european cement research academy

Newsletter 2/2005

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Clinker microscopy – A powerful tool for process optimisation

Influences of alternative fuel combustion on clinker properties can be explained properly

Clinker microscopy is a very useful tool to see changes in the product performance due to changes in the clinker burning process. Because of the high effort required microscopy cannot be established as a routine method in the quality control systems of a cement plant. However, if any processing parameter is changed, e. g. the fuel mix, effects on the product may be detected by microscopical examination.

A microscopical analysis gives information on the composition, homogeneity and porosity of a clinker. Also the morphology of the different clinker phases can be examined. As a consequence clinker microscopy gives information about the setting and hardening behaviour of the clinker and finally the cement. Microscopy also provides insights into the homogeneity of the raw mix, the fuel mix and the burning and cooling conditions. Moreover, by means of microscopy reducing burning conditions can be detected at a very early stage, i. e. before any deteriorating effects on product properties happen.

In any case optical microscopy reaches its full potential in combination with various other techniques like X-ray diffraction, chemical analysis and scanning electron microscopy. Such an approach might be helpful to solve complex problems, e. g. to estimate effects of major process changes on the clinker quality and the resulting properties of the cement.

Use of secondary fuels

In recent years, the aim of cost cutting and CO_2 reduction has led to several changes in the process of clinker burning. As a rule, the main target of this development is to minimise the need for primary fuels while maintaining the level of clinker performance in cement. In addition, the given geochemical conditions of any cement plant can affect the clinker properties. As a third factor, an effect of plant operational conditions on product properties can be expected. However, in many cases the change of hydraulic clinker characteristics can be seen by microscopical techniques.The following example, describing influences of animal meal as a phosphate bearing fuel on clinker properties and on cement performance, provides a good insight into the potentials of clinker microscopy.

Phosphate-bearing fuels

Due to the current restrictions on using animal meal for feeding cattle, there has been growing experience in handling and utilising animal meal as a secondary fuel. Other phosphate-bearing secondary fuels, like sewage sludge, are about to be available to the cement industry. The clinker burning process is very well suited for an environmentally harmless utilisation of bone meal and animal fats. A secure burnout rate is guaranteed due to gas temperatures of up to 2,000 °C and the high residence time in an oxidising gas atmosphere.

Regardless of these favourable parameters, there are still various underlying conditions that must be taken into account while using animal meal. The variable limiting the quantities of animal meal used in rotary kilns are not the combustion properties of the material. The maximum input is mainly restricted by the input into the clinker. Under practical conditions, phosphate contents of up to 1 % by mass P_2O_5 are known to have no detrimental effect on the clinker properties.

Changes in clinker properties

Phosphate plays an active role for the clinkering reactions of the burning process. Its high mobility leads to an almost even distribution of phoshate over the granules' whole cross sections. Phosphate is mainly incorporated into the silicate phases. By means of scanning electron microscopy combined with EDX-analysis it can be seen, that especially belite can incorporate amounts of phosphate (**fig. 1**).
At high phosphate contents the formation of alite is inhibited and belite is stabilised. Typical microstructural features are belite clusters containing finely dispersed free lime

