7.6 Using strength-enhancing cement additives

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The process effects and the economic benefits of chemical additives are well understood, but their potential to reduce the carbon footprint of cement is a new frontier for many producers. Chemical additives improve the reactivity of cement, allowing increased clinker replacement with limestone and other supplementary cementitious materials (SCMs) without loss of strength. This is an important lever for reducing cement plant CO_2 emissions. This article discusses the mechanisms and sustainability benefits of strength-enhancing cement additives, including an industrial case study.

The versatility and sustainability of concrete as a construction material is well established. With constituents readily available in most parts of the world, concrete can be reliably produced and placed with relative ease in a variety of environments with various structural performance characteristics to provide a long service life.[1] Due to these benefits and the wide-spread use of concrete, cement demand is responsible for around seven per cent of global industrial energy use and approximately seven per cent of direct global CO_2 emissions.[1] With rising population and infrastructure development needs, global cement production is expected to grow by 12-23 per cent by 2050.[2]

Clinker production is the most energy- and carbon-intensive step in the manufacture of cement. Fuel combustion to heat the kiln and calcination of limestone accounts for almost 90 per cent of the CO_2 emissions, with the balance being attributed to electricity and transport.[3] At present, efforts to minimise the carbon footprint of concrete must focus on reducing the clinker content of either the finished cement or of the concrete.[4,5] This chapter discusses the ability of strength-enhancing cement additives to allow reductions in cement clinker contents.

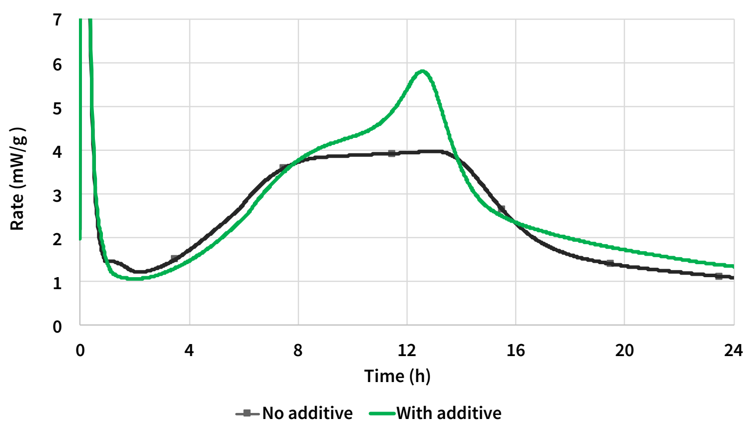
Cement additives

Cement additives are typically liquid chemical formulations that are interground with 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. Dosages vary widely but are generally low, ranging from about 400-3000g/t of finished cement.[6]

Cement additives were first introduced to improve the efficiency of the grinding process. As such, they are often referred to as grinding aids, particularly if they are not also chemical strength enhancers. Cement grinding aids are typically polar organic compounds. During the grinding process, the crystalline structures of the clinker compounds are fractured, generating electrically unbalanced surfaces that tend to adhere to each other and to other surfaces such as the grinding media in the ball mill. Grinding aids adsorb onto the newly-fractured cement particle surfaces, reducing the attractive forces and improving particle dispersion.[6]

When using a grinding aid, the finest particles are more efficiently removed from the mill at the separator, which improves the production rate of the mill. Other benefits include flowability and reduced pack set of the finished cement and improved particle size distribution with fewer coarse particles.[6] Because these benefits tend to be quite cost-effective, most cement is produced using some type of grinding aid.

Figure 7.6.1: isothermal calorimetry plot of cement paste made without additive (markers) and with an alkanolamine based quality improver (no markers). The enhanced heat output with the additive is a good indication of a greater degree of hydration and strength development



Source: internal GCP data

Performance-enhancing additives

Cement additives can also contain chemicals that will enhance the strength development of the concrete. Such additives are often referred to as strength enhancers. It should be noted that strength enhancers will also be designed to act as grinding aids, so it is not necessary for a cement producer to choose between grinding enhancement and strength enhancement.

