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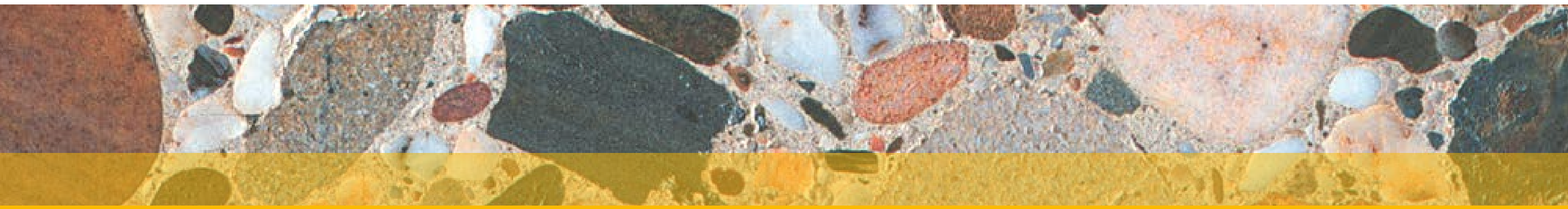
european cement research academy



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NEWSLETTER

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Upcoming ECRA seminars:

- Cement Grinding Technology
  6–7 November 2018
- Analysis and Evaluation of Clinker and Cement Properties
  27–28 November 2018

Further developments in existing grinding technology

The operation of efficient grinding circuits requires knowledge of the principles and ideal operation parameters

During the past decades several new developments in grinding technology have occurred, for example vertical mills for the finish grinding of cement and Horomills for finish grinding. High pressure grinding rolls emerged mainly in combination with ball mills, but also in finish mode for the grinding of raw material and cement. Besides the new equipment, further developed existing machinery was also introduced onto the market with the aim of improving energy efficiency in the grinding process.

Grinding still consumes the biggest amount of electrical energy in the cement production process. New cement types with high fineness levels require advanced mills as well as a highly efficient separation process. Besides the machinery, the operation of the circuit also plays an important role. The influence of process parameters and even auxiliary equipment becomes more important if the system is running at full capacity.

The most widely used operating mill type is still the ball mill, even if this machine has a history of more than 100 years. Its easy operation and maintenance as well as its proven high quality cement properties are the reasons why the ball mill is still used despite its higher energy demand. Newly installed grinding circuits for cement in Europe are often still ball mill systems. The ball mill may seem old fashioned, but even this tried and tested mill has not stopped evolving. Further developed machine parts, improved wear parts and the integration of modern separator systems have raised the efficiency level of ball mill systems.

VRM and HPGR

In the past decades further grinding mills emerged in the cement industry. The vertical mill, which is based on a grinding principle already used in the Roman era, was originally used in coal grinding, but then advanced into raw material and cement grinding. Nowadays, the vertical mill has the biggest market share in newly installed grinding circuits worldwide.

The high pressure grinding roll, which was introduced in the 1980s, started out as only a pre-grinder in combination with the ball mill. In the past 10 years, more and more installations have been commissioned with HPGRs in finish mode, i.e. without the ball mill. Such developments were enabled through further optimised circuits and separators with degglomeration functions. Although most of the newly installed high pressure grinding rolls are still used in combination with balls mills, for example in upgrade projects of existing systems, more and more new installations comprise only one grinding machine.

In the 1990s one more developed grinding machine appeared on the cement horizon. The Horomill uses the concept of high pressure comminution like the HPGR at a lower level and uses the centrifugal forces principle for the material transport like the vertical mill. With several dozen installations the Horomill has proven its ability to grind different cement types, raw material and granulated blast furnace slag in an efficient way. A comparison of the energy requirements are shown in **Fig. 1**.

Separators are key

The separator is one of the key components of the grinding circuit besides the mill. Even the distribution of the material and air flow is a very critical issue for the sharp separation of fine and coarse material. With high proportions of unclassified fractions – also known as bypass – it is impossible to operate any grinding circuit efficiently. Such inefficient operation can be detected only by measurements and auditing which have to be performed regularly. Further developments in the design of cage and rotor blades enable new conditions between centrifugal forces and air drag forces.