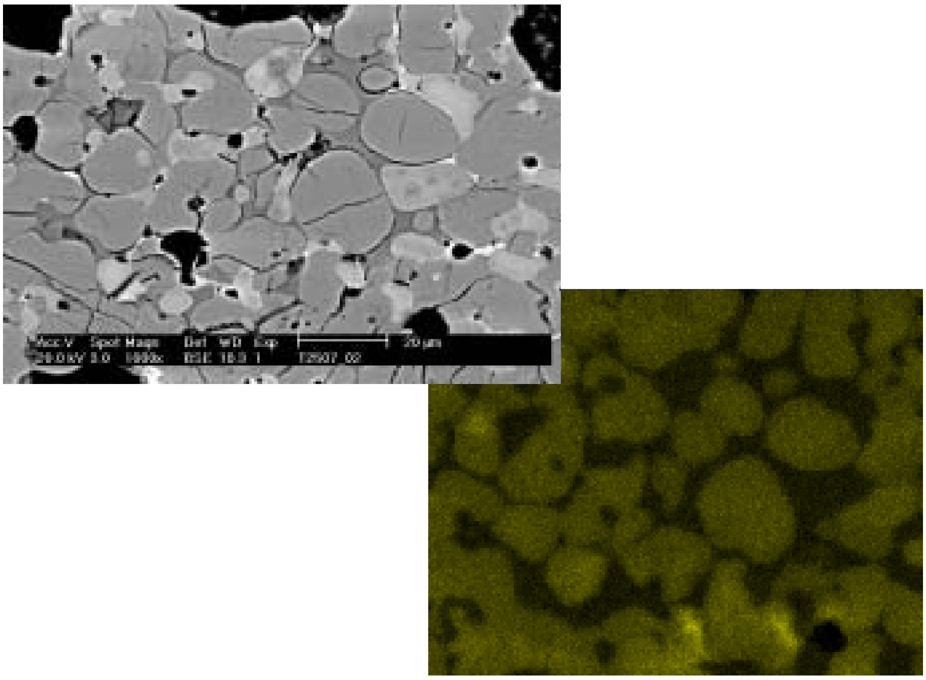

Fig. 1: SEM-micrograph (BSE mode) and phosphorous distribution in a clinker. The phosphate is concentrated in the rounded belite particles.

(**fig. 2**). This appearance differs clearly from free lime clusters caused by large limestone grains in the raw mix. The decrease of alite content can be partially compensated by increasing the clinker's lime saturation factor.

Moreover phosphate lowers the viscosity of the melt. For this reason the mean crystal size of the alite increases (**fig. 3**). Thus, phosphate has a similar effect on the characteristics alite as a high sulfate content of the clinker.

If phosphate is present, also aluminum tends to be incorporated into calcium silicates to a higher degree. As a consequence, phosphate bearing clinkers can contain less C_3A than expected. Besides other analytical techniques such as X-ray diffraction, the decrease of C_3A can also be observed by comparing optical micrographs. To maintain the setting properties of cement, it can be advantageous to increase the alumina ratio of the clinker.

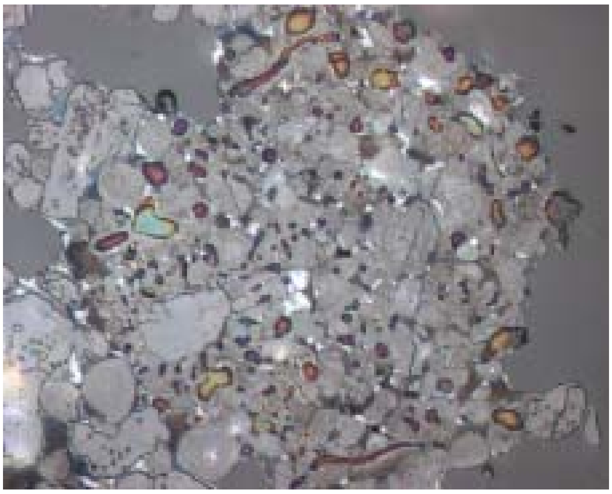

Fig. 2: Micrograph of a belite cluster with finely dispersed free lime in a phosphate bearing clinker

