A new generation of strength

Triisopropanolamine-based grinding additives are known to improve the strength of limestone blended cements. Cements are produced with a narrower particle size distribution with lower fineness, allowing for enhanced mill throughput and improved energy efficiency of the mill. These grinding additives boost silicate reactivity and encourage carboaluminate formation.[1,2] A new generation of triisopropananolamine-based quality improvers allows for early strength improvement of up to 30 per cent. This increased cement strength can be used to allow higher rates of clinker substitution and lower production costs, further reducing the carbon footprint of cement.

■ by **L Jardine Buzzell and J Cheung,** *GCP Applied Technologies Inc, USA*

The impact of clinker production on CO_2 emissions is well known and despite significant reductions from clinker substitution and improved energy efficiency, increased cement output has only seen this impact intensify.[3,4]

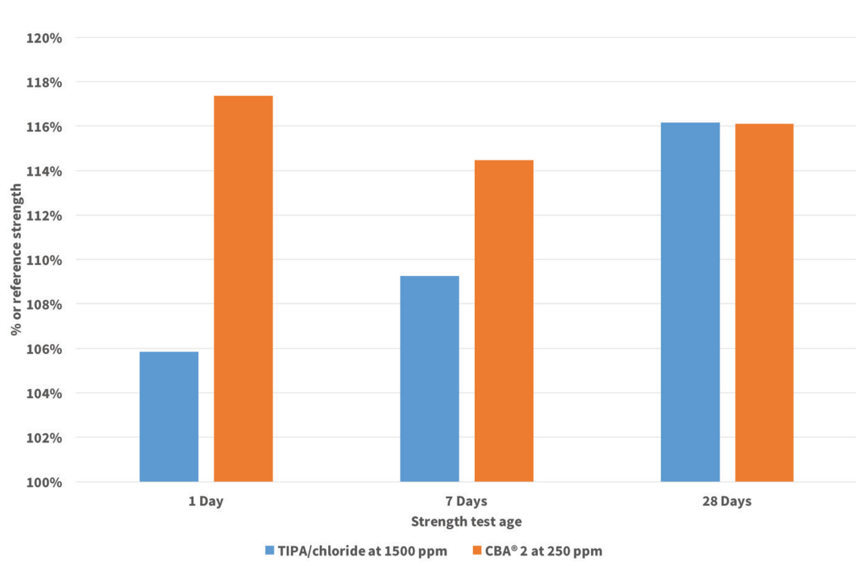
While many cement plants have installed more fuel-efficient kilns, applied alternative fuels and made partial substitution of non-carbonate sources of calcium oxide in the kiln raw materials,[5] a further efficient method for lowering CO_2 levels is clinker substitution.

Limestone is known to react with aluminate phases to form carboaluminates.[6] Gartner et al [1,2] showed accelerated hydration of limestone-blended cements at later ages via formation of calcium carboaluminates in the presence of triisopropanolamine (TIPA).

Although TIPA gives good late strength enhancement, it causes elevated air contents in some cases. A new generation of quality improvers, designed to reduce the tendency for air build with the use of TIPA, has been introduced. Early strength increase is higher than would be predicted by the common observation that a one per cent decrease in air is accompanied by a five per cent increase in strength.[7,8] Studies were completed comparing the new generation of quality improvers, described by their trade name CBA® 2, with TIPA-based quality improvers, CBA®.

> *"Although TIPA gives good late strength enhancement, it causes elevated air contents in some cases. A new generation of quality improvers designed to reduce the tendency for air build with the use of TIPA has been introduced."*

Figure 1: compressive strength with amine-based additives in CP II 40 cement mortars



Results and discussion

Laboratory studies

CBA 2 was compared with a similar CBA in two laboratory studies. In these experiments the additives were added during the preparation of mortar with the gauge water.

Study 1

Non-chloride CBA 2 was compared with a blend of TIPA and chloride in a CP II F 40 cement comprised of 83 per cent clinker, 12 per cent limestone and five per cent gypsum. Mortar strength was measured according to EN-196. Quality Improvers were added with the mix water.

As Figure 1 shows, the low-dosage CBA 2 improves one-day strength by 1.9MPa (11 per cent) more than the TIPA-chloride blend. Seven-day strength enhancement is 2.0MPa (five per cent) greater with CBA 2 than the TIPA/chloride blend. Twenty-eight day strength is comparable for both additives.

