

# Cement additives for lower CO<sub>2</sub> emissions

The use of cement grinding additives reduces energy consumption in cement plants and allows a decrease in clinker content. As a result, they enable a reduction in CO<sub>2</sub> emissions during the cement production process.

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In the cement industry, CO<sub>2</sub> emissions are limited by the cap-and-trade EU Emissions Trading System, which aims to make the EU climate-neutral by 2050.<sup>1</sup> Within the cement production process, the highest emission rate occurs in the calcination of clinker, as shown in Figure 1, while the rest originates from the excavation, transport, crushing and grinding processes.<sup>2</sup>

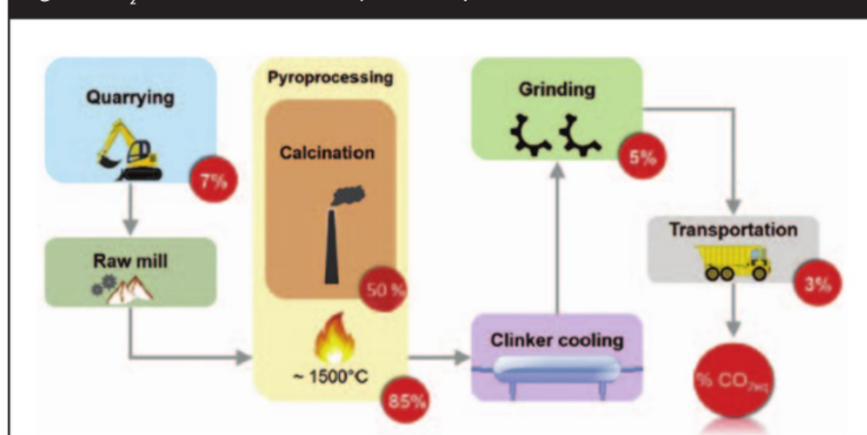
Cement grinding additives increase the efficiency of the material crushing process by neutralising the surface charge of the cement particles formed during the grinding process, thus reducing the surface free energy of the ground material.<sup>3</sup>

Furthermore, cement grinding additives are capable of accelerating the hydration reactions of the cement and, therefore, of increasing the compressive strength at different curing ages. This effect reduces the amount of clinker in the cement recipe, so that it leads to a reduction in CO<sub>2</sub> emissions/t of cement, not only in terms of energy savings in the grinding process but also derived from a clinker saving.

The adsorption mechanism of the additives on the surface of the cement particles is based on weak electrostatic forces that favour repulsion and steric hindrance between particles, avoiding their agglomeration and the total or partial effect of the coating on the mill balls, thus increasing grinding efficiency.

Proquicesa is one of the few companies in the world dedicated entirely to the

Figure 1: CO<sub>2</sub> emissions in the cement production process



development, manufacture and sale of additives for the cement industry.<sup>4</sup> Currently, Proquicesa's technical department is focussed on the development of a new family of additives capable of promoting a particularly significant increase in compressive strengths to minimise CO<sub>2</sub> emissions from the cement production process, as well as to minimise energy costs.<sup>5</sup> This new generation of additives will help reduce CO<sub>2</sub> emissions by optimising the production process and reducing the percentage of clinker by improving the compressive strength of cement.

To characterise the mechanism of action of the additives, advanced material characterisation techniques are used, such as simultaneous thermal analysis DSC/TGA to analyse the evaluation of hydration

reactions in cement, as well as scanning electron microscopy (SEM) and X-ray diffraction (XRD) to evaluate the structure of the cement paste by comparing various additives. These tests are carried out both on dry cement and on cement pastes with a water-cement ratio of 0.4 (w/w), evaluating the results at two, seven and 28 days of curing.

## Results and discussion

The physical characterisation (fineness, compressive strengths and the standard method to measure setting time in cement – EN 196-3:2005) of the cements manufactured in the Proquicesa pilot plant was carried out according to the European Standards (UNE-EN). On the other hand, the structural characterisation tests and thermal analysis were carried out at the Research Support Services (SAI) in La Coruña and at the Technological Research Centre (CIT) in Ferrol, respectively.

The composition of the additives used in this study is shown in Table 1.

