# Reducing pre-hydration

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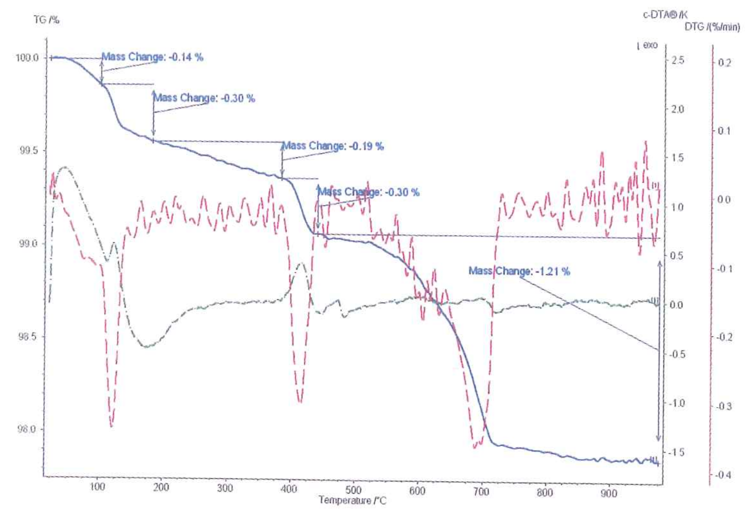
*Considering the exponential growth in the number of vertical roller mills (VRMs) installed at cement plants over the years, in 2010 Mapei introduced a new product line on the cement additives market specifically with VRMs in mind. The combination of these particular products and the introductory technology that has been described in past publications (direct dosage together with the water flow instead of 'traditional' dosing on the raw material conveyor belt) has enabled several cement plants to obtain results which had previously not been achievable using standard products originally developed for ball mills. This article outlines one specific industrial case study which demonstrates the effectiveness of this products as well as its intrinsic versatility.*

In recent years, during the installation of grinding plants, VRMs have begun to outnumber 'traditional' horizontal ball mills. The main advantages of VRMs compared to ball mills lie in their higher levels of output, lower specific energy consumption, lower housing costs and a higher versatility.

However, VRMs also present certain challenges. For example, high pressures of the roller presses are demanded in case high Blaine values are required. On top of this, VRMs are significantly more sensitive towards materials entering that have a very high fineness (the threshold is set at around a maximum of 50 per cent material <4mm). Particularly in the case of fine raw materials, a significant amount of water has to be added in the grinding process to keep the vibration level of the whole grinding system low at all times[1]. As could be reasonably expected, high amounts of injected water are likely to trigger the pre-hydration of ground cement inside the mill, with signficant consequences on the product's compressive strength.

Water amounts (usually expressed in percentage terms) of 0.5 up to 1.5 per cent are generally considered to be safe and do not negatively impact cement quality. Nevertheless, suitable higher amounts of water (up to 5-6 per cent) are sometimes needed to stabilise the vertical mill. This is particularly true of grinding plants where the control of clinker and granulometry quality are limited.