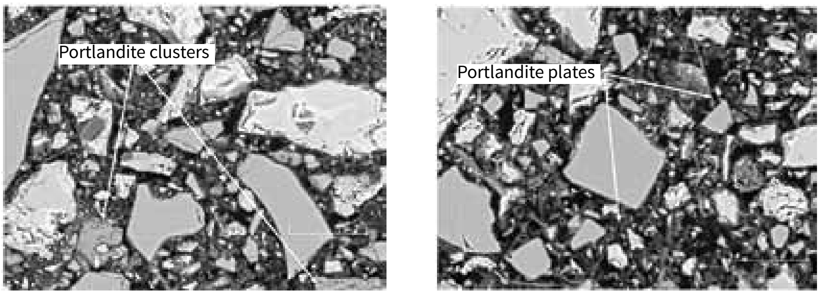
Strength enhancers increase strength by dissolving into the mix water when the concrete (or mortar) is made and changing the cement hydration process. These changes generally fall into three categories:

- increased degree of hydration of the cement minerals – In general, more hydration means more strength. The increased hydration may occur primarily at early ages by a hydration accelerating effect, or the effects may be observed at later ages because the chemical allows one or more of the cement minerals to react more completely. Figure 7.6.1 shows an example of an isothermal calorimetry plot for a cement with and without a quality improving additive. The greater heat flow during the first day leads to a higher early strength.
- improved morphology of the hydration products – Not all hydration products lead to the same amount of strength. Phases with small, interlocking grains give the best strength. Larger blocky crystals provide less strength, although they can confer some benefit by reducing the pore space. An example of different portlandite morphologies is shown in Figure 7.6.2.
- improved pore size distribution (see Figure 7.6.3) – Formation of hydration product reduces both the total porosity and the size of the pores in the cement paste. Cement additives can enhance this pore refinement process, leading to higher strength.

Types of strength enhancers

There are many different chemicals that can enhance cement strength. Using multiple chemicals in a formulation can provide synergistic effects and also allows the development of customised products that are optimised for a particular cement. Three general types of chemicals that enhance strength are discussed below: tertiary alkanolamines, retarders and accelerators.

Figure 7.6.2: backscattered SEM images of young (10h) cement paste made without DEIPA (left) and with DEIPA (right).[7] Without DEIPA the portlandite forms as large clusters. With DEIPA the portlandite forms as well-spaced, thin plates



Tertiary alkanolamines

Tertiary alkanolamines are perhaps the most widely used class of strength-enhancing chemicals for cement, with the most commonly used being triethanolamine (TEA), diethylisopropanolamine (DEIPA) and triisopropanolamine (TIPA). These compounds are also effective grinding aids, giving them a double benefit when used in cement additive formulations. Alkanolamines remain in the pore solution of cement or concrete for an extended period (days or weeks), during which time they facilitate the hydration process of the cement minerals, leading to a greater degree of hydration and thus greater strength. As such, the required dosages of these chemicals for strength enhancement are quite low, with typical values being 0.01-0.03 per cent by mass of cement. Higher dosages may, in fact, lead to different and possibly negative effects. A more detailed discussion of the effects of these chemicals is beyond the scope of this article, but more information is available.[8] An example of the effect of an alkanolamine on the hydration rate is shown in Figure 7.6.1.

Retarders

Retarders are chemicals used to extend the set time of cement and concrete, thus increasing the window of initial workability. An example of a retarding effect on early hydration is shown in Figure 7.6.4. They are frequently admixed into concrete at the time of mixing for this purpose, for example when placing concrete in hot weather or when the time between mixing and placement at a job site is expected to be long. Retarders act by interfering with the nucleation and growth of hydration products. They do this by adsorbing directly onto the surface of the cement particles, slowing their dissolution, or by adsorbing onto the newly-formed hydration product, slowing its further growth.

The most commonly-used retarding chemicals are lignosulphonates, carboxylic acids and carbohydrates, particularly sucrose, glucose and sodium gluconate.[8] Smaller doses of the same chemicals are sometimes included as a component of cement additive formulations for the purpose of increasing strength. While the exact mechanism for strength increase is not well understood, the retarders are believed to lead to a better overall distribution of hydration products and greater hydration levels at later ages. One study[9] found that sucrose, a powerful set retarder, was a "delayed accelerator", in that it causes longer set times but then gives a higher degree of hydration, and presumably higher strength, at later ages.