Study 2

In a second study, CBA 2 was compared

Figure 2: compressive strength with amine-based additives in limestone cement mortars

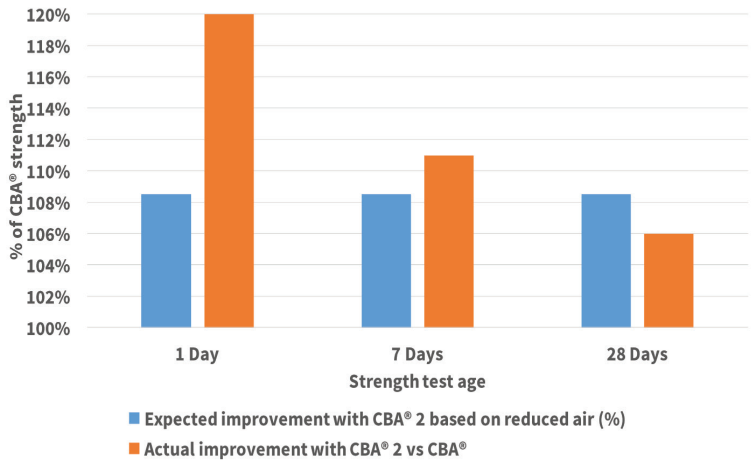


Figure 3: EN-196 compressive strength of type II/B-M (L-P) cement, interground amine-based additives

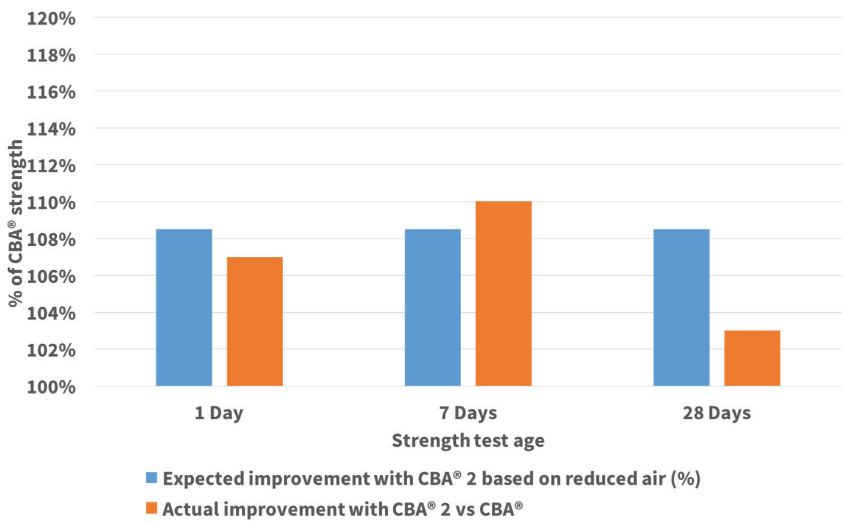
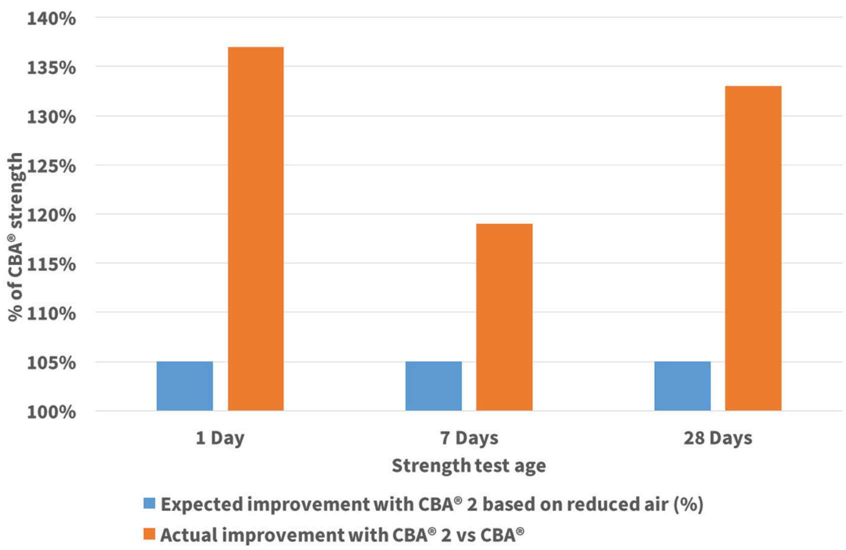


Figure 4: compressive strength of type II/B-M (L-P) cement, interground amine-based additives in concrete



"For a technology to be useful as a cement additive, it must survive the harsh conditions (high temperature, with the possibility for alkali degradation) found in a cement mil."

with CBA in a cement with seven per cent limestone. Mortar strength was measured according to EN-196. Based on the 1.7 per cent decrease in mortar air, strength of CBA 2 is predicted to be 108.5 per cent strength of CBA.

Actual strength increase, with CBA 2 vs CBA, at one day is 120 per cent (see Figure 2). Strength with CBA 2 was 1.3MPa higher than that of CBA at one day, 2.7MPa higher than at three days and 3.7 MPa higher at 28 days.

Comparative study at a cement plant

CBA 2 was compared with CBA in a cement plant trial in a type II/B-M (L-P) cement with 17 per cent limestone, 66 per cent clinker, six per cent gypsum and 11 per cent slag. Additives were interground with the cement during milling. Mortar strength of the cements produced was measured according to EN-196. Based on a decrease in mortar air of 1.8 per cent with CBA 2, mortar compressive strength with CBA 2 is predicted to be 109 per cent strength with CBA (see Figure 3). Actual strength increase is comparable at 107 per cent and 110 per cent at one and seven days, respectively. Strength with CBA 2 was 0.5MPa higher than that of CBA at one day, 1.9MPa higher at two days and 1.3MPa higher at 28 days.

