Enhanced performance

by Mapei SpA, Italy

In recent years, alongside with the use of the traditional grinding aids (whose principal effect is on the mill capacity), the use of a special type of grinding aids has spread, which we could name as 'performance grinding aids', characterised by having a chemical effect on the mechanical strengths of the cement, highly concentrated, chloride free and a low dosage (0.01-0.03 per cent). In this article Mapei proposes a technical solution regarding the optimisation of performance grinding aids in terms of increases in mill capacity, leaving unchanged the effects on the mechanical properties.

This article will examine the following arguments for the optimisation of performance grinding aids in cement manufacture:

1. *highly concentrated grinding aids*: dilution with water and effects on mill capacity and cement cost production
2. *cement quality:* analysis of the characteristics of the cement ground with the dilution technique
3. *water dilution technique*: for performance grinding aids

Water dilution

The first consideration is the water dilution of the performance grinding aids at the moment of use, with the aim of achieving an improved dispersion of the active substance of which they are composed and to optimise the contact between the additive and the cement surface. These additives, which due to their high concentration are often used at very low dosages (0.015-0.025 per cent), are not always able to express their full potential, because of the difficulty of the dispersion of the liquid onto the solid material. In industry, it often happens that very low flow rates of additive, come in contact with only a part of the material entering the mill. in these conditions the additive struggles to disperse during the grinding process.

The type of dilution to which is being refered to is the following:

- dilution made on the spot by using a double head pump
- additive-water ratio between 1:3 to 1:10 or, in order to introduce into the mill a dosage of liquid (additive + water) between 1.000g/t and 2.000g/t (0.10 per cent and 0.20 per cent on the weight of the material to be ground).

A typical example is represented by an additive/water mixture of 1.500g/t composed by 300g/t additive and 1200g/t of water.

When is the dilution successful and which type of additives to dilute?

In Europe, side-by-side with newer installations, there still exist a great number of small mills that often are maintained in service to grind high fineness cements (eg CEM I 52.5 R). It is in these installations, characterised by a small hourly capacity, that the dilution of the grinding aid gives the greatest benefits. In fact, a very small amount of grinding aid enters into these mills (eg 9-15kg/h for a mill producing 30-50tph with a dosage of 300g/t). In these conditions the amount per minute of the grinding aid varies between 150 and 250g/min if, for different reasons, even a small quantity of the additive does not reach the material to be ground, the mill performances decrease quickly.

Based on these considerations Mapei started to perform a large amount of industrial tests using the technique of diluted grinding aids, both on small and big mills, and this opinion has been formed:

The dilution of grinding aids with water is always recommended, but is particularly efficient in the following cases:

- highly concentrated grainding aidss
- low additive dosage, eg lower than 300g/t (0.03 per cent)
- low mill diameter (<3m) or with limited production (<60tph)
- mills without cooling water addition in the first chamber
- limestone or high fineness cements
- hot clinker at the mill entrance

Dilution effects on grinding performances

The dilution of the performance grinding aids with water may be carried out with the intent of reaching two different goals: a) to reduce the additive dosage while maintaining the same mill capacity

Figure 1: grinding aid production increase

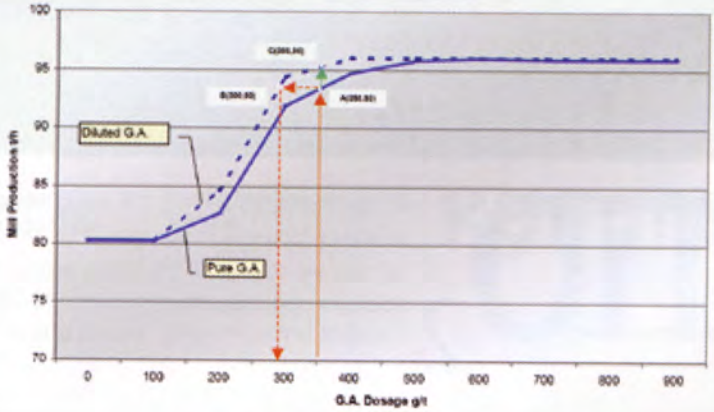
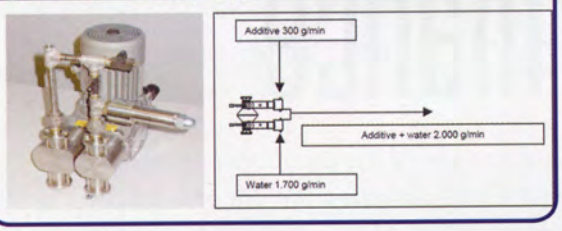