Accelerators

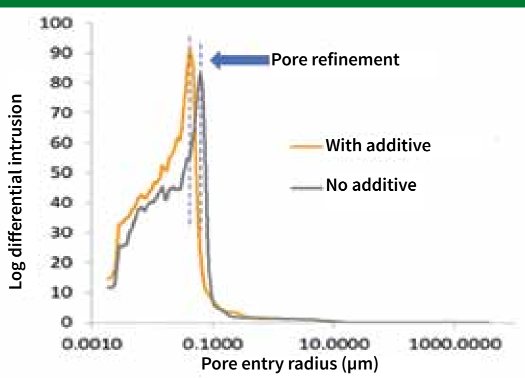
Accelerators are chemicals that shorten the time to set and increase the early hydration rate. They are often added at the time of mixing when concrete is being placed in cold weather or when early high early strength is required. An example of an accelerating effect on early hydration is shown in Figure 7.6.4. Due to the faster hydration, accelerators increase early strength, particularly up to one day. However, the later strength is usually not enhanced or may even be lower, especially when high doses are used. A variety of soluble inorganic salts can be used as accelerators, with calcium chloride and calcium nitrate being two commonly used examples. Accelerators can be included in cement additive formulations when the cement producer wishes to increase the early strength or shorten the set time of the as-produced cement. Accelerators can also be used to counteract the set time extension caused by retarders that are in the formulation.

Reducing the CO_2 footprint through clinker replacement

According to internal GCP estimates, approximately 70 per cent of the total carbon emissions associated with the use of concrete comes from the manufacture of the Portland cement. Therefore, clinker substitution can have a rather dramatic effect on the carbon footprint of concrete. The most obvious and attractive method of clinker substitution is limestone replacement, as limestone is readily available at nearly all cement plants. With this approach, limestone is typically interground with the clinker and gypsum. When the amount of limestone added is in the order of 2-4 per cent, there is little effect on the strength, because the surface of the limestone particles provides a beneficial location for hydration product to nucleate and grow. However, larger levels of limestone replacement have a negative effect on strength, due to the reduced amount of clinker. This strength decrease can be addressed by finer grinding, which increases energy usage and decreases production, or by using a strength enhancer, which adds cost.[10]

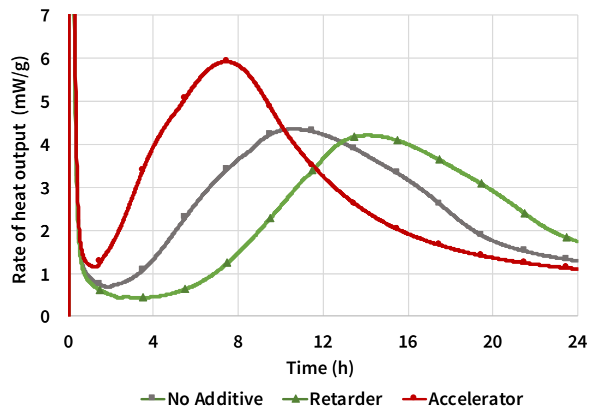
The effect of limestone addition on strength is illustrated by Figure 7.6.5. In this set of experiments, run in GCP laboratories and published here for the first time, different amounts of ground limestone were blended into an industrial cement that was manufactured with four per cent of

Figure 7.6.3: pore size distribution of cement paste made with and without an alkanolamine additive (DEIPA), as measured by mercury intrusion porosity. In the presence of the additive, the pores are smaller



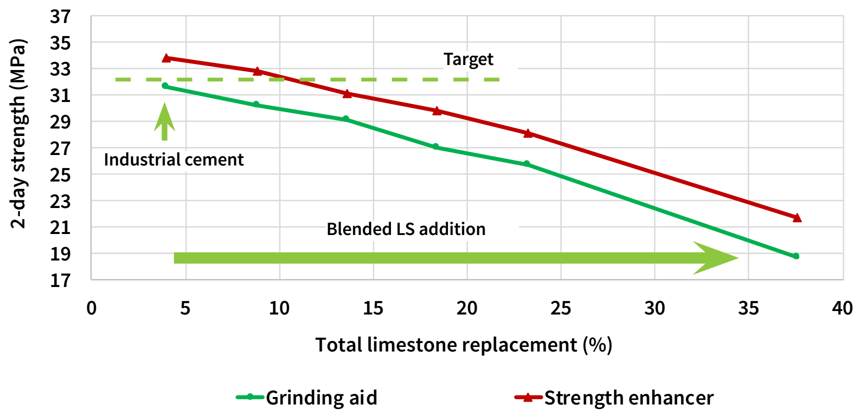
Source: internal GCP data

Figure 7.6.4: isothermal calorimetry plot of cement paste made with no additive, with a set retarder, and with an accelerator



