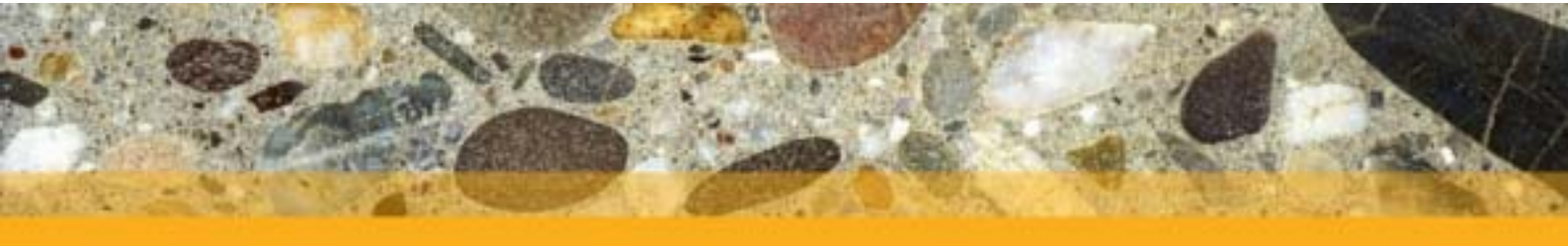




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Newsletter 3/2005

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- Modern Grinding Techniques
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- Pretreatment, Handling, Storage
and Feeding of Waste Fuels
November 9-10, 2005

Experiences with animal meal as secondary fuel in clinker production

Product properties can be maintained, if clinker phosphate content is less than 1 %

Since the ban on feeding animal meal was put into force all over Europe in 2001, considerable amounts of stock-farming waste materials have become available as secondary materials for non-agricultural purposes. More than 3 million tons of animal meal and 1,5 million tons of animal fat are to be disposed of each year in Europe. Out of this, a total of 890,000 t was used as secondary fuel in European cement plants in the year 2001.

The clinker burning process has proven to be a safe and effective way to utilise these waste materials. Along with the use of animal meal, a supplementary entrainment of phosphorous bearing compounds has to be expected. In practice, as long as phosphate contents are less than 1 wt.-% in cement clinker, no detrimental effects on product quality are found. This corresponds to similar experiences in several European countries using other phosphate bearing secondary fuels, e.g. sewage sludge, in clinker production.

Research activities

To support current positive practical experience with cements containing up to 1 wt.-% P_2O_5 , and to extend the knowledge about cements with a phosphate content exceeding 1 wt.-%, a research programme has been conducted by the Research Institute. Because of this, the knowledge on the basic mechanisms of phosphate entrainment has improved.

In a laboratory kiln cement clinkers with phosphate contents between 0 and 8 wt.-% were synthesised and examined. Depending on temperature, the influence of phosphate on the progress of chemical and mineralogical reactions during the clinkering process was observed. Subsequently, the clinkers containing up to 2,0 wt.-% phosphate were used to prepare cements, the product properties of which were investigated. The majority of cement investigations covered classical, standardised test methods. Particular emphasis was placed on testing conditions to be close to the ones during building and construction application. Thus, also the influence of temperature on the hydration and strength develop-

ment of cement, as well as interactions with commercial concrete admixtures, were part of the research programme.

Effects on clinker phase formation

The examinations revealed an active participation of phosphate in the reactions during clinker burning. The stability ranges of clinker phases can be modified. Due to the high mobility of phosphate it can be distributed almost homogeneously within the clinker nodules. At the beginning of the clinkering process, phosphate is bound in the mineralogical phase hydroxylapatite. With increasing temperature apatite becomes instable and releases its phosphate. A reaction with the silicates is initiated and leads to the formation of mixed crystals between dicalcium silicate and tricalcium phosphate (C_2S-C_3P). This solid solution exhibits a complete miscibility with $\beta-C_2S$. If sufficient CaO is available, the phosphorous bearing solid solution can continue to react and form phosphate bearing alite

(C_3S). As phosphate lowers the viscosity of the clinker melt, the growth of alite crystals is fostered.

Increased phosphate contents lead to the formation of C_2S-C_3P with the crystal structure of $\alpha'-C_2S$ and $\alpha-C_2S$ (fig. 1). These compounds can incorporate phosphate in excess of the stoichiometrical values. As a consequence, the free lime content increases slightly with increasing phosphate contents of > 2 wt.-%, but decreases again, if P_2O_5 contents exceed 5 wt.-%, due to the formation of α' - and α -modifications of belite (fig. 2).

With rising uptake of phosphate, the alite content is reduced. Likewise, the dicalcium silicates can incorporate more aluminum. This leads to a decreased content of matrix phases, mainly of C_3A . The aluminate and ferrite phases do not incorporate phosphate.