## Granulometry tests

The evolution of the fineness of the cement R32μm (per cent) with the grinding time

Table 1: composition of the different additives

	Additive A	Additive B	Additive C	Additive D
Water (wt %)	30-40	20-30	–	5-15
Organic compounds (wt %)	50-60	60-70	85-95	85-95
Acid (wt %)	5-15	5-15	5-15	–

Figure 2: comparison of additive cements vs non-additive cement (white) from the residue on a 32 $\mu$ m sieve (A) and the particle size reduction rate (B)

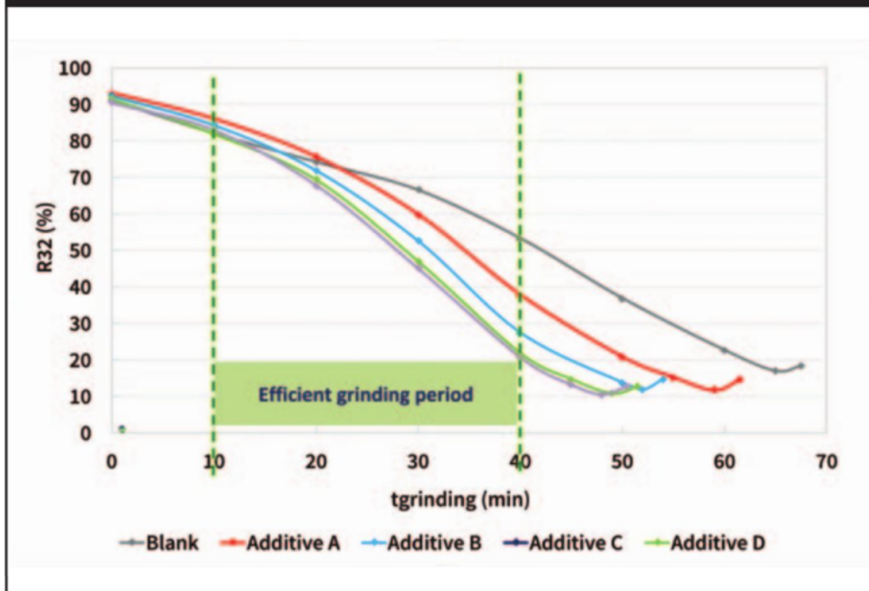


Table 2: results obtained for cement with different additives compared to blank test

Additive	Grinding time (min)	Blaine (cm <sup>2</sup> /g)	R32 $\mu$ m (wt %)	R45 $\mu$ m (wt %)	C <sub>R32</sub> (/min)	$\Delta C_{R32}$
Blank	67.5	5163	18.4	9.0	0.0109	-
A	61.5	4949	14.6	7.4	0.0172	58
B	54.0	4819	14.8	6.9	0.0209	91
C	50.5	4884	12.8	5.9	0.0229	110
D	51.5	4893	12.8	5.9	0.0241	121

(min) of the cement produced on a pilot scale is shown in Figure 2.

The tested additives have shown a very remarkable adjuvant effect, presenting values for the speed of reduction of the particle size (C<sub>R32</sub>) that are much higher than those obtained in the blank. Among them, additives C and D presented the most notable performances in terms of milling efficiency.

The granulometric properties of the cements (Blaine, R32 $\mu$ m and R45 $\mu$ m), the grinding time of the test and the

speed of reduction of the particle size (C<sub>R32</sub>) are shown in Table 2, in addition to the percentage of improvement in the adjuvant power ( $\Delta C_{R32}$ ). Keep in mind that the dose of additive used during the tests is always constant (480ppm).

As shown in Table 2, the grinding time is reduced with respect to the blank in all cases, by increasing the speed of particle size reduction (C<sub>R32</sub>), which implies a greater efficiency of the grinding of cement, due to the action of additives.

Additives C and D achieve the highest

particle size reduction rates (adjuvant power), improving 110 and 121 per cent, respectively, compared to the blank sample. This implies a reduction of the grinding time with respect to the blank of 17min (25 per cent), which supposes, from the industrial point of view, a significant improvement in the energy efficiency of the grinding process, which would lead to the minimisation of emissions (CO<sub>2</sub>) in cement plants.