Figure 2: double head pump



(recommended solution) or
b) to further increase the mill capacity while maintaining the same additive dosage.

When the additive dosage is relatively high (eg >0.3 per cent) dilution is recommended in order to reduce the dosage at the same mill output, while when the dosage is already quite low (<0.3 per cent) it is better to aim towards increasing the mill production.

Typical results of the dilution can be as follows:

- a reduction of the additive dosage of 10-20 per cent at equivalent mill performance or
- a further increase in production of 2-5 per cent at the same additive dosage. Figure 1, taken from a real industrial case history, clarifies the previous notions.

Let's consider a mill producing 80-81tph of CEM II/A-LL 42.5 R ground at 3.600Blaine in a stable operating regime without an additive. With a dosage of 350g/t of pure grinding aids and at the same fineness the production obtained is 92-93 tph as represented by point A (350,93). By increasing the additive dosage the production stabilises in an asymptotic way on 96-97tph.

With the dilution there following options are available:
a) passing from point A (350,93) to point B (300,93) through the red line by reducing the grinding aid dosage and maintaining the mill production unaltered. In this case, a dosage decrease of 14 per cent is obtained at the same level of production. Recommended solution.
b) Passing from A (350,93) to point C (350,96) through the green line with the same grinding aid dosage and obtaining a production increase of 2.3 per cent. In this case the percentage increase is less remarkable due to the fact that the mill is already close to its structural limit of 97tph (for that type of cement and at that fineness).

Figure 3: additive dosage/mill production

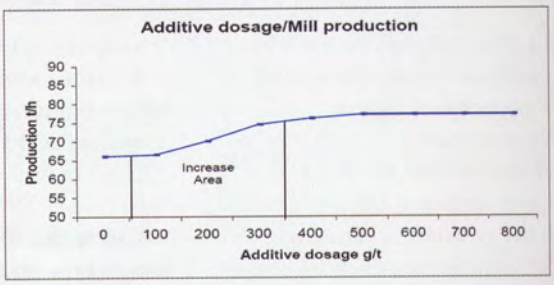


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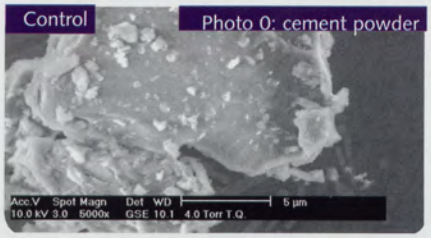
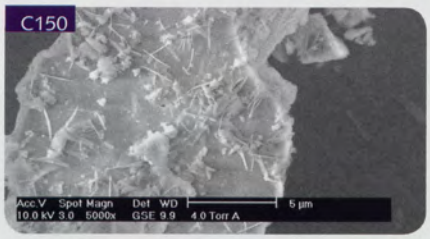
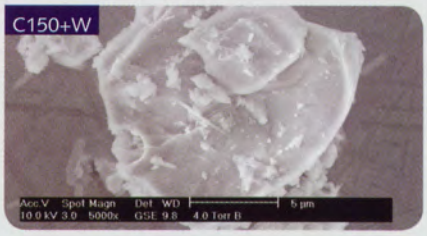
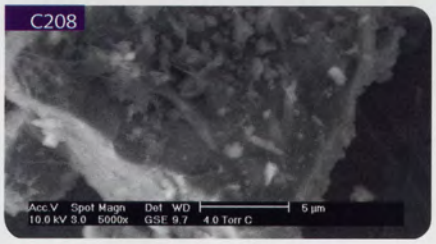
Table 1: clinker chemical analysis