Effects on product properties

The influences of increasing phosphate entrainment into clinker on the product properties were tested

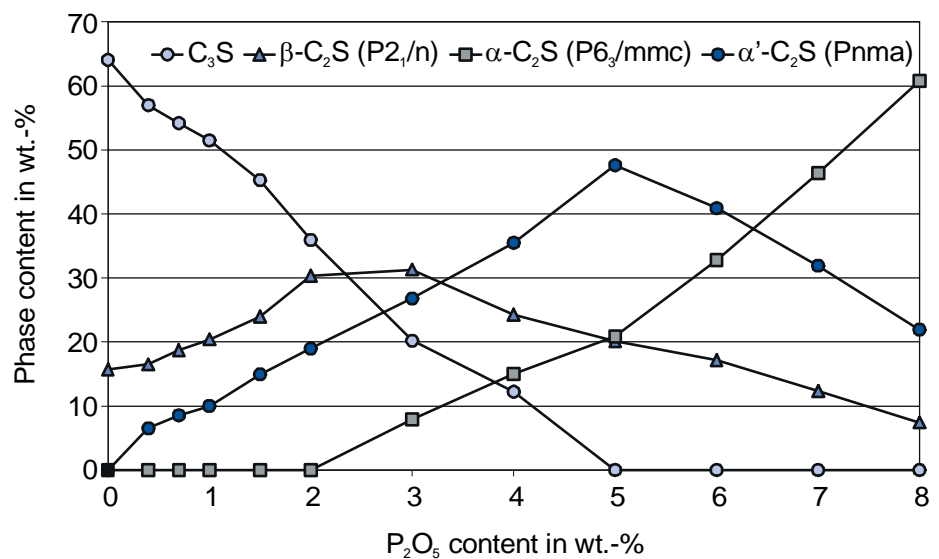


Fig. 1: Contents of silicate phases vs. phosphate content in laboratory clinkers

on laboratory cements made of clinker with up to 2,0 wt.-% P_2O_5 . Up to 1,0 wt.-% P_2O_5 in the clinker there is only a slight loss of early strength due to the decreased alite content, which can be compensated by increasing the clinker's lime saturation factor. Stronger effects on the early cement strength can only be observed at higher phosphate contents and can still be counteracted to a certain degree by an excess calcium supply in the raw meal. The decay of alite and the subsequent early strength loss can be compensated to a certain degree, if the clinker's lime saturation factor is increased. The 28-d-strength is slightly increased for clinkers with up to 1,0 wt.-% P_2O_5 and will be reduced with further increasing phosphate content, until at roughly 2,0 wt.-% the strength level of the phosphate-free reference cement is attained again.

Due to the decreasing C_3A content, the demand of sulfate for an optimised cement setting behaviour is reduced. By adjusting the content and composition of sulfate agents in the cement, the setting behaviour

can be controlled in the same way as for cements with low phosphate contents.

As a further result of the examinations it could be shown that the entrainment of phosphate into the clinker does not strongly affect the primary ettringite formation. A supplementary effect on the activity of superplasticising admixtures could

not be detected. The generally known retarding effect of superplasticisers on CSH formation was not significantly changed by high phosphate contents in the clinker. At 20 °C and at 8 °C no impact of phosphate on the hydration behaviour of cements with superplasticisers based on polycarboxylate or sulphonate could be observed.

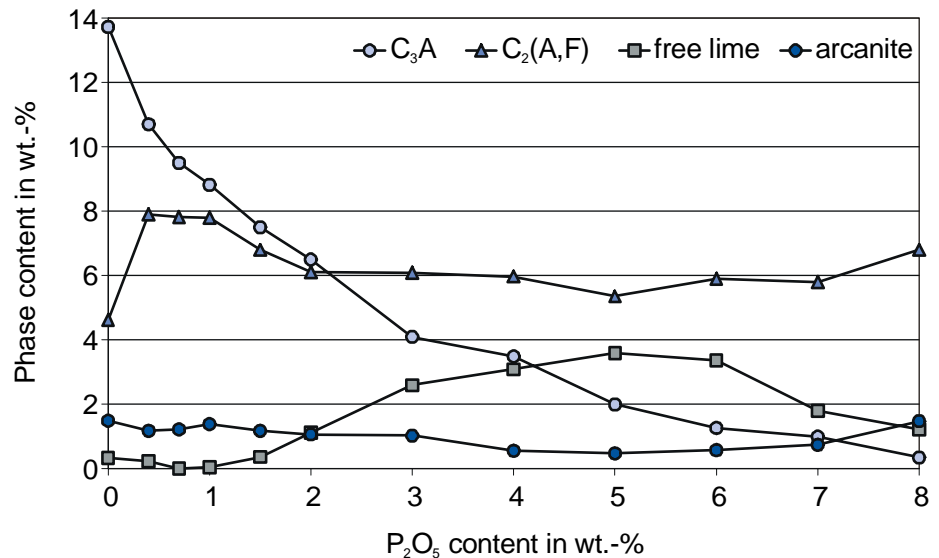


Fig. 2: Contents of non-silicate phases vs. phosphate content in laboratory clinkers

Continuous Emission Monitoring

New requirements for quality assurance of automated measuring systems

The continuous monitoring of the emissions of cement kilns is a matter of growing concern for the European Cement Industry. Especially when wastes are used as fuels, the plant operators have to meet the very stringent requirements of the European Directive 2000/76/EC on the incineration of waste. Furthermore it has to be pointed out that in September 2004 the new European CEN Standard EN 14181 on quality assurance for automated measuring systems has been published. This standard contains various important items that have to be taken into consideration by monitoring bodies as well as plant operators in the future.