Concrete results (see Figure 4) showed a greater relative increase in strength with CBA 2. Strength with CBA 2 is 119-137 per cent strength with CBA. Based on the one per cent decrease in mortar air, strength of CBA 2 is predicted to be 105 per cent strength of CBA. Concrete strength with CBA 2 was 3.4MPa higher than that of CBA at one day, 3.2MPa higher at seven days and 6.1MPa higher at 28 days.

These results show that it is important to compare plant cements interground with this technology in concrete as well as mortar.

Heat stability of CBA 2

For a technology to be useful as a cement

Table 1: concrete mix parameters					
Cement factor: 290kg/m³ – water-to-cement ratio: 0.63 Concrete admixture ADVA Flex 0.6% by weight of cement					
Additive	**Dosage (ppm)**	**Air (%)**	**Slump (min)**		
			6	**30**	**60**
CBA	500	2.3	100	75	65
CBA 2	500	1.3	100	85	65
Air (%) CBA 2 – CBA	-	-1	-	-	-

Table 2: air entrainment with cements from heated grinds				
Additive	**Dosage (ppm)**	**Air (%)**		**Change in air (%) Air for heated grind - air admixed test**
		Admix	**Heated grind**	
None	-	2.4	2.4	0
CBA	200	4.0	3.6	-0.4
CBA 2	240	1.5	2.0	+0.5
CBA 3	240	2.8	2.4	-0.4
CBA + non-commercial heat-unstable technology	240	1.7	3.4	+1.7

additive, it must survive the harsh conditions (high temperature, with the possibility for alkali degradation) found in a cement mill.

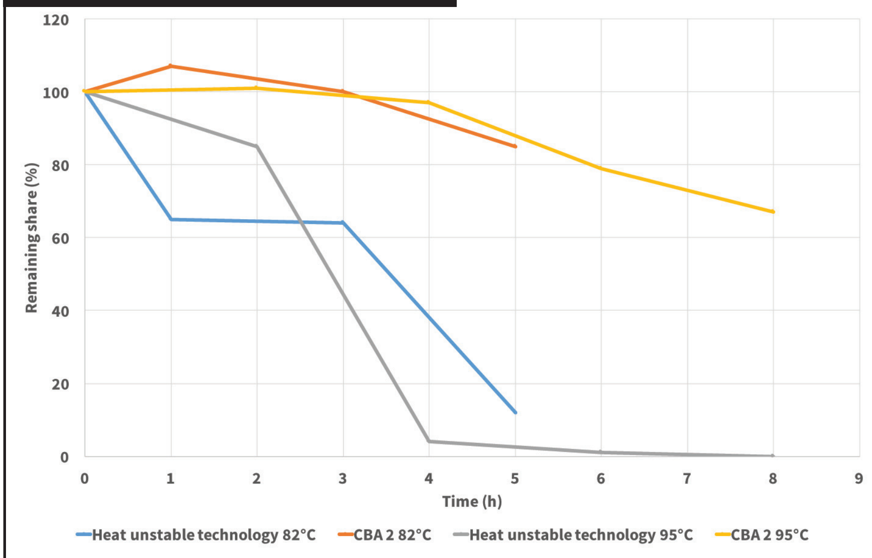
CBA 2 and a non-commercial alternative technology with poor heat stability were compared under alkaline conditions at 82 and 95˚C. Alkaline conditions were used to generate an exaggerated cement mill environment.

High-performance liquid chromatography (HPLC) was used to observe degradation under the test conditions. Samples were exposed for various intervals of time, and analysed by HPLC.

Figure 5 shows the share of each technology that survives without degradation after exposure to heat and alkaline conditions.

These results are supported by physical testing results measured on cements ground in heated laboratory mills. For the admix testing, additives are added to mortar prepared with the blank grind. For the heated grinds, additives were interground with cement clinker and gypsum for 2h 15min at 160˚C. CBA® 3 is another mill-stable quality improver designed to reduce the tendency for air build with the use of TIPA. When the heat-unstable technology is interground with cement clinker in a heated mill, there is no reduction in the tendency for air build with the use of TIPA. Air is comparable to air with CBA (3.4 vs 3.6 per cent). With heat-stable CBA 2 and CBA 3, air remains below three per cent.

Figure 5: thermal stability of technologies



Conclusions

A new generation of TIPA-based quality improvers, with a heat-stable compound able to reduce the air entrainment generated by TIPA, is shown to lower air entrainment and increase compressive strength of mortar and concrete, especially at early ages. Additional investigation is needed to understand the strength increase by this technology, beyond what is expected from air loss. ■

Acknowledgements

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