### Compressive strength tests

The results of compressive strength (CS) tests are shown in Table 3, presenting the MPa values reached by the cements ground with different additives, at the curing ages of two, seven and 28 days, as well as the degree of improvement in per cent caused by the effect of the grinding aids.

These results imply a notable increase in the CS in this cement, which would allow an increase in its performance, or a reduction in the clinker factor of the cement, which would enable a significant reduction in the CO<sub>2</sub> emissions associated with its production.

Additives C and D achieve the best results in terms of CS, with the difference that, after two and seven days of curing, additive C allows a slightly higher result to be achieved, while at 28 days of curing, additive D presents CS greater than additive C. The difference between the formulations of these two additives is the acid content, so, in view of the results obtained, the CS at two days would be improved with additives that contain organic salts in their formulation, while after 28 days of curing the results are optimised with additives that present a higher concentration of free organic compounds.

### Thermal analysis

The thermal analysis technique explains the mechanism of action of the additives

Table 3: data of compressive strength at two, seven and 28 days of curing

Additive	Compressive strength (MPa)								
	2 days			7 days			28 days		
	CS (MPa)	$\Delta CS$ (MPa)	$\Delta CS$ (%)	CS (MPa)	$\Delta CS$ (MPa)	$\Delta CS$ (%)	CS (MPa)	$\Delta CS$ (MPa)	$\Delta CS$ (%)
Blank	23.2	-	-	34.1	-	-	44.6	-	-
A	24.8	1.6	7	35.6	1.5	4	46.7	2.1	5
B	25.7	2.5	11	37.8	3.7	11	48.0	3.4	8
C	27.3	4.1	18	38.3	4.2	12	50.1	5.5	12
D	26.7	3.5	15	38.4	4.3	13	51.3	6.7	15



Figure 3: thermal analysis – derived from the weight loss of dry cement (A) and in pastes (B) with different additives and blank test

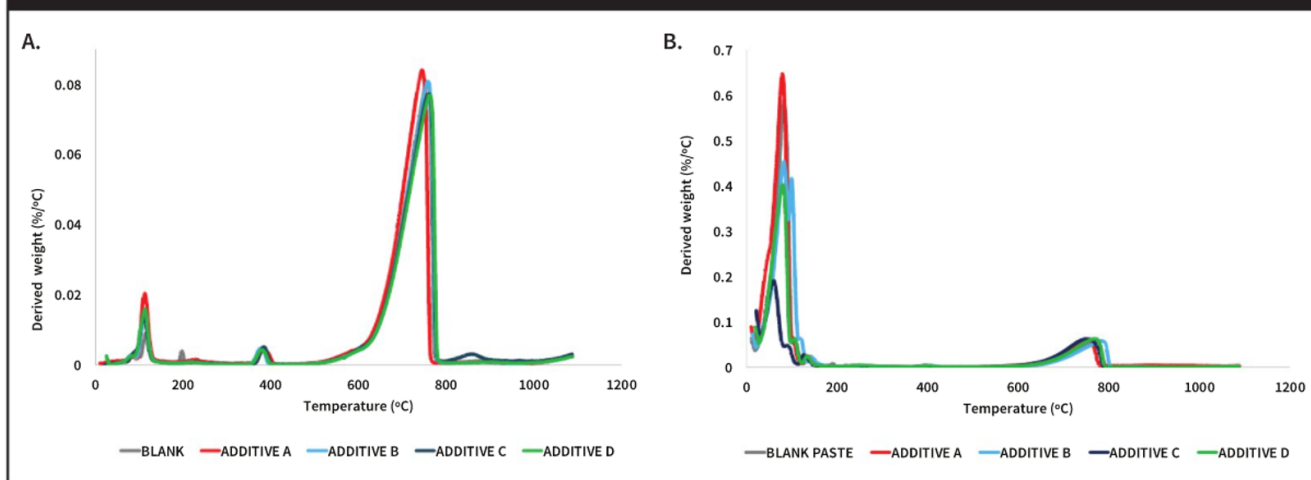
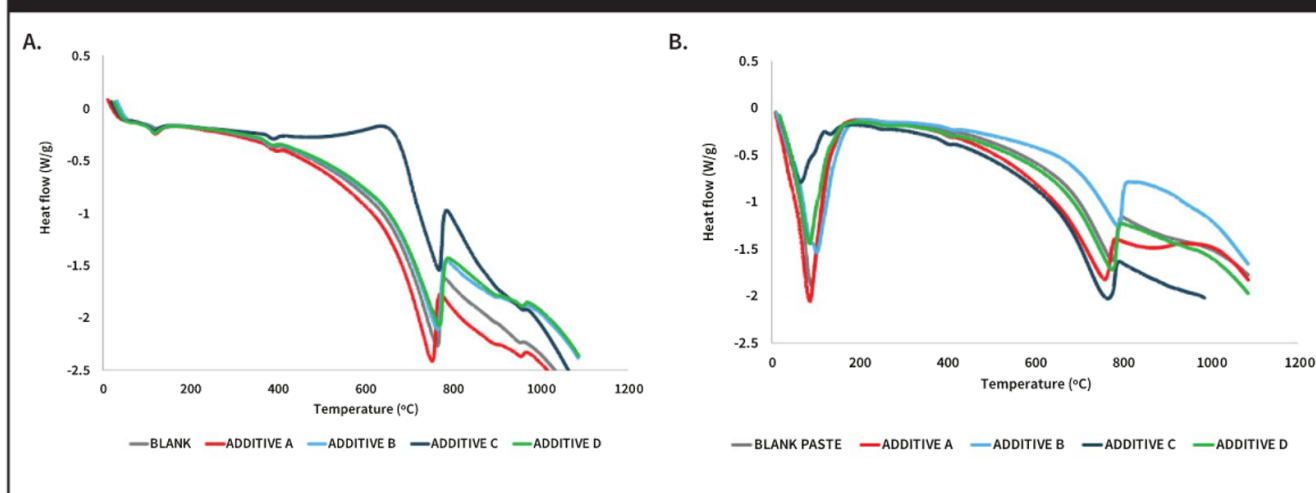