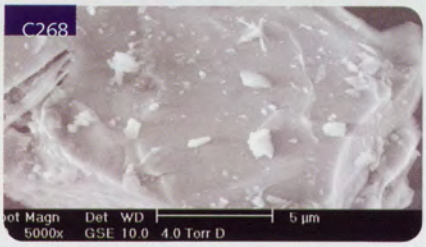
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI	Free CaO	Total
20.95%	6.32%	269%	65.55%	1.45%	0.87%	0.23%	1.10%	0.23%	0.84%	99.16%









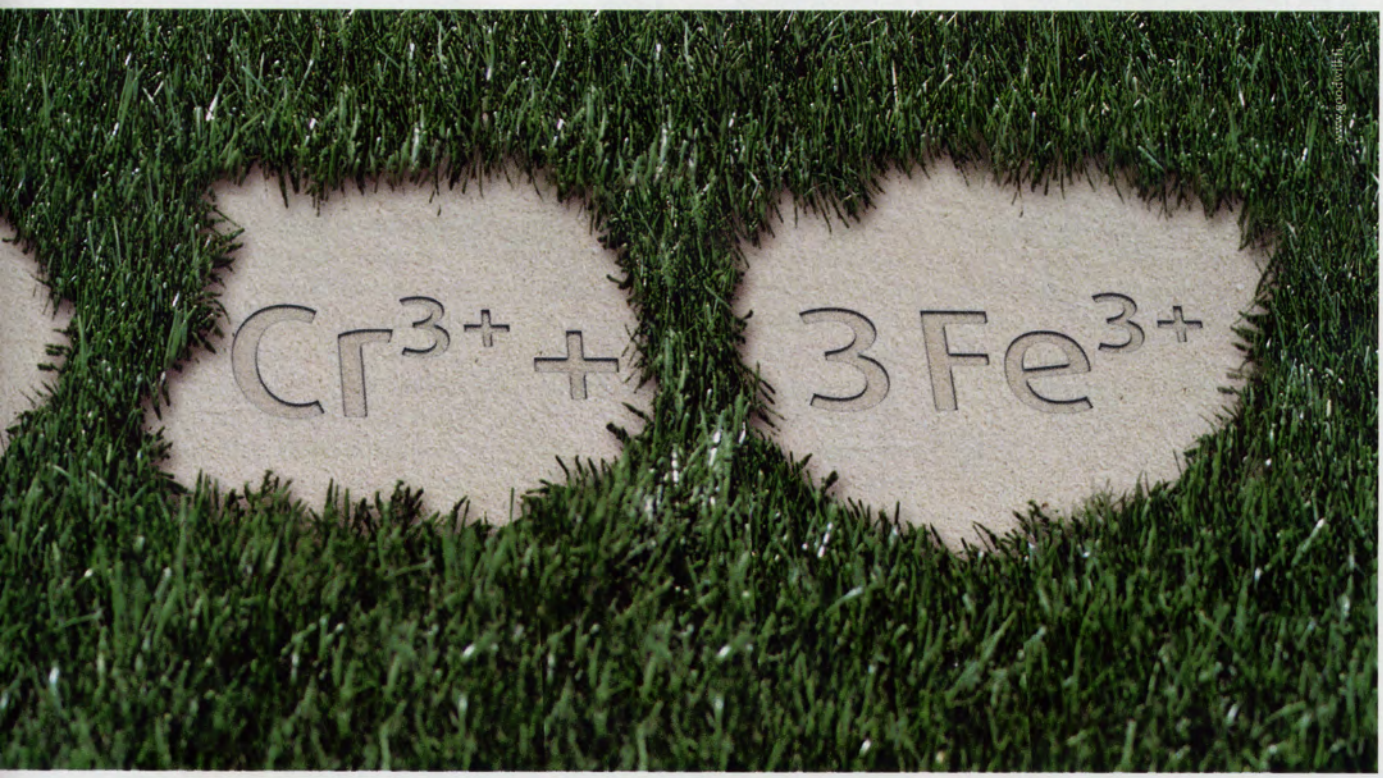


In practice, through water dilution, we obtain a 'shift to the left' of the curve additive dosage/mill production tph. The curve with the pure additive is the blue line, the broken line represents a dilution 1:6 between the grinding aid and water.

