KEEPING UP QUALITY

Abstract

Due to the stringent requirements of energy saving, the use of vertical roller mills (VRMs) for cement grinding is now common. Modern VRMs provide good reliability and operational stability. However, cements produced in VRMs can sometimes perform less well than cements with a similar composition and mineralogy produced via different grinding systems. This is usually due to factors related to grinding temperature and prehydration during cement manufacturing. This article will detail Mapei's approach to improving the quality of cements produced by VRMs. It will also include a case study on a typical cement produced in different grinding systems, focusing on the main elements affecting cement quality when transitioning from a traditional ball mill to a vertical roller mill.

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OUTLINES AN INVESTIGATION INTO THE COMPARATIVE STRENGTHS OF CEMENTS PRODUCED BY DIFFERENT GRINDING SYSTEMS.

Introduction

Mainly due to their lower specific energy consumption (measured in kWh/t of produced material) and higher production (tph) values, vertical cement mills are slowly but steadily outnumbering 'traditional' horizontal ball mills.

Vertical cement mills can reach production values that are significantly higher than those achievable with traditional ball mills. For example, ball mills can provide an indicative maximum output of 180 – 200 tph, while vertical mills can provide up to 300 tph. Consequently, VRMs have a lower energy consumption, resulting in a lower specific cost (€/t cement produced).

Vertical mills can also offer versatility – transition times between different cement types/compositions are significantly shorter if not nonexistent. From the point of view of grinding efficiency, vertical mills are less sensitive to the possible high moisture content of raw materials, due to high hot gas flow through the mill (given that a sufficient energy source is present).

Nevertheless, vertical mills also present certain disadvantages when compared to traditional grinding systems. In a nutshell: high roller pressures are required in case high Blaine values are desired; vertical mills are more sensitive to materials that present a very high fineness (with 'dusty' clinker having a significant mass fraction below 4 mm, very high vibration levels are possible); a significant amount of water has to be added to the grinding process in order for the vibration level of the whole grinding system to remain low at all times. The latter can have major repercussions on the cement grinding temperature, and an external heat supply is needed to guarantee a certain exit temperature. Although this means an increase in specific production costs, lower cement performances can sometimes result from an insufficient grinding temperature.

Case study

A European cement plant produces a CEM I 52.5 R type in both a VRM and a traditional ball mill, using the same clinker and mineral additions sources (gypsum and a few percent limestone).

Since the VRM began operating, notwithstanding the lower specific energy consumption, the CEM I it produced had a lower compressive strength at all ages (2 – 3 Mpa on average). The main parameters of the VRM are summarised in Table 1.

The cement plant contacted Mapei for technical support, with the specific aim of increasing the strengths of the VRM cement in order to match the results obtained by the ball mill.

If the clinker quality is the same, the cause of the differences in strengths can lie in the modification of particle size distribution (PSD) or in the type and amount of calcium sulfate. Mapei's approach began with a detailed analysis of cement samples.

Table 1. **Main VRM parameters**

Average mill output	135 tph
Vibration range	2.0 – 2.5 mm/s
Water flow	4.0%
Pressure drop ΔP	50 mbar
Average Blaine fineness	4400 ± 100 cm²/g

Details of analysis performed

Samples of CEM I 52.5 R – produced in the same period with the ball mill and VRM – were analysed using the following techniques:

- X-ray diffraction analysis (XRD): powder diffraction is a widely used analytical tool for cement-based materials. It helps to determine the mineralogical composition of cement, clinker and secondary cementitious materials, as well as allowing for the study of cement and hydraulic binders hydration. The usual Bogue calculation presents severe limitations. Firstly, it cannot be used for cement. In addition, when used for clinker, it assumes that equilibrium conditions are reached during clinker formation in the kiln and does not take into account the effect of minor elements in the clinkerisation process.[1, 2]
- Thermogravimetric analysis (TGA): TGA is a very useful technique for the analysis of dry and hydrated cements.[3] 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 and hydrated phases.
- Electron scanning microscopy (ESEM-FEG): cement powder morphology was observed by an environmental scanning electron microscope equipped with a field emission gun.
- Laser diffraction: this is a well-known analytical technique that allows for the measurement of the particle size distribution of cements.