Figure 4: heat flow of dry cement (A) and paste (B) with different additives and blank test



in the hydration reactions of the cement. For this, the simultaneous DSC-TGA of TA Instruments SDT 2960 was used, with 100-120mg of sample and a heating rate of 10 °C/min up to 1100 °C, using alumina crucibles, under the flow of 100ml/min of dry nitrogen.

Analyses of the dry cement samples, cement pastes with a water-cement ratio of 0.4 (w/w) and cement pastes with the same w/c ratio cured at two, seven and 28 days, were performed and compared to evaluate the influence of the additives in the cement during the grinding process itself, and in the development of hydration reactions.

The derivative of the weight loss shown in Figure 3 gives information about the processes that occur during the temperature ramp. In the case of dry cement (A), three main peaks are observed for cement ground with additives, while an additional peak at 200 °C is detected in the blank. On the other hand, in the case of cement pastes (B), the peaks disappear

around 400 °C and those of 100 °C gain importance. The peak at 200 °C is also observed only in the blank test.

The peaks of around 100 °C in the dry cement are due to the dehydration of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). This process is divided into three steps, involving the formation of an intermediate hydrate  $\text{CaSO}_4 \cdot 0.15\text{H}_2\text{O}$ , which only appears in the blank test at around 200 °C. This peak is not present in the cement with additive, because the additive prevents agglomeration of the particles (therefore, it has a greater specific surface area), while accelerating the dehydration reaction of the gypsum through the formation of an organic complex with  $\text{C}_3\text{A}$ , avoiding the formation of the intermediate hydrate and accelerating the formation reaction of the Aft phase. On the other hand, around 400 °C, the final decomposition of the semi-hydrated gypsum ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) in anhydrite ( $\text{CaSO}_4$ ) occurs.

In the case of cement pastes, the peaks between 50-100 °C are due to multiple

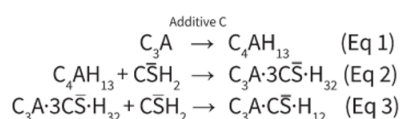
processes, such as the loss of free water present in the pastes, the dehydration of the gypsum and, to a lesser extent, the formation of CSH and Aft formed in the first cement hydration reactions. Additive C presents less intensity in the loss of free water, which suggests a greater acceleration of the hydration reactions in the cement, and therefore, a greater consumption of free water to form hydrated phases of cement, which would explain the higher two-day CS result obtained for this additive.