All mills have in common that the understanding of the physical principles of the equipment, smart integration into the process, excellent maintenance, and the smart setting of process parameters enable operation at the highest efficiency with excellent product quality.

Product quality

In particular the European cement market demands very high fineness, which requires skilled operators if using VRMs, Horomills or HPGRs.

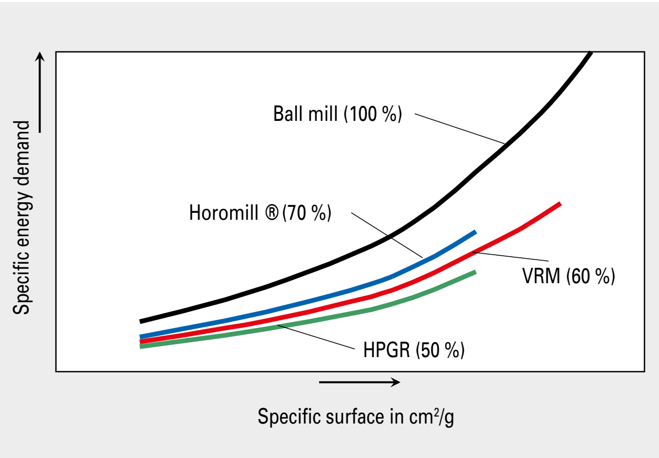

Figure 1: Energy comparison of grinding systems

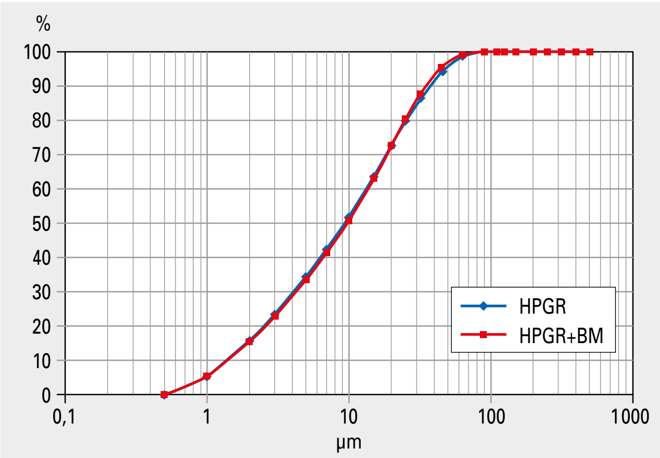

Figure 2: Comparison of PSD of CEM V cement ground in a HPGR and HPGR plus ball mill

Vibrations can occur if the system doesn't run at the ideal set point. Such disturbances can create high material recirculation in the circuit which narrows the created particle size distribution. Since for example the water demand depends on the particle size distribution, it has to be ensured that trouble free operation is ongoing. In **Fig. 2**, particle size distributions of a HPGR finish grinding product and a ball mill + HPGR product are shown. This cement type contains clinker, limestone and trass and is ground to a fineness level of more than 5000 Blaine. These PSD analyses prove that it is possible to grind even very fine composite cement types in a highly efficient way if the system runs smoothly. Comparable water demand could be measured for both cements as well as similar strength developments. Only the setting times differed from each other, which could be levelled with sulphate adjustment and different system temperatures.

Future Grinding Technologies

In 2015 ECRA began a research project on Future Grinding Technologies in order to understand and take on the challenges of grinding in today's and tomorrow's industry. The project was launched with a roundtable event in Duesseldorf, attended by over 50 experts from the cement industry, equipment suppliers, universities and other industries such as the mining and chemical industries to discuss the future of grinding.

The evaluation of the round table event was published on the ECRA website in a report which highlighted all discussion points and studies for the project. One outcome of the report was the requirement of a grinding model to better understand the process of comminution in the plant. As a first step a literature study was done to validate different modelling concepts for fine comminution and also to analyse the possible challenges of the model development. In the meantime the first model steps have been completed and are currently undergoing fine adjustment. The next step is the evaluation of the model parameters and the alignment with experimental data. The model will basically be used for ball mill comminution but it will also be possible to implement it into other grinding machinery.

Can Ono's method for the analysis of clinker be transferred to XRD?