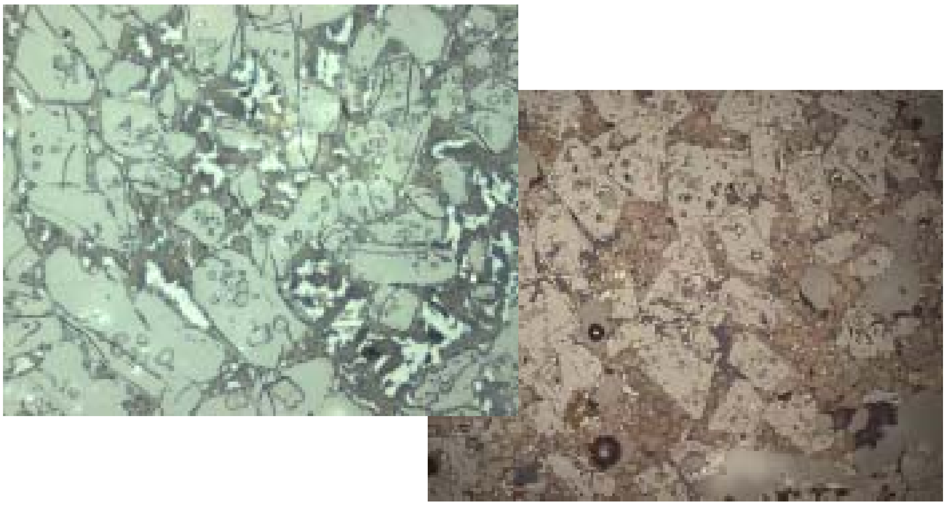

Fig. 3: Comparison of the alite crystal size in a clinker without (left) and with 1.5 % by mass phosphate. Magnification left: 500 x, right: 100 x

Secondary fuels require new burner design and operation

Effects on clinker quality, emissions and chlorine/sulphur cycles have to be considered

Burning conditions in the sintering zone of a cement kiln have a significant impact on the clinker quality. Therefore cement kiln operators have given special attention to burner technology for many years. In the nineteen-eighties multi-channel burners substituted the old burner pipes aiming at a better adjustability of the flame shape. When NO_x emissions became more important during the nineties the so-called low-NO_x-burners (or low-primary-air burners) were developed. Today the increasing utilization of waste fuels again requires a new burner design and an adapted burner operation.

Since the multi- (mostly three) channel burner was developed three decades ago the cement kiln burner technology has been based on the idea that the flame shape can be influenced by the separate adjustability of at least two air channels (swirl air, axial air) and of the injection velocity of the fuel. Multi-channel burners are mostly used for conventional fuels like coal, petcoke, gas or fuel oil. Multi-channel burners allow attainment of a distinct and hot flame and therefore a good clinker quality. This flame type is attained by injecting a larger volume of combustion air into the core flame, meaning that the injected fuel is ignited very quickly and that the combustion of the flame is very intense. This requires a primary air ratio of about 15 to 20 % of the total combustion air. The disadvantage of this flame type is the relatively high NO_x formation.

Low NO_x burners

During the ninetees NO_x emissions became more important and emission limits for NO_x were implemented at European level, for example by the Waste Incineration Directive. As secondary reduction measures are costly the burner sppliers developed new burner types based on a lower primary air ratio of 7 to 13 %. Scientific investigations have been carried out at the International Flame Research Foundation in the "CEMFLAME" project. The project was financed by a consortium of European cement producers and burner suppliers. As a result it turned out that for low NO_x emissions and a stable kiln flame the ignition distance of the flame from the burner tip should be as short as possible. This requires a low primary air ratio, a low fuel injection velocity, a high axial and a medium or low swirl air monumentum. Furthermore a high fuel/air ratio in the core flame should be implemented by positioning the fuel channel in the centre of the burner. The idea is that this leads to an early ignition of the fuel, lower maximum temperatures in the sintering zone, a longer flame and therefore lower NO_x emissions. In some cases a NO_x reduction of up to 30 % has been achieved by these burner types. On the other hand experience shows that under certain conditions clinker quality was affected negatively and burner operation had to be changed again.