Due to the water content in the cement pastes, the formation of the semi-hydrated gypsum does not take place, since, in this case, the gypsum would have dissolved, beginning to precipitate, to subsequently form Aft phase.

Around 700 °C, the peaks, both in dry cement and in pastes, are due to the decomposition of calcite ( $\text{CaCO}_3$ ) in  $\text{CO}_2$  and  $\text{CaO}$ . Additionally, in dry cement, a peak around 850 °C is shown in additive C, due to the decomposition of  $\text{CaCO}_3$ .

located in the internal structure of the cement, which could be due to the fact that additive C triggers to a microstructure with higher density, where phases such as calcite could be trapped, displacing the peak to 850 °C.

Figure 4 represents the heat flow of dry cements and cement pastes. In dry cement with additive C (Figure 4A), an exothermic process is observed around 650 °C, in contrast to the other additives and white. This process could be due to the fact that additive C causes a previous reaction to hydration reactions as such, so that the aluminate phase could react with part of the gypsum dihydrate, creating Aft and/or AFm ( $C_3A \cdot C\bar{S} \cdot H_{12}$ ) (Equations 1-3).



The exothermic peak disappears in the cement pastes, as seen in Figure 4B, since the presence of water promotes the dissolution and subsequent reaction of gypsum and  $C_3A$ , reducing the amount of free gypsum, and favoring the formation of Aft.

In Figure 5, four main peaks can be seen for the cement paste at all cure ages.

Around 100 °C, some peaks appear due to the loss of free water but mostly due to the dehydration of the CSH and Aft gel. Dehydration of the CSH gel occurs at about 120 °C and two different phases can be obtained as a result of this decomposition: tobermorite ( $Ca_5Si_6O_{16}(OH)_2 \cdot nH_2O$ ) and jenita ( $Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O$ ).

These peaks are overlapping with the Aft decomposition peak, between 25 and 120 °C. Moreover, peaks around 250 °C are due to the thermal decomposition of  $CxASHy35$ .

At 400 °C occurs the portlandite decomposition. This peak only appears in cement pastes cured, because the hydration reaction time was not enough to observe it in cement pastes that had just been mixed with water.

Peaks about 700 °C are due to calcite decomposition in  $CO_2$  and  $CaO$ .

It should be noted that at seven and 28 days, the blank test has the lowest peak height inbetween 25-120 °C. This highlights the lower CSH gel formation and increased portlandite formation, as discussed later with the PXRD results.

### Scanning electron microscopy

The morphology of the different phases

that appear in the cement samples are studied by scanning electron microscopy, coupled to energy dispersion spectroscopy (SEM-EDS) in the JEOL JSM 6400 microscope.

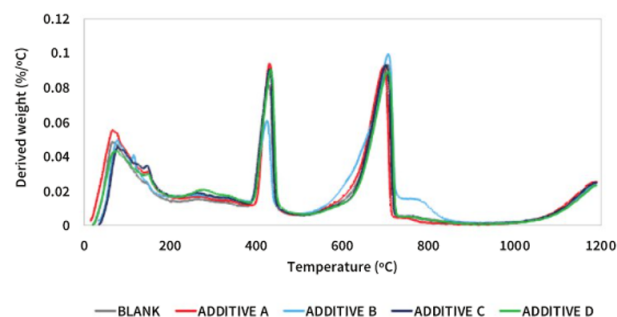
Comparing the SEM images at two, seven and 28 days of curing, it is possible to study the influence of the additives, focussing on the porosity, hydration and formation or disappearance of phases (eg, Aft, portlandite, CSH gel, anhydrous phases).

Based on the observations made, it is contemplated that the presence of acid in the additives would favour the densification of the Aft, so that the porosity of the cement would be reduced at two days (see Figure 6). This happens because the acid interacts with the organic compounds, which have a certain basic character, neutralising the charge difference between the surfaces of the Aft, due to the formation of ions. This phenomenon would minimise the porosity of the cement, causing an increase in the compressive strength at two days, as shown in the section about compressive strength.