Table 2. **XRD and TGA results**

Sample	Grinding system	XRD		TGA		
		Nat. gypsum ($CaSO_4 \cdot 2H_2O$)	Hemi-hydrate calcium sulfate ($CaSO_4 \cdot 0.5H_2O$)	Weight decrease 100 – 200°C	Weight decrease 200 – 400°C	Calculated weight decrease according to XRD
CEM I	Ball mill	5.1%	1.2%	1.15%	0.05%	1.14%
CEM I	VRM	6.7%	–	1.38%	0.22%	1.40%

Table 3. Laser particle size distribution

Sample	Grinding system	Particle diameter 10% passing material (d10 – µm)	Particle diameter 50% passing material (d50 – µm)	Particle diameter 90% passing material (d90 – µm)
CEM I	Ball mill	10.2	15.6	55.4
CEM I	VRM	10.7	15.7	56.1

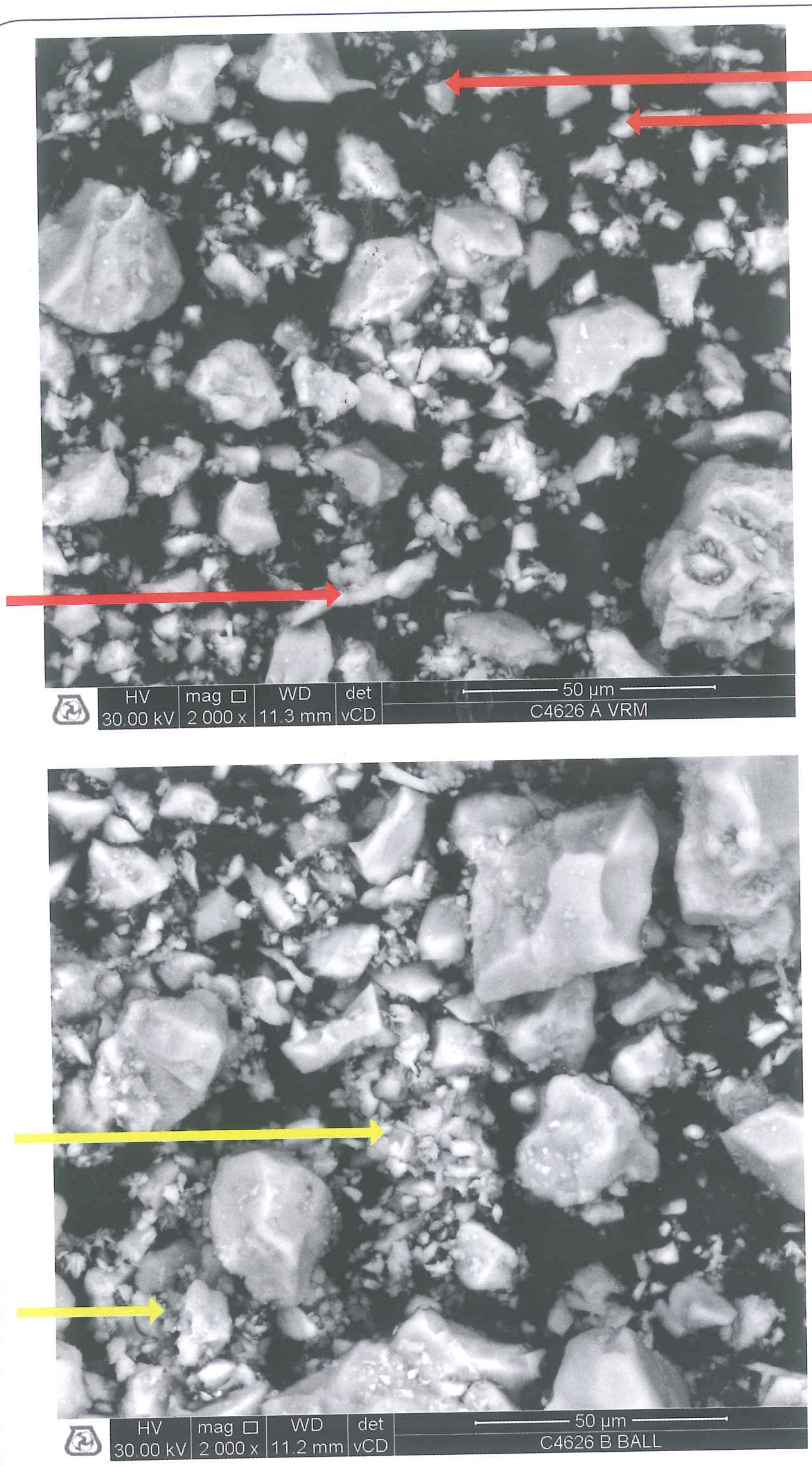

Figure 1. Above: VRM cement particle morphology; below: ball mill cement particle morphology.

