CEMENT ADDITIVES

POWERFUL GRINDING AIDS

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Practical experiences with all major cement producers around the world show that stronger grinding additives enhance cement particle dispersion. Besides higher production rates, this also results in more favourable particle size distribution (PSD) which physically accelerates strength development and allows for higher clinker replacements. Consequently, stronger grinding additives are particularly suitable for blended cements.

A three per cent increase of the production rate could mean a reduction of specific energy consumption of around 1.2kWh/t and thus save a 1Mta plant €0.07m in energy costs. If the market environment allows, the resulting 30,000tpa increased sales volume could result in an extra profit of €0.3m per year. Alternatively, this grinding potential could be used to target a higher fineness at the same production rate. The resulting higher strength could be used to reduce the clinker factor by two per cent, adding €0.4m of profit. Additional potential could be taken from maximising production at times with lower electric energy cost or shifting capacities to more efficient mill systems while reducing or stopping the usage of inefficient mills.

Standard vs solution provider
Standard grinding additives are based on existing raw materials from mass production. The cost of purchase is compensated by energy cost savings of approximately €0.2/t. Every €0.01/t less treatment cost leads to €10,000 in annual savings for a 1Mta plant. Hence the target is to find the cheapest possible products leading to the typical 10 per cent production increase.

Stronger technologies are based on customised raw materials that need special production. Their higher cost will be compensated by the additional benefits they deliver, eg raw material savings, reduced CO₂ emissions, increased cement sales or minimised claim costs. In this case, the target is to find a technical solution under economic conditions. Consequently, a stronger grinding aid will be a solution provider.

Three-fold approach
To gather comprehensive knowledge for developing high-performance grinding aids, Sika has followed a three-fold approach: the basis has been the evaluation of the physical and chemical background of forces between cement particles. Then, extensive screening with all types of compounds has been carried out at its central cement laboratory, using its own batch grinding equipment. Finally, molecular modelling, in cooperation with the University of Akron and the Institute for Building Materials of the ETH Zürich (Swiss Federal Institute of Technology) was performed to provide insights into the atomistic interactions. More detailed information has been published by Weibel and Mishra.²

Physical and chemical background
Critical to the understanding of the working mechanisms of grinding additives are the first and second laws of thermodynamics: ‘Everything tends towards a state with the lowest possible energy and the greatest possible disorder.’ These general principles of nature are also valid for all aspects of grinding. Coated mill internals represent the lowest energy level for grinding without chemical additives. The presence of a grinding aid leads to a different minimum energy state which leads to blank mill internals without coating and hence higher mill efficiency.

From a scientific perspective, a cleavage with significant charge separation is only possible in the complete absence of water and even then would be very unlikely. Surface atoms of freshly-cleaved polar surfaces reposition themselves in accordance with minimum energy and optimised charge equilibration very quickly. Consequently, surface charges – as frequently mentioned – cannot be the reason for particle agglomeration. Atoms, molecules and ions always interact with one another. Within homogeneous solids and liquids, the internal forces cancel each other out. The bulk energy is zero. At the surface, there is a resulting force directed inwards.

In liquids this force is called surface tension. It has the same value and dimension as the surface energy. The
most important are the calculations of the agglomeration energy. This energy is released when particle surfaces come together to achieve the lowest energy level. Alternatively expressed, it is the energy which is required to separate agglomerated particles.

Figure 2 shows the values for dry C₃S – the dominant part of clinker composition – in comparison with hydroxylated C₃S surfaces (HC) without and with chemical compounds. Already one monolayer of the various grinding additives significantly reduces the agglomeration energy to approximately 25-50 per cent compared to hydroxylated C₃S surfaces. The agglomeration energy correlates inversely with the grinding performance of the laboratory screenings. Consequently, lower agglomeration energy leads to a better particle separation and hence increases mill output.