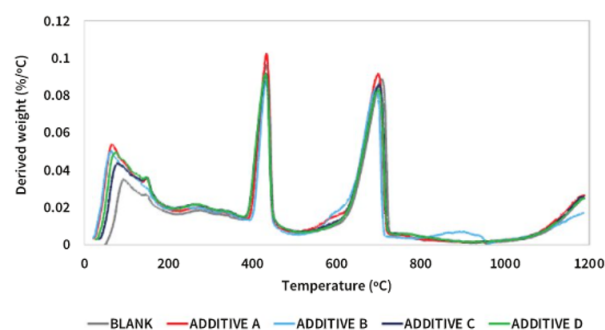
The additives formulated with organic compounds and acids, react with the potentially soluble gypsum in the cement, favouring the hydration of the aluminate phases, and promoting the formation of Aft after two and seven days of curing.

Figure 5: derived of weight loss in the cement past at two, seven and 28 days of curing with different additives and a blank

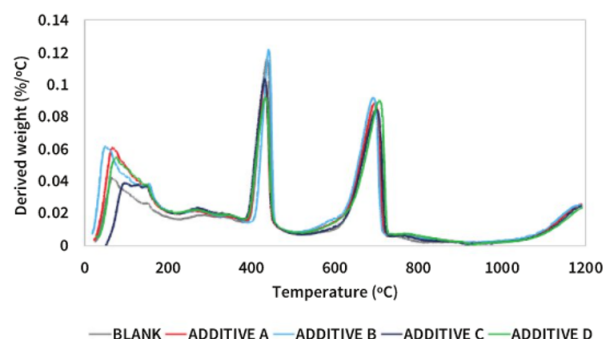
#### After two days of curing



#### After seven days of curing



#### After 28 days of curing



This effect is observed more notably with additive C, since it has a higher concentration of organic compounds and acid, while in cases A and B, phase  $C_3A$  is observed still unreacted, while in additive D, not containing acid,  $C_4AF$  phase is observed, also unreacted.

The use of additives promotes the densification of the CSH gel structure, reaching complete hydration after 28 days of curing. The densification of the gel causes a decrease in porosity (see Figure 8). In addition, it can be seen that after 28 days, unreacted phases continue to appear, especially in the blank test and in



additive A. However, for additives C and D, a high formation of portlandite and CSH gel is observed, which would explain the higher 28-day CS results obtained by these additives.

### X-ray diffraction

X-ray powder diffraction (PXRD) at room temperature was performed on a Siemens D-5000 diffractometer, using Cu K $\alpha$

radiation ( $k = 1.5418 \text{ \AA}$ ).

The results of PXRD are shown in Figure 9, where the most important phases present in the cement pastes at two, seven and 28 days of curing are represented, with different additives and the blank.

Alite and belite are the phases with the greatest presence in clinker. The hydration reactions of these crystalline

phases have different kinetics since the hydration reaction of the alite begins before the hydration of the belite, as shown in Figure 9. The decrease or increase of these phases at different curing times leads to the formation of amorphous phases such as CSH gel, which are not detected with PXRD, or portlandite, whose evolution can be studied using this technique.

The presence of additives seems to decrease the content of the portlandite phase in the cement, at seven and 28 days of curing, this would be explained by an increase in the Ca/Si interaction, which would therefore promote the formation of CSH gel.

The rate of formation of portlandite at initial ages is boosted in additive cements with respect to the blank test, producing an increase in CS at two days. Meanwhile, at seven and 28 days of curing, a significant increase in this phase is observed in the blank, due to the low mobility of Ca<sup>2+</sup> and Si<sup>4+</sup> due to the absence of additive, thus leading to less CSH gel formation and, therefore, obtaining lower compressive strengths.

In all the tests carried out, the calcite remains constant due to its filler action used to disperse the clinker grains, accelerate the hydration of the cement and fill the intergranular holes, obtaining more compact and homogeneous cement pastes but remaining inert during the hydration process.

In all cases, except with additive C, the highest amount of alite phase appears after two days of curing, and then decreases up to seven days due to the hydration of this phase. However, for additive C, the hydration reaction of alite is accelerated before two days of curing, so the amount of unhydrated alite is practically constant at two, seven and 28 days of curing. This would explain the increase of the CS to two days of curing for additive C.

On the other hand, due to the low kinetics of the hydration reaction of the belite, its reaction is more intense after seven days of curing, both in the additive cements and in the blank test.