XRD could be integrated into automated quality control, unlike microscopical methods

Process control is of high importance in cement manufacturing. Among the different techniques and procedures, Ono's method is known to provide good process information. However, the method requires an experienced microscopist and cannot be fully automated. Nevertheless, some parts of the Ono method can be based on automated measuring schemes such as XRD and can help to better integrate this method into the quality control system of a cement plant.

Ono's method was developed to evaluate the quality of Portland cement clinker as well as the conditions of the production process. Four burning conditions (heating rate, time at high temperature, maximum temperature and cooling rate) are evaluated with the help of four parameters analysed microscopically (alite size, belite size, alite birefringence, belite colour). The relationship between the burning conditions and the microscopical parameters were established empirically by Ono and other researchers.

Research programme

The four parameters analysed in a clinker are connected with crystallographic properties of the clinker phases. In a research programme including laboratory clinkers as well as technical clinkers sampled during kiln trials in which the burning conditions were varied deliberately, correlations between Ono's parameters and results from XRD with Rietveld refinement were looked for. Such correlations were found for two burning conditions, heating rate and cooling rate.

Heating rate and alite size

In Ono's method, heating rate is evaluated with alite size measurements. Higher heating rates are assumed to lead to smaller alite crystals. It was found that Rietveld refinements of XRD measurements performed on relatively coarsely ground clinker result in preferred orientations (PO) of alite that roughly correlate with the alite size measured microscopically (**Fig. 1**). As PO is a textural parameter, this correlation is basically caused by a preparation artefact. The c-axis of larger alite crystals tend to face away from the surface of the pressed pellet due to the pressure applied during preparation (schematically shown in **Fig. 2**). A perfectly randomised orientation of crystals would lead to a PO of 1. The stronger the preferred orientation, the lower the PO value.

The data in **Fig. 1** show that the alite size can roughly be estimated from the PO value. However, additional measurements showed that the effect vanishes with increasing fineness of the clinker sample.

Cooling rate and belite colour

In Ono's method, the cooling rate is evaluated with the belite colour. High cooling rates are associated with clear and colourless belite crystals. With decreasing cooling rates belite crystals become more and more coloured (light yellow – yellow – amber).

The analysis of belite with XRD and Rietveld refinement showed complex interdependencies between the cooling rate, the belite modification (α, α', β), and the amount and composition of the ground mass (C_3A, C_4AF) of the clinker. There seem to be correlations, but the available data do not allow straightforward interpretations at present.

Cooling rate, C_3A and C_4AF

The cooling rate can also be evaluated on the basis of the crystal sizes of the ground mass phases, i.e. C_3A and C_4AF. Both clinker phases are formed from the clinker melt upon cooling. Lower cooling rates lead to the for-

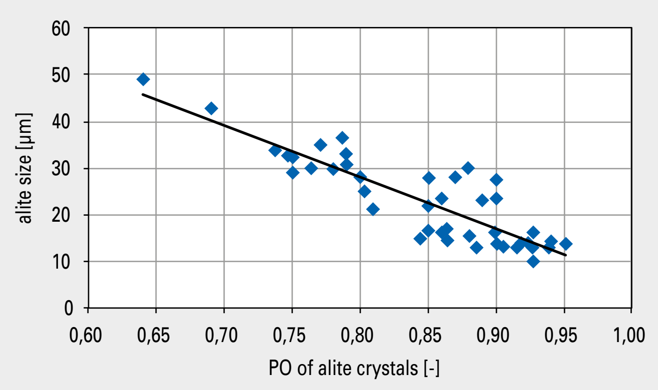

Figure 1: Correlation between preferred orientation (PO) determined with Rietveld refinement and alite size measured under the microscope

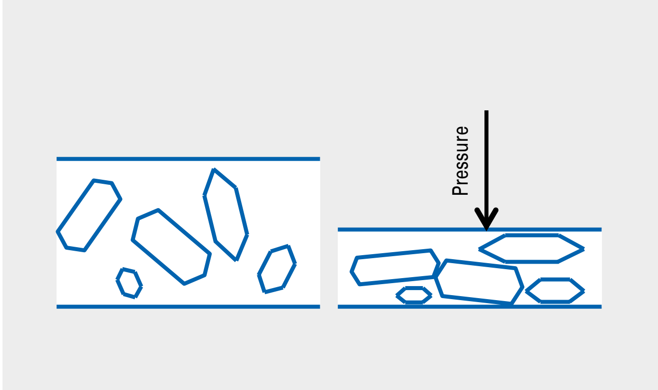

Figure 2: Schematic representation of alite crystal rotation upon application of pressure during pressed tablet preparation

mation of larger crystals, whereas higher cooling rates arrest further crystal growth resulting in smaller crystals.