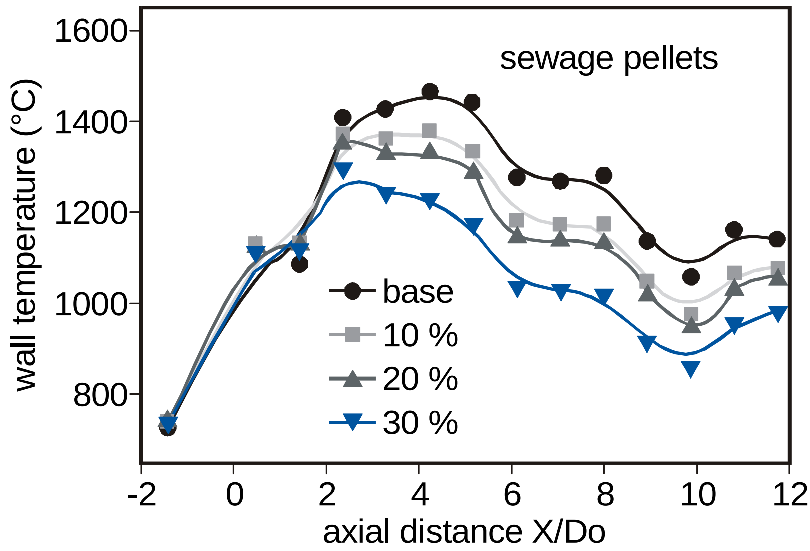

Fig. 1: Wall temperature profile with co-incineration of sewage sludge pellets

Burners for secondary fuels

The development during the last years shows that in many European countries the cement kiln operators have changed or are changing their fuels from conventional fossil fuels to waste fuels. Often, a number of different fuels are used meaning that there is not only a change from one fuel to another but also from one fuel to a multi-fuel mix combustion. In the beginning, trials have been made with separate pipes for the injection of waste fuels. Depending on the fuel this could lead to an insufficient mixing and therefore a stretched temperature profile in the flame. Under certain conditions also a second sintering zone could be the consequence.

Fuel properties of wastes, even if prepared, are mostly different from the properties of traditional fuels like coal dust. Particle size distribution, humidity, volatile or ash content as well as ignition properties can vary significantly. Burner operation and design has to meet the fuel properties. But – on the other hand – flexibility of changing physical fuel properties can also be used as the results of a further CEMFLAME research project show. **Fig. 1** shows the wall temperature profile of a pilot scale cement kiln co-incinerating different rates of sewage sludge pellets. The coarse particles need more time to be heated and to be ignited. This leads to a significantly lower maximum temperature in the sintering zone at high substitution rates. If the sewage sludge is finely ground (**fig. 2**), much higher substitution rates can be attained without negative effect on the temperature profile.

The different fuel properties combined with the demand to burn different fuels at the same time have led to a new burner design and require an adaption of the burning process. Depending on the fuel type it can be necessary to increase the primary air ratio again and to further increase the momentum of axial or swirl air. A higher air ratio in the sintering zone can also be necessary in order to provide a complete combustion as well as to avoid clinker burning under locally reducing conditions.

Under the same burning conditions, the combustion of coarse or humid waste fuels lead to longer flames, lower maximum temperature in the sintering zone as well as higher temperatures in the kiln inlet. This can cause major problems due to sulphur cycles and coating formation in the kiln inlet and the riser duct. New burner systems have various injection systems and allow a higher flexibility concerning fuel properties and adjustability of the flame shape by changing the injection momentum of air and fuel. In some cases NO_x emissions can increase slightly by adapting the flame shape according to multi-fuel combustion. In these cases it can be necessary to use secondary measures like SNCR technology to meet NO_x emission. Summarized, nowadays the selection of a suitable burner type or design for multi-fuel combustion as well as the optimization of the combustion itself have to meet a greater number of criteria than 20 years before.

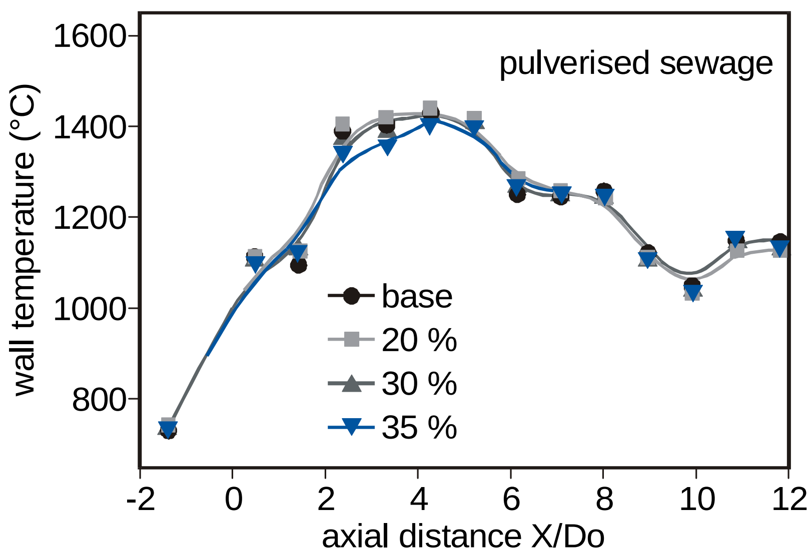

Fig. 2: Wall temperature profile with co-incineration of pulverised sewage sludge