Practical realisation of the dilution

The double head pump represents the most suitable system for diluting grinding aid on the spot. It is constituted by a single motor and two pumping heads with separate dosage flow rates (see Figure 2). Additive and water join together in a single pipe, where the dilution takes place.

To avoid unexpected inconveniences we recommend using low-pressure water: the best solution is to pump water from a small reservoir with a free surface, such as



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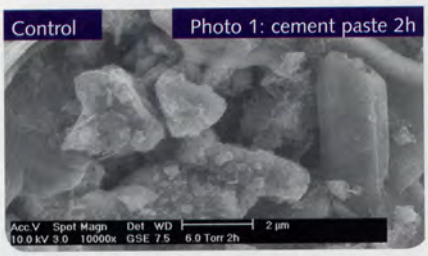
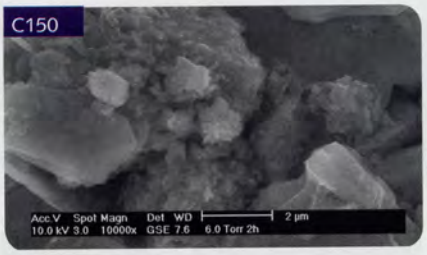
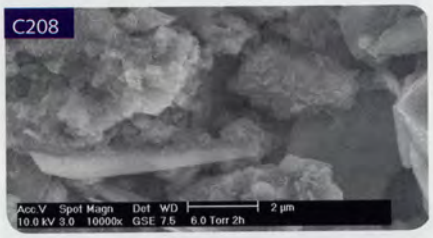
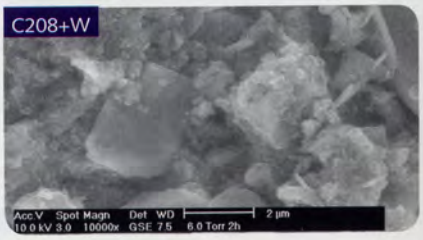








a plastic tank or other recipient, with the aim of maintaining automatically the same water level by means of a float system such as used in sanitary appliances. With high pressure water we risk:

- water passing into the mill even when the pump is off and the mill is at rest
- irregular dosage of the additive and flow rate.

Industrial trials

The dilution of grinding aid with water is to be considered as a procedure for the optimisation of grinding aid performances.

- as a first step it is advisable to use the pure additive in order to obtain reliable results without water.

In this first phase, that should last at least one week, it will be possible to identify not only the optimum dosage but also the maximum dosage above which it will not be possible to obtain tangible benefits. In practice we could build an additive dosage/mill production tph curve, like in the following example.

- once the performances of the pure additive are verified it will be possible to add water following the above-mentioned instructions and decide on whether to decrease the additive dosage or to increase the mill production.

Cement quality

As previously mentioned, the additive dilution technique was applied to the performance grinding aids. In other words, on products that improve the mechanical properties of the cements. This type of additive is usually employed to improve cement quality or to reduce the clinker content in blended cements while maintaining the same quality. Together with the mill production increase, it is of interest to verify if the mechanical properties of the cement produced can be further improved using the dilution technique.

With this aim, irrespective of different indications derived from industrial cases, Mapei decided to carry out a series of lab grinding tests (Bond type mill) under the following conditions:

- defined composition: 95 per cent clinker and five per cent (natural) gypsum
- same grinding fineness: 3.100 ±100 Blaine

Using two types of additives (MA GA/C150 and MA GA/C208) the following were ground:

- reference cement
- cement with 0.03 per cent pure additive
- cement with 0.03 per cent additive + 0.12 per cent water.