Source: internal GCP data

Figure 7.6.5: effect on 2-day mortar strength of blending ground limestone (BSA = 600m²/g) into an industrial cement interground with four per cent limestone (BSA = 450m²/g) and made with a glycol-based grinding aid that does not enhance strength. The green results are for the as-received cement, and the red results are with an admixed quality improver. Use of the strength-enhancing additive could allow an additional seven per cent limestone replacement while maintaining the target 2-day strength



Source: internal GCP data

interground limestone. The resulting two-day mortar strength is observed to decrease in an approximately linear fashion with limestone addition. Addition of a strength-enhancing additive at the time of mixing provided a consistent strength increase of about 2MPa. As illustrated by the horizontal dotted line, the additive would allow the target two-day strength value of 32MPa to be maintained while increasing the limestone content from four to 11 per cent. Clinker reductions can also be realised by adding other SCMs, such as ground granulated blastfurnace slag (GGBS), fly ash, and natural or calcined pozzolans. These materials have some reactivity when combined with Portland cement and thus can make some contribution to the ultimate strength, but their use tends to result in lower early age strengths, depending on the type and quantity used. In comparison to limestone, these materials tend to be limited in their availability and significantly more expensive.

Industrial case study

A GCP customer in Europe was producing an ordinary Portland cement (CEM I 42.5R) with four per cent limestone using a standard quality improver. They wished to start producing a CEM II/A-P cement by adding a local natural pozzolan, but needed to compensate for the resulting loss of strength.

In an initial industrial trial, a more powerful CO_2ST® Reducer additive from GCP Applied Technologies was tested on the CEM I. CO_2ST Reducer additives are specifically formulated to maximise strength and allow for greater clinker substitution.

As shown in Table 7.6.1, with constant particle size distribution and limestone content, the strength was increased by the new additive, particularly at 28 days where the increase was nearly 6MPa.

A long-term trial was then conducted to determine the optimum pozzolan addition. It was determined that eight per cent clinker replacement with pozzolan (in addition to the four per cent limestone) could be achieved while maintaining the early and late strength (see Table 7.6.2).

As a result of the pozzolan addition, the cement carbon footprint was reduced from 683 to 623kg/t, a significant reduction of nine per cent.

Summary

In an environment that is increasingly focussed on sustainability, cement producers need to utilise every avenue available to increase manufacturing efficiency and reduce carbon emissions while maintaining the required performance, quality and handling of their finished cement. This involves careful consideration of energy consumption, cement composition, additive cost, emission levels, production capacities and market needs, and the enablement of other technologies such as alternative fuel and raw material sources. This article has shown that the use of strength-enhancing cement additives can allow for greater levels of clinker replacement, providing direct and meaningful reductions in the carbon footprint of concrete.

Table 7.6.1: results of initial industrial trial conducted on CEM I 42.5R cement

Additive	Dose (g/t)	Blaine (cm²/g)	R45 (wt%)	$CaCO_3$ (%)	Strength development (MPa)		
					2-day	7-day	28-day
Reference quality improver	500	3480	3.8	4.1	29.5	42.7	53.5
CO_2ST® Reducer	1000	3505	4.1	4.8	30.2	45.6	59.4

Table 7.6.2: results of the long-term trial comparing the new and old cement types

Cement	Additive	Dose (g/t)	$CaCO_3$ (%)	Pozzolan (%)	Strength development (MPa)	
					2-day	28-day
CEM I 42.5 R	Reference	500-600	4.0	0	27-29	53-56
CEM II/A-P 42.5 R	CO_2ST® Reducer	900-1000	4.0	8.0	28	56

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More information

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WBCSD Cement Technology Roadmap
www.wbcsd.org/Sector-Projects/Cement-Sustainability-Initiative/Resources/Technology-Roadmap-Low-Carbon-Transition-in-the-Cement-Industry