### Conclusions

From the results obtained, it is concluded that the use of Proquicesa grinding additives reduces CO<sub>2</sub> emissions in the cement manufacturing process.

The reduction of CO<sub>2</sub> emissions induced by using grinding aids is achieved

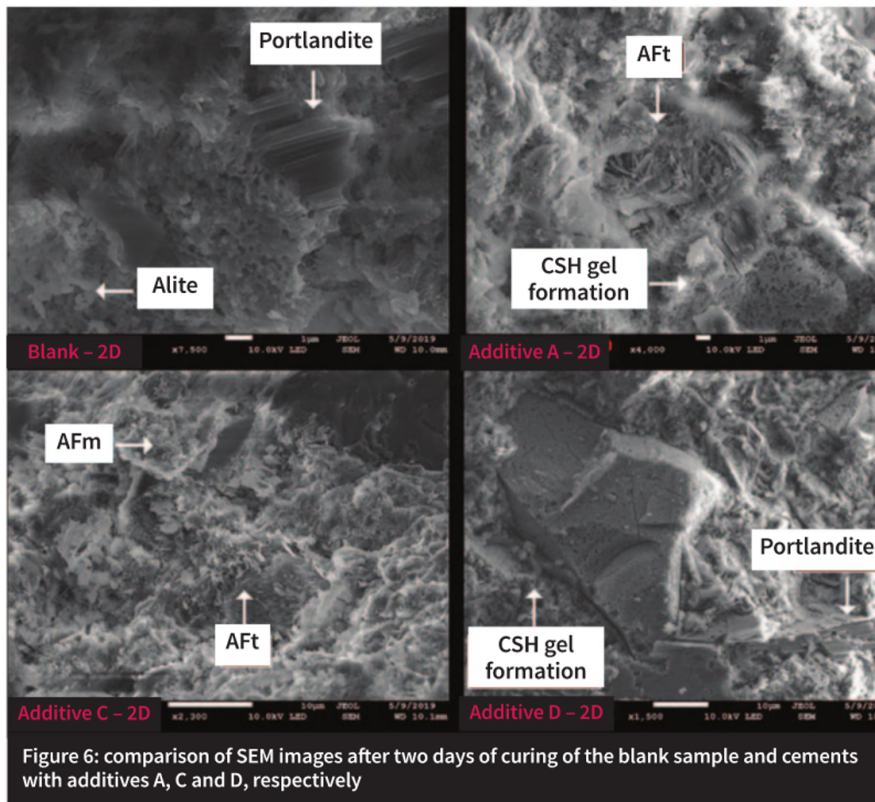


Figure 6: comparison of SEM images after two days of curing of the blank sample and cements with additives A, C and D, respectively