The two additives are characterised by the same grinding capability but they have a different chemical effect: the first (C150) is able to increase early strengths the second (C208) is more suitable for ultimate strengths. The study has been carried out with four different types of clinker using the following techniques:

- morphological analysis of the ground cement powder with a ESEM-FEG electron microscopy
- morphological analysis of the hydrated paste of cement at different hydration times with a ESEM-FEG electron microscopy
- temperature curves of the cementitious paste during hydration
- mechanical strengths according to the EN 196 standard.

The first two techniques provide a 'qualitative' idea of the effect of the additive (pure or diluted), while the last two enable technicians to 'quantify' the additive effect. To simplify the data, it has been decided only to illustrate, in this paper, the results of the below mentioned clinker, which Mapei considers the most representative.

Morphological analysis of the powder and cement paste

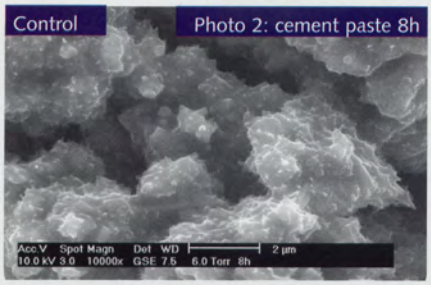
The intention was to verify if there are differences between the cement powder ground with and without an additive (pure or diluted). Because it was impossible to obtain the identical granulometric distribution with and without an additive, Mapei carried out the experiments at the same Blaine fineness. The following photos (0,1,2) show the results obtained (10,000x).

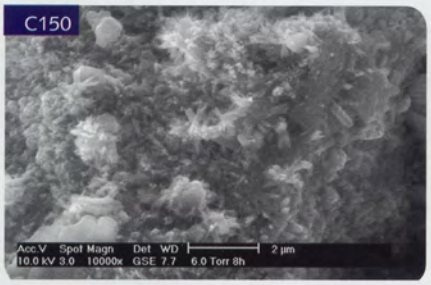
On the surface of the cement particles ground with additives some traces of a sort of pre-hydration (in particular in the 'C150' photograph) can be observed which would merit further investigation.

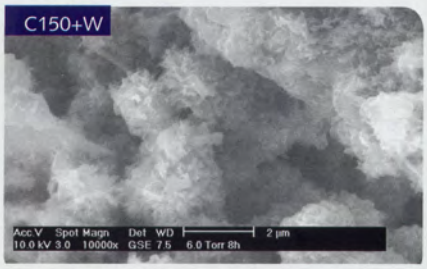
As far as the hydration is concerned, the different degree of calcium silicates hydration with the additive can be observed. From the photos 1 and 2, it can be seen that until two hours the additive has a minor effect on the hydrated products, but from eight hours on the cement ground with performance grinding aids presents a much more advanced hydration status (hydration of calcium silicates, important for early mechanical strengths). In fact photo 3, taken at eight hours, the cement ground with both additives shows a larger development of the silicates needle structure (C-S-H).

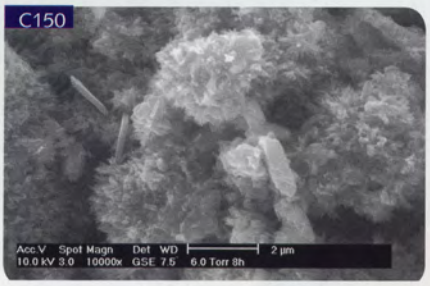
Temperature curves

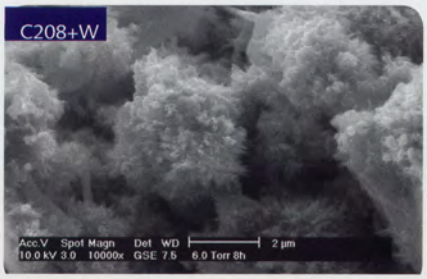
The points were reported on the temperature curves corresponding to the 'hydration times' at which the pictures were taken. The heat of hydration of the cement with additives (integral of temperature curves) is always higher than that of the control cement. The minor difference between the cement ground











with pure additive and with diluted additive is probably due to the slight difference in fineness (see Table 2).