The EC waste incineration directive had to be implemented by the EU member states by December 28, 2002. For existing plants, a transitional period until December 28, 2005 at the latest is granted. The directive contains ambitious requirements particularly referring to the performance of automated measuring systems.

According to the EU directive the components dust, SO_2 , NO_x , TOC, CO, HCl and HF have to be measured continuously in the exhaust gas of so-called "co-incineration plants" like e. g. cement kilns using secondary fuels.

In addition to these stack gas emissions the oxygen concentration, pressure, temperature and water vapour content of the exhaust gas have to be continuously recorded. These parameters are needed to standardise the measured concentrations at a temperature of 273 K, a pressure of 101,3 kPa and 10 % oxygen (dry gas).

Further to these continuous measurements, periodic measurements of heavy metals, dioxins and furans, and - in some cases - polycyclic hydrocarbons or other pollutants have to be carried out regularly.

Continuous measuring techniques

Relevant continuous measuring principles are the IR and the UV photometry as well as the FTIR spectrometry and the flame ionisation detection.

According to article 10 of the EU directive, the installation and functioning of the automated monitoring equipment has to be controlled by an annual surveillance test (AST). In addition to this, a calibration has to be accomplished by means of parallel measurements with standard reference methods (SRM) at least every three years. Based

upon the results of these parallel measurements, the analytical function of the complete monitoring equipment has to be calculated by a so-called regression analysis. This mathematical correlation is fed finally into the emission data acquisition unit.

New European standard

At least for cement kilns using wastes as fuels the AST as well as the periodic calibration have to be carried out by the beginning of 2006 according to the new European standard EN 14181. This standard contains various new requirements which have an impact on the independent monitoring bodies (i. e. external laboratories) as well as on the plant operators.

To begin with, the annual AST will no longer be a more or less standardised functional test of the measuring device. In fact it will cover also a set of at least five individual measurements with SRM in the future. Moreover, these measurements shall be uniformly spread over the whole measuring day. This requirement leads to an excessive increase of labour time needed to carry out the annual AST.

Based upon the new standard, the periodic calibration will also be more time consuming than before. In principle, the calibration of an automated measuring system (AMS) covers the following items:



Fig. 1: Continuous emission monitoring is a matter of growing concern

- Installation of the AMS
- Calibration of the AMS by means of parallel measurements with SRM
- Determination of the variability of the AMS and check of compliance with the required uncertainty

Especially the requirements on the parallel measurements with SRM have been tightened by the new standard. It will, e. g., be necessary to spread the parallel measurements over a minimum period of three days. Furthermore, at least 15 valid measurements will be needed (which means that the actual number of samples which have to be taken might be even higher). After all, this requirement will lead to a much higher labour time for the external monitoring body than

before and consequently also to higher costs.

Additional tasks for the plant operator

Besides the new requirements mentioned above, the plant operator will have to observe procedures to permanently maintain the quality of the AMS. He will be obliged to check the drift and the precision of the measuring devices regularly in the future. To be able to meet these requirements he will have to get accustomed to the application of control cards to continuously compare his values from the current process with the target value.

To sum up the situation, it can be said that it is of crucial importance for the plant operator to know his duties arising from the new standard. Furthermore it must be pointed out that the plant operator and the external laboratories should work together as closely as possible in order to avoid any unnecessary additional work. By doing so it should be possible to carry out the required control procedures without losing cost control.

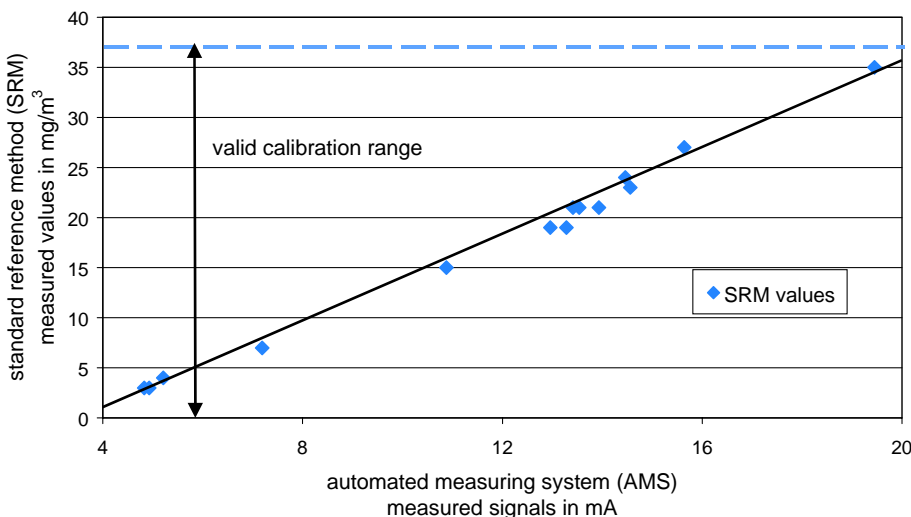


Fig. 2: Calibration function according to EN 14181

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