**Agglomeration energy**

C₃S > HC > HC-glycerine > HC-TEA > HC-TIPA > HC-MDIPA

**Grinding performance**

Clinker < HC < HC-glycerine < HC-TEA < HC-TIPA < HC-MDIPA

Not all clinker phases behave the same. In the case of tricalcium aluminate (C₃A, Figure 3), the agglomeration energy without grinding additives is approximately twice that of C₃S. This confirms that C₃S should be easier to grind, as it is assumed in Engelsen (2008). Also the performance rankings of individual chemical compounds are quite different compared to C₃S (red arrows).

Customised multi-compound grinding aids (blends) ensure that the agglomeration energy of all clinker phases is significantly reduced. Consequently, these blends can achieve a stronger grinding performance compared to pure chemical compounds.

**Particle separation**

Figure 4 shows the computed distribution of glycerine molecules on 50 per cent-covered clinker surfaces. As a result, the particles are separated by one complete layer (100 per cent coverage) and can approach each other to a minimum distance of typically about 4Å. The necessary quantity of a chemical...
The blank production rate of CEM I 32.5 R (3200cm²/g according Blaine) was rated at 108tph. Dosing 300g/t TEA based grinding aid already achieved a good profit to the cement plant. The technical solution of a PCE-powered grinding aid offers an extra €0.8m annual profit to the cement plant.

Further improvement can only be achieved by spatial means. Crushed clinker particles are jagged. To separate them most efficiently larger polymers like PCEs (polycarboxylate ethers) are necessary. Figure 5 displays the calculated distance which is double compared with glycerine.

PCEs improve grinding in two ways. On the one hand, they reduce the agglomeration energy like traditional compounds. On the other hand, they cause a steric separation of the clinker particles due to size and configuration.

We can conclude that the combination of the physical and chemical background, empirical testing and molecular modelling provides comprehensive understanding of the working mechanisms of grinding aids. This allows the development of further improved grinding aids and customised cement additives.

**Case study: Portland cement**

To verify these conclusions, Sika executed and analysed plant trials which compare traditional grinding additives and blends with PCE. The grinding system at this 1.2Mta plant (serving a sold-out market) was a traditional ball mill in a closed-circuit system with a third-generation separator. The blank production rate of CEM I 32.5 R (3200cm²/g according Blaine) was rated at 108tph. Dosing 300g/t TEA based grinding aid already achieved a good value of a 13 per cent higher production rate. The same amount of a TEA/PCE blend performed significantly better and reached a 20 per cent production increase compared to the blank benchmark (Figure 6). This confirms the findings of the molecular modelling.

The technical improvement of a six per cent higher production compared to a traditional TEA leads to two advantages: 2.3kWh/t reduced energy consumption and 70,000t higher volume. The economic value is calculated by €0.14/t less energy cost minus €0.06/t additional treatment cost for the higher value grinding aid and accumulates to an annual saving of €0.1m. Additional sales generate a further contribution of €0.7m. In total, the technical solution of a PCE-powered grinding aid offers an extra €0.8m annual profit to the cement plant.

**Summary**

Extensive theoretical analyses combined with vast laboratory trials and molecular modelling have made it possible to improve the understanding of the working mechanisms of grinding aids during the cement grinding process. Energy on the clinker surface is larger than inside the particle. As a consequence, powder particles agglomerate to reach a lower energy level. The energy which is released is called agglomeration energy. The strong agglomeration energy of dry clinker is usually reduced by the moisture existing in the grinding atmosphere. The remaining agglomeration energy is still so high that it negatively affects the grinding and separating process (coating, agglomeration).

Traditional grinding aids reduce agglomeration energy to a level where most particles are dispersed and coating is reduced to a large extent. The performance of Sika’s new grinding aid technology is boosted by specific ‘sterically acting molecules which extend the distance between the particles due to large PCE molecules. Molecular modelling confirms these results.

Stronger grinding aids offer opportunities to improve cement plant profitability, especially when producing blended cements.

**References**