Figure 1: TGA analysis of a pre-hydrated cement sample



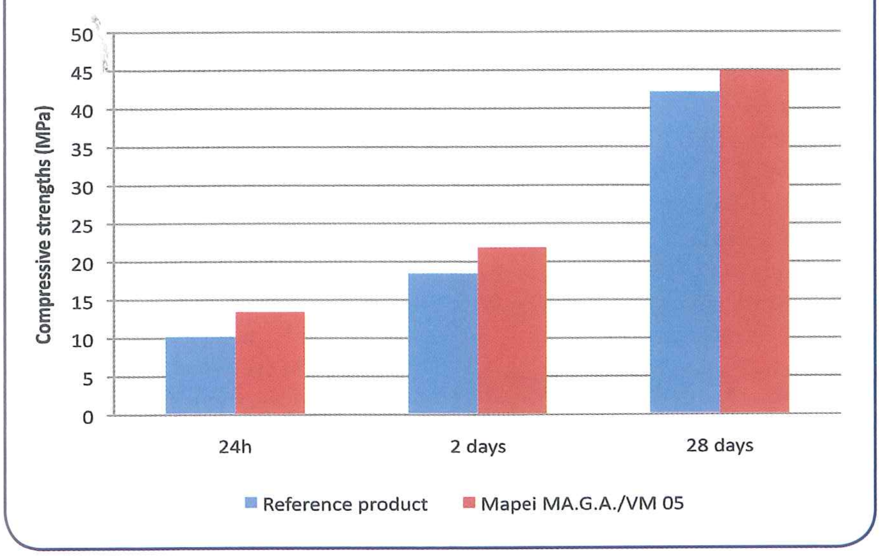

## Case study

Last year Mapei was contacted by representatives from a medium-sized grinding facility situated in southern Europe. The plant was facing problems with the production of a CEM I 42.5 R cement blend on a vertical grinding system. Due to the high degree of fineness of the purchased clinker, the plant was forced to add a considerable amount of water to the grinding process (up to seven per cent) to keep the vibration levels of the mill within the structural limits of the installation. A standard grinding aid for ball mills was in use, with a positive but rather small effect on the mill's output level. The plant would dose the product on the clinker conveyor belt just before entering the mill, as is usually the case with horizontal grinding systems.

**Table 1: effect of MA.G.A./VM 05 on the main process parameters**

| | | |
|---|---|---|
| Average mill output (tph): | 65.0 | 72.0 |
| Vibration range (mm/s): | 2.0-2.6 | 1.6-2.2 |
| Water flow (%): | 6.4 | 2.5 |
| Additive flow (g/t): | 500 | 450 |
| Average Blaine fineness ($cm^2/g$): | 3820 | 3836 |

Figure 2: effect of MA.G.A./VM 05 on the development of compressive strengths




The main problem lay in the low compressive strengths, which were most probably due to pre-hydration of the cement caused by the very high amounts of injected water.

During Mapei's first visit to the plant, the company obtained samples of freshly-ground cement as well as raw materials (clinker, gypsum and limestone). These materials were fully determined by XRD, XRF and thermogravimetric analysis (TGA) analyses.

The TGA analysis showed a very high level of pre-hydration in the cement sample. The results of this analysis as well as a general description of how the pre-hydration level can be reasonably estimated using this technique is described below.

**Pre-hydration of cements in VRMs**

Reduction of vibration for stabilisation of the grinding bed is usually obtained through the use of water sprayed on clinker during milling operation in VRMs. This addition has some side effects, which can be quite unfavourable:

- *reduction of dehydration of gypsum*[2, 3, 4] – different forms of calcium sulphate have a significant impact on cement performances and reactivity of cement/concrete additives. Temperature and moisture in cement mills should be carefully controlled to have the right conversion rate of natural gypsum to hemi-hydrate or anhydrous calcium sulphate. If too much water is added during grinding, gypsum dehydration can be influenced and reduced, leading to important modifications of the cement behaviour during hydration

• *pre-hydration of cement* – if too much water is used, it can be partially bound in calcium silicate hydrates promoting a partial pre-hydration of cements with a consequent reduction of mechanical properties.

A very interesting tool for measuring and controlling cement pre-hydration is TGA. This technique is very useful for the analysis of dry and hydrated cements[5]. A sample of cement is heated from room temperature up to 1000°C and the decreases in weight (due to the release of water or $CO_2$) are measured. It is then possible to quantify the amount of gypsum, calcium hydroxide, limestone, hydrated phases. For instance:

• at 125°C and 170°C natural gypsum is dehydrated in two steps, losing first 1½ molecules of water being converted to calcium sulphate hemihydrate, then losing ½ molecules of water giving anhydrite (anhydrous calcium sulphate). Therefore, a weight decrease between these two temperatures (below 200°C) can be related to the sum of the following reactions:

$CaSO_4{\cdot}2H_2O = CaSO_4{\cdot}0{,}5H_2O + 1.5H_2O$
$CaSO_4{\cdot}0{,}5H2O = CaSO_4 + 0.5H_2O$

• hydration of tricalcium silicate produces a family of different compounds usually described as C-S-H (calcium silicate hydates). Water bound in such structures is usually lost over a wide range of temperatures, due to the extreme variety of compositions of the C-S-H. Generally speaking, we can associate the weight decrease between 200° and -400°C to the water lost from C-S-H

• Calcium hydroxide $Ca(OH)_2$ (also known as portlandite) is present in hydrated cement pastes as consequence of tricalcium silicate and free lime hydration. Water from calcium hydroxide is released in a strict range of temperature (around 500°C). Thus, weight decrease between 450 and 550°C is associated to the water bound in portlandite, lost according to the following reaction:

$Ca(OH)_2 = CaO + H_2O$

• above 600°C, the weight decrease is associated to the decarbonation of limestone (calcium carbonate $CaCO_3$), according to the reaction:

$CaCO_3 = CaO + CO_2$

• limestone is present in cements as mineral addition intentionally added (as envisaged in the international standards on cement composition), or it is originated from hydration of free lime, according to the following reactions:

$CaO + H_2O = Ca(OH)_2$
$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$

TGA analysis (performed with TGA – Netzsh TG209F1 Iris) on the samples show that with the use of a suitable grinding aid (for example Mapei's MA.G.A./VM 05, as described below) there is a consistent decrease of water in the range 200-400°C.

**Table 2: weight decreases at different temperatures evaluated using TGA**

| 100-200°C | 200-400°C | 450-550°C | >600°C | |
|---|---|---|---|---|
| No additive (%) | 0.30 | 0.19 | 0.30 | 1.21 |
| With MA.G.A./VM05 (%) | 0.28 | 0.08 | 0.27 | 1.85 |

Taking into account all these different aspects, Mapei has identified one particular product that could improve the situation: MA.G.A./VM 05, which is characterised by a combined effect on the production process (grinding aid plus strengths enhancer). In addition to this, Mapei proposed a modification of the dosing system at the plant according to the technology developed by Mapei[1].

MA.G.A./VM 05 has been tested on the production of a typical CEM I 42.5 R type cement blend (92.0 per cent clinker, 4.5 per cent gypsum, 3.5 per cent limestone). The product has been dosed at 450g/t (suggested dosage range for this product is 300-500g/t) directly on the grinding table together with the water flow. Two separate pumps permitted Mapei to control the flow of the two liquids independently. The results of the industrial trials are reported in Table 1.

As can be seen, the combination of MA.G.A./VM 05 (chemical enhancement of the hydration process) and the reduction of the injected water (reduced pre-hydration of cement) has been able to deliver consistent increases of the compressive strengths at all ages (see Figure 2).

The positive effect of water reduction is confirmed by comparing the weight decrease between 200 and 400°C in cements ground with and without MA.G.A./VM 05, as reported in Table 2.

In addition to this, Mapei has observed a solid increase of the mill output (+1.7 per cent) while keeping the same targeted fineness. Finally, it should be also noted that the average vibration level of the mill was reduced following the introduction of the product in the system.

## Conclusions

The industrial case study presented in this article demonstrates how, by choosing the correct cement additive and the most effective introduction technology, solid improvements of the process parameters of VRMs can be achieved.

As a direct consequence, the reduction of the percentage of injected water (ie reduced pre-hydration degree) combined with the chemical effect of MA.G.A./VM 05 on the cement hydration process has enabled good increases in the cement's compressive strengths.

A reduction in the amount of injected water has been possible thanks to the positive influence of the cement additive on the stabilisation of the cement mass on the grinding table.

**References**

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