Starting from this observation, crystallographic parameters of C_3A and C_4AF were evaluated in detail. No good correlations between these parameters and the crystal sizes observed microscopically were observed in data gathered from clinker samples in their original state. The reflexes caused by C_3A and C_4AF in the XRD pattern are often strongly overlapping with reflexes of the main clinker phases alite and belite.

The clinker phases C_3A and C_4AF can be strongly enriched for further analysis by a selective dissolution step in methanol and salicylic acid (M/S digestion). Alite, belite and free lime are dissolved with this procedure. Correspondingly, in the XRD patterns of the M/S-residues the reflexes of C_3A and C_4AF can be evaluated in greater detail.

It could be shown that the crystallite sizes (CS) of the dominating i.e. more frequent, ground mass phase – measured by XRD – increase with increasing crystal size as observed under the microscope.

The CS is a measure for the size of coherently scattering domains in a crystal. It can be limited by lattice distortion (defects, incorporation of foreign ions) and by crystal boundaries, i.e. by the actual crystal size. Large CSs are visible in the XRD pattern as sharp and high reflexes, whereas small CSs cause wider, smaller reflexes (**Fig. 3**).

Conclusions

Onos method shows correlations between

- alite size and PO of alite crystals
- cooling rate and CS of the dominating ground mass phase (C_3A or C_4AF) in the M/S residue.

The alite size can therefore be monitored with a method already available and automated in many cement plants. The preparation procedure must produce samples with sufficient coarseness. To avoid influences of the special preparation on other XRD results, the PO should be evaluated in a separate measurement with a dedicated preparation program.

The CS of C_3A/C_4AF and correspondingly the cooling rate cannot be evaluated based on automatised XRD measurements because the correlations are based on the evaluation of the M/S-residue of clinker samples. However, most cement plants have laboratories that are able to perform the necessary preparation step (M/S digestion) as well as XRD measurements.

The results show that important process conditions traditionally evaluated with microscopical methods can also be monitored with XRD. It should be noted that the variability of the respective parameters seem to differ strongly from plant to plant. Correspondingly, the procedures described here can be more valuable for some plants than for others.

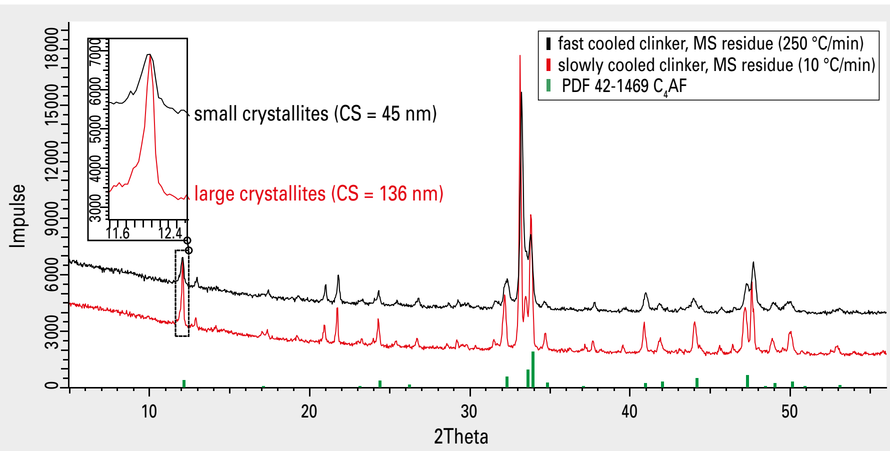

Figure 3: X-ray diffraction patterns of M/S-residue of two clinker samples cooled with different cooling rates (fast cooled: 250 °C/min; slowly cooled: 10 °C/min); Detail indicates the differences in a C_4AF reflex at 12.2° 2Theta

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