinker photomicrographs shown in Figures 2 and 3 show the compositional and microstructural changes of the original clinker and the clinker produced after the addition of alternative fuels.

Both clinkers showed moderately slow cooling characteristics.

The original clinker, as shown in Figures 2a and 3a, exhibited a more homogeneous and moderately hard burnt clinker.

The new clinker produced with alternative fuels, as shown in Figures 2b and 3b, appeared to be a more heterogeneous clinker.

Microstructural and morphological features typically associated with reducing kiln conditions, are often found associated with the use of alternative fuels.

In this case, despite evidence from positive chemical reduction tests to indicate reducing kiln conditions were indeed present in the resulting clinker produced with RDF, it still did not exhibit many 'classic' reduction-derived microstructural features. Higher amounts of low reactivity alite, likely resulting from increased Fe take up in the crystal lattice, and the

Table 1. GCP's experience with some of the downsides of the most common AFs.

Alternative fuel	Potential limitations and downsides relative to clinker composition
Used tyres, rubber waste	Unsteady kiln conditions Iron and sulfur content
Spent solvents	High chlorine levels High heavy metal content
Refuse derived fuel	Chlorine
Animal meal	Phosphorous Chlorine and metals
Sewage sludge	Can cause clinker mineralisation issues Phosphorous, chlorine High heavy metal content, spec. Al and Fe

Table 2. Downsides of minor elements.

Minor element	Typical negative impact on cement quality and performance.
Cl	Setting (acceleration), early strength, corrosion
B, Y, La	Setting (acceleration)
P, As, Zr, Zn	Setting (delay)
Pb	Setting (delay), late strength
F	Mineralisation, setting (delay), late strength
Na, K	Early strength (increase) and late strength (decrease)
Cr, Co	Cement's EH&S
Cr, V, Mn	Colour
Mg	Expansive behaviour
Sr, As, Bo, P	Alite destabilisation
Sr, Ba	Belite stabilisation

Table 3. Typical performance benefits using a modern cement additive.

Quality parameter	Expected benefit by the cement additive
Process (Coating, pack-set, mill output, PSD)	+5 to +30%
2-day compressive strength	+10 to +30% (2 – 8 MPa)
28-day compressive strength	+5 to +20% (2 – 12 MPa)
Initial setting time (acceleration)	-15 to -60 minutes
Initial Setting Time (retardation)	+15 to +90 minutes
Concrete water demand	-2 to -5%
Slump retention	+20 – 70 mm @ 45 min

Table 4. XRF, microscopy and QXRD data.

Analyte	Method	Original fuel mix	85% petcoke, 15% RDF	Analyte	Method	Original fuel mix	85% petcoke, 15% RDF
SiO_2	XRF	21.06	21.00	C_4AF	XRF-calculated	11	12
Al_2O_3	XRF	4.62	4.94	LSF	XRF-calculated	0.95	0.94*
Fe_2O_3	XRF	3.56	3.83	LSF	Microscopic assessment	0.95	0.96*
CaO	XRF	63.58	63.19	AR	Microscopic assessment	1.25	1.25
MgO	XRF	2.48	3.71	SR	Microscopic assessment	2.6	2.6
SO_3	XRF	1.17	1.25	C_3S	XRD	55.0	58.2
Na_2Oeq	XRF	0.71	0.80	C_2S	XRD	24.4	21.0
TiO_2	XRF	0.22	0.24	C_4AF	XRD	10.5	10.6
C_3S	XRF-calculated	63	59	C_3A cubic	XRD	2.7	3.2
C_2S	XRF-calculated	14	16	C_3A orthorhombic	XRD	1.0	0.8
C_3A	XRF-calculated	6	7	MgO	XRD	1.7	3.3

Note: *- Raised LSF by microscopy compared to XRF calculated figure.

Table 5. Additive solution allowing a further strength enhancement at all ages.

Additive	Dosage ppm	1-day MPa	2-day MPa	28-day MPa
None	-	23.8	36.5	60.8
Current QI	3300	28.3	41.0	64.2
$CO_2ST^®$ Reducer	1500	30.3	43.6	71.6

reduced flux content likely leading to difficulties in the cement mineral phase combinability, as indicated by raised amounts of well-defined belite and free lime clusters, were still observed, confirming that reducing kiln conditions were indeed present and were likely the primary cause for the lower strength development.

The differences observed in the XRF and microscopy/QXRD based cement ratios between the original and RDF fuel clinkers are considered primarily the result of the reducing kiln conditions. The raised magnesium content may also result in raised expansion potential in resultant mortars and concretes.

Overall, the observed changes in clinker chemistry and morphology fit broadly with the measured loss of strength. Select XRF, microscopy and QXRD data are reported in Table 4.

GCP was then asked to help resolve the strength loss issue, which was particularly challenging as the plant was already utilising a high-performance cement additive, delivering a 4 – 5 MPa enhancement at all ages from 1 to 28 days. Upon running a series of laboratory tests, GCP eventually developed a customised CO_2ST Reducer solution, allowing a further strength enhancement at all ages, as shown in Table 5. Notably, the strength at 1 and 2 days was increased by approximately 2 MPa on top of the previous additive, meeting the plant's requirements by 6 – 7 MPa on top of the 'blank' (no additive) cement. The strength at 28 days was increased by 5 MPa on top of the reference additive, and by over 10 MPa on top of the 'blank' cement. The plant has enjoyed a safe use of the new fuel mix since then.

Conclusions

Most cement plants are striving to reduce their use of fossil fuels, in order to attain a lower carbon footprint, and to lower their production costs. The introduction of an alternative fuel often poses the cement plant several challenges, including potential detrimental effects on the final quality of the resulting cement and concrete products. Many of these downsides can be balanced by the use of an appropriate cement additive, allowing the cement quality to remain unchanged, whilst achieving significant economic savings, environmental improvements and carbon reductions. ■

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