Mechanical strengths

Mechanical performances with the pure and diluted additive are listed in the table. There is no significant difference in strengths between the cement ground with pure additive and with diluted additive. At the same grinding time samples ground with diluted additive are slightly finer, as expected.

The C150 (pure or diluted) has a positive effect on early strengths. It is normally used on high strength Portland cements (eg CEM I 52.5 R) and in any case where an increase in strengths at 1-2 days is required (or to reduce the clinker content in favour of an 'active' addition: slag, etc).

The C208 (pure or diluted) is more suitable for increasing ultimate strengths. It is normally used on Portland cements or to reduce the clinker percentage on blended cements (eg limestone cements).

Conclusions

a) the grinding aid dilution technique may allow increases in production of 2-5 per cent or, alternatively, savings of 10-20 per cent on the additive cost. The results depend on the grinding system available and on the type of cement.

b) the quality of the cement ground with the diluted additive remains unchanged. More sophisticated analysis is under way.

c) grinding aids allow cement manufacturers to improve the quality of cements or, alternatively, to reduce the clinker content in cement while maintaining the same cement quality.

d) some other industrial trials are already planned. Contributions from readers are most welcome.

Figure 4: CEM I 52.5R (LAB) temperature curves; 20°C; C=500g; W/C=0.35 (Rich 2004340)

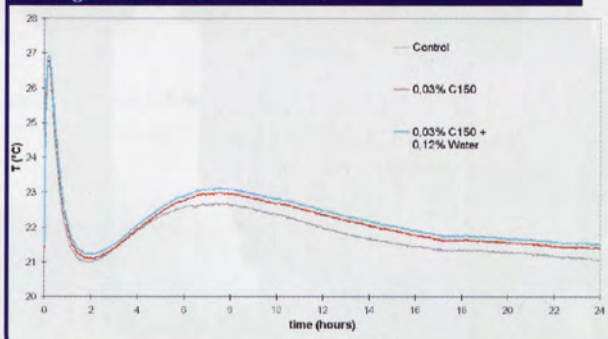


Figure 5: CEM I 52.5R (LAB) temperature curves; 20°C; C=500g; W/C=0.35 (Rich 2004340)

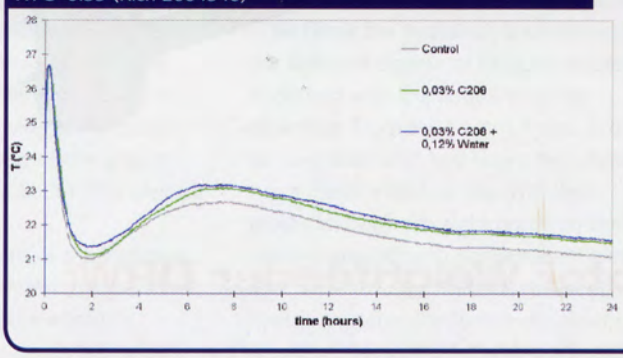


Table 2: cement physical data

	Blaine	Grinding time	Alpine residuals	I Setting time	F Setting time	Strength i day	Strength 2 days	Strength 28 days
	cm^2/g	min	32µm	min	min	N/mm^2	N/mm^2	N/mm^2
Ref.	3.160	45	43.3	160	225	14.4	25.7	52.8
C150	3.080	34	41.3	150	210	16.9	27.6	53.4
C150+W	3.150	34	39.7	150	210	17.1	27.4	53.6
C208	3.120	35	41.1	155	220	15.8	27.2	55.6
C208+W	3.190	35	37.4	155	215	16.1	27.3	56.2

Note: results in terms of strength reflect the typical values obtained with those types of additives