Results

The main results of the XRD and TGA analysis are provided in Table 2. The amounts of the main mineralogical phases of both cements (not shown in the table) are similar. This was expected as the samples were produced using the same clinker. On the other hand, the calcium sulfate balance is different. In the VRM sample, only natural gypsum (calcium sulfate di-hydrated) is present, while in the ball mill sample, XRD analysis revealed the presence of a blend of natural gypsum and hemi-hydrate calcium sulfate.

Further information can be obtained from the TGA results: the weight decrease in the range of 100 – 200°C is consistent with the sulfate balance obtained by the XRD analysis. Additionally, and more interestingly, the decrease in the 200 – 400°C range is remarkably higher in the VRM.

The particle size distribution of the cements can be considered similar, as evidenced by the main parameters obtained via laser analysis (Table 3).

Electron scanning microscopy details the morphology and shape of cement particles ground with different milling systems (Figure 1). In cement ground in the VRM, some 'flat' particles can be seen (shown by the red arrows), along with a lower tendency for the agglomeration of small particles. In VRM cements, particles appear to be spread over the surface with a higher number of lone, fine particles. In ball mill cements, there are less lone, small particles and more cluster formations. Clusters of agglomerated particles are indicated by the yellow arrows.

Comments and discussion

Depending on the temperature conditions (more precisely – depending on temperature/humidity), several modifications take place in the cement during grinding. First of all, natural gypsum (chemically di-hydrate calcium sulfate) added as a set regulator is partially dehydrated to hemi-hydrate calcium sulfate, according to the following reaction:

$$CaSO_4 \cdot 2H_2O = CaSO_4 \cdot 0.5H_2O + 1.5H_2O$$

By increasing the grinding temperature and reducing the moisture content in the gas stream through the mill, the extent of gypsum dehydration (and therefore the conversion of di-hydrate to hemi-hydrate) becomes more evident.

The hydration of cement (with particular reference to plastic phase behaviour and strength development) is strongly affected by the balance between gypsum and hemi-hydrate. Different forms of calcium sulfate have different dissolution kinetics: the sulfate supply during clinker hydration is modified when gypsum is converted to hemi-hydrate and this can potentially affect compressive strength development, as described elsewhere.[4, 5, 6]

In addition, excess water during grinding can react with cement, promoting a partial pre-hydration. Typical signals of pre-hydration can be found in TGA analysis. Water bound in C-S-H (calcium silicates hydrates) and in other hydrated phases (ettringite, calcium aluminates hydrates) is usually released in the temperature range 200 – 400˚C. Cement ground in the VRM shows no conversion of di-hydrate to hemi-hydrate and a remarkably higher water content in the aforementioned range can be noticed.

Both of these observations are consistent with a grinding temperature that is too low and/or a moisture content that is too high in the gas flow through the kiln. This situation, quite typical with a VRM, is usually related to water commonly added to the grinding bed. If the amount of water is too high, it cannot be completely evaporated and it remains as pre-hydration water, despite the positive effect on vibration reduction.

On the basis of the XRD and TGA results it can be concluded that lower compressive strengths obtained in CEM I 52.5 R produced via the VRM are related to different gypsum dehydration and to pre-hydration of C_3S, as a result of too much water being sprayed on the grinding table. This leads to the following:

- Low temperature of cements in the VRM, and consequently insufficient gypsum dehydration. Optimum strengths development is strictly related to the correct supply of sulfate during C_3A and C_3S hydration. Different balances of gypsum/hemi-hydrate have different sulfate supply rates, thus influencing strengths.
- Presence of water in the finished cement that promotes partial pre-hydration (as can be seen in the TGA analysis). Although the pre-hydration level is not extremely high in the VRM cement, it is remarkably higher than in the cement produced in the ball mill.

Conclusion

Reducing the amount of water sprayed on the grinding table would be beneficial for both pre-hydration and gypsum dehydration. On the other hand, this would reduce the mill output and the fineness, as the grinding bed vibrations would be less controlled.

Although an increase in gas flow temperature would increase the grinding temperature (benefitting cement quality), the cost of gas heating would be detrimental.

The easiest way to improve the quality of CEM I 52.5 R produced in a VRM is related to the use of a suitable cement additive: this allows for the stabilisation of vibrations and a reduction in the amount of water sprayed. Details of the use of cement additives in VRMs (with a particular focus on dosing points and the results that can be obtained) have already been outlined on several occasions, such as in the article 'Vertical Roller Mill for Verifiable Success' featured in *World Cement*'s December 2011 issue.[7] The additives from the MA.G.A./VM series, coupled with the innovative introduction system developed on the field by Mapei technicians, have been proven to overcome these particular issues.

References

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