



ecra

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NEWSLETTER

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Next ECRA events to come:

- Hydration of Blended Cements
5 October 2010
- Influence of Alternative Fuels and Raw Materials
on the Properties of Clinker and Cement
9–10 November 2010

The potential of calcined clays as main constituent in cement

Calcined clays exhibit pozzolanic activity which depends on the clay's constitution and the tempering process

The use of blended cements has a long and successful tradition in many countries around the world. Today, in Europe as an example the dominant main constituents besides clinker are limestone, ground granulated blast furnace slag (GGBFS), fly ashes and natural pozzolanas (**Fig. 1 and Fig. 2**). Cements produced from these materials are well tried and proven, like other cements given e.g in EN 197-1, which contain main constituents of lesser availability. This also applies to calcined clays, which might have a growing potential to be used in the cement industry.

The European cement standard EN 197-1 also allows the manufacturing of cements with different types of pozzolanic materials. Members of this pozzolanic family are natural and natural calcined pozzolana as well as siliceous and calcareous fly ash. For the production of cements containing pozzolana a fundamental knowledge of the materials themselves and their hydration reactions in cement clinker based matrices is essential. Therefore, numerous research projects concerning the use of different pozzolanic materials as cement main constituents are carried out. As an example a project dealing with clay as a pozzolanic material in cement is presented.

Calcined Clay as a cement constituent

Today, clays are used primarily as a raw material in the ceramics industry to produce clay bricks and as raw meal components in the cement industry. However, calcined clay may also be used as a main constituent of cement according to EN 197-1 if the content of reactive silicon dioxide is at least 25 wt.-%. Although suitable raw material deposits seem to be available, calcined clays are used in cement production only to a small extent. The reason is that these materials must be thermally treated first; also the pozzolanic reactivity might not be sufficient. In principle however, the availability of clays is sufficient, thus potentially providing valuable raw materials for natural calcined pozzolana. The composition of suitable clay deposits should be between those for ceramics and those for cement raw meals. Thus, the use of such clays as natural calcined pozzolana would not interfere with other applications.

The pozzolanic activity of calcined clays depends on the type and mineralogical constitution of the clay minerals in the material. The main factors are their chemical composition and degree of crystallisation. During calcination water is expelled from the clay minerals. This causes a degradation of their crystalline structure and

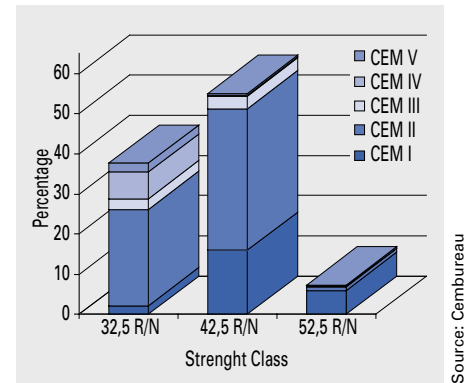


Fig. 1: Cement production in Europe 2007 by type and strength

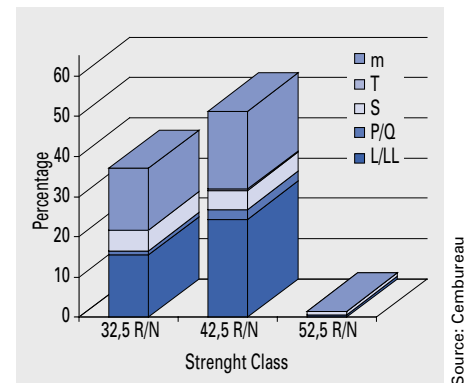


Fig. 2: CEM II production in Europe 2007 by type and strength

a conversion to amorphous aluminosilicate phases. With increasing amorphous character of the dehydrated phases their pozzolanic activity develops. At high temperatures crystalline phases with less pozzolanic reactivity will be formed. The optimum tempering temperature of clay is thus between the dehydration temperature of the clay minerals and the beginning of its recrystallisation. Apart from the calcination temperature, the period of calcination is also decisive for the reactivity of calcined clays. If the period is too long, the specific surface area of the calcined particles will be reduced due to the beginning of sintering processes. This also reduces their pozzolanic activity.

Case study

In the following example, the burning conditions to achieve at least 25 wt.-% of reactive silicon dioxide were determined. A simultaneous thermal analysis (STA) was carried out on the starting material (**Fig. 3**). The DTA and TG signals show endothermic mass losses at temperatures around 550 °C and 800 °C. These are due to dehydration reactions of various clay minerals. Around 900 °C an exothermic signal marks the start of the re-

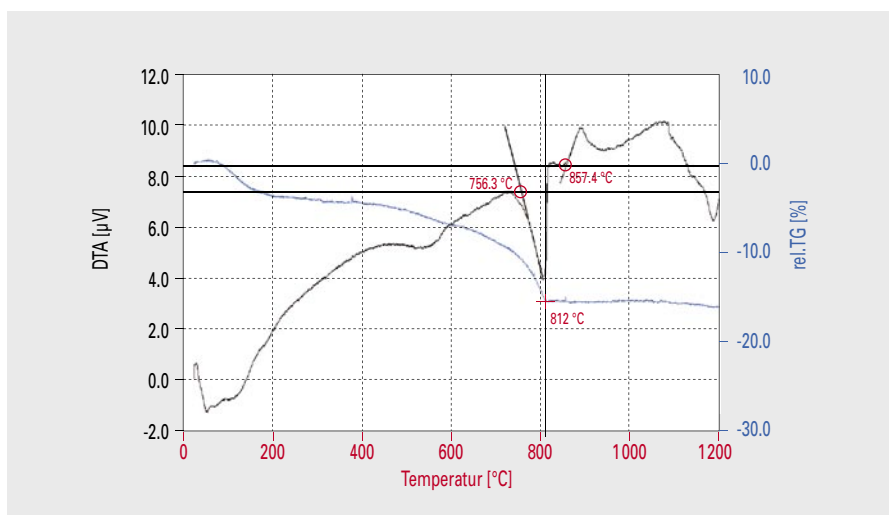


Fig. 3: STA measurement of untreated clay

crystallisation of new phases. Temperature and duration of burning of the clay samples were defined according to these results.

The samples, 100 g each, were tempered in corundum crucibles in a Nabertherm kiln under different burning conditions. After the heat treatment the samples were finely ground and the content of reactive silicon dioxide was determined according to EN 197-1. The mineralogical compositions of the calcined samples were investigated by X-ray diffractometry (XRD). **Table 1** shows the content of reactive silicon dioxide of the calcined samples depending on the burning conditions.

At a temperature of 1000 °C the clay minerals were completely dehydrated and also new phases were formed. However, under these conditions the amount of reactive silicon dioxide was the highest (29 wt.-%). Hence, complete dehydration of the clay minerals is primarily decisive for their pozzolanic reactivity. The negative effect of the formation of non-reactive crystalline phases seemed to be of minor importance for the investigated material. On the whole, a relatively

Sample	Burning temperature in °C	Burning time in min.	Reactive silicon dioxide acc. to EN 197-1 in %
1	750	60	21,9
2	750	180	20,0
3	810	5	21,2
4	810	30	23,3
5	810	60	22,6
6	850	30	24,6
7	850	60	24,3
8	1000	30	29,0

Table 1: Influence of burning conditions on the content of reactive silicon dioxide according to EN 197-1

short treatment (30 minutes) at high temperatures was most effective for the creation of a high content of reactive silicon dioxide in the sample.

Practical application

Calcined clays can be used as pozzolanic main cement constituents according to the specifications of EN 197-1. However, the standard demands a content of at least 25 mass % of reactive silicon dioxide in calcined clay. In individual cases, burning conditions (temperature and

duration) must be adjusted to the respective raw material.

In summary, calcined clay may qualify as main constituent in cement. Its pozzolanic activity depends on the quality and composition of the starting material as well as the conditions of thermal treatment. Even if the requirements of the cement standard can be fulfilled, the final decision for its use in cements depends on the availability of appropriate clay deposits. Also the energy demand for tempering must be taken into account.

Impact of Burning and Cooling Conditions on clinker quality

How fuel ashes and the composition of raw materials can influence the clinker characteristics

Any type of fuel and raw material has an impact on the burning and cooling conditions and consequently the clinker characteristics. Since cement performance is determined to a high degree by the clinker reactivity, a continuous and detailed monitoring of the clinker characteristics is essential and state of the art nowadays. Experiences show that the knowledge and understanding of the clinker microstructure is the base for maintaining good product quality.

Among many parameters, the sulphate and alkali intake via fuel and raw materials into the kiln has an effect on the reactivity of C_3A and consequently on the clinker properties. It

is the setting behaviour of Portland cement which is mainly controlled by the reactivity of C_3A in the clinker component and the dissolution characteristics of the sulphate bearing phases in the cement. The reactivity of C_3A as well as its modification is determined by its alkali content, which itself depends on the total amount of alkalis and the degree of sulphatisation. These parameters also control the amount of highly soluble alkali sulphates in the clinker. Fluctuations of the alkali and sulphate contents in the clinker due to inhomogeneities in the fuels can therefore change the C_3A modification (**Fig. 1**, **Fig. 2**) and the amount of highly soluble sulphate in the cement, each with immediate effects on the setting behaviour. Both effects can be observed directly by X-ray diffraction (XRD).

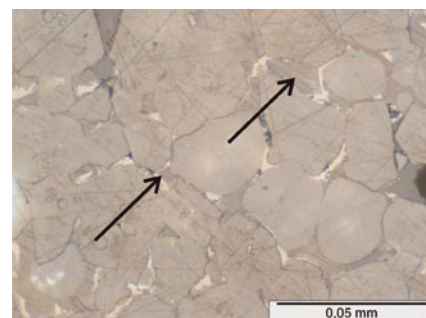


Fig. 1: Isometric crystals of the cubic modification of C_3A in the interstitial mass of clinker (black arrows), low reactivity