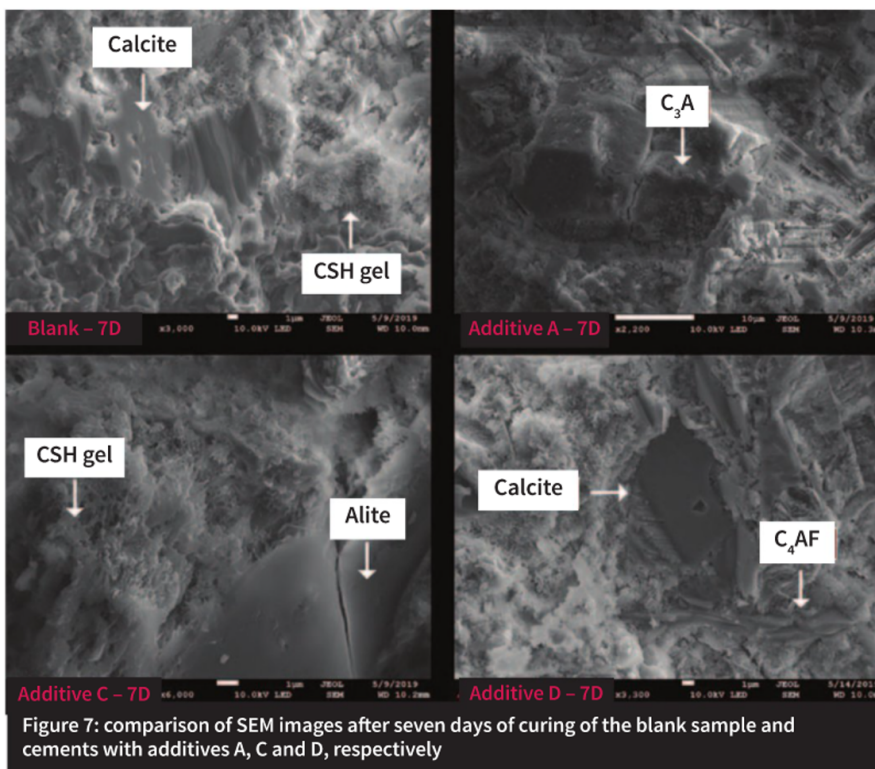


Figure 7: comparison of SEM images after seven days of curing of the blank sample and cements with additives A, C and D, respectively



through decreasing the clinker factor, thanks to the increase in compressive strength, reaching more than 12 per cent improvement at all ages.

On the other hand, an outstanding increase in production has been observed using Proquicesa cement additives, reducing grinding time by over 20 per cent. This leads to a reduction in emissions thanks to the energy optimisation of the cement grinding process.

The additive that has provided the best performance at initial ages is additive C, as a consequence of the addition of acid, which promotes the densification of the ettringite phase, minimising porosity and increasing the CS to two days. This additive promotes the conversion of Aft to AFm by forming a complex between gypsum and organic compounds in dry cement. It also accelerates the reaction of the alite according to PXRD.

On the other hand, the formation of CSH gel due to the action of additive D provides the greatest increase at final curing ages due to its higher content of free organic compounds, which would lead to a higher conversion of  $\text{Ca(OH)}_2$  into CSH gel. ■

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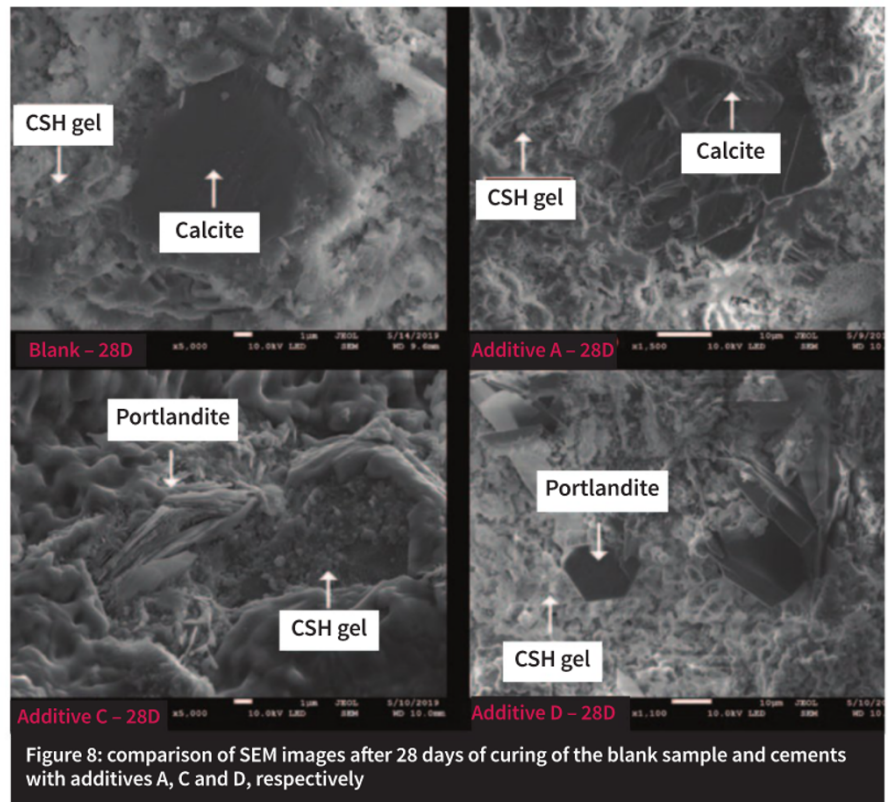


Figure 8: comparison of SEM images after 28 days of curing of the blank sample and cements with additives A, C and D, respectively

Figure 9: share of cement phases (in per cent) at two, seven and 28 days of curing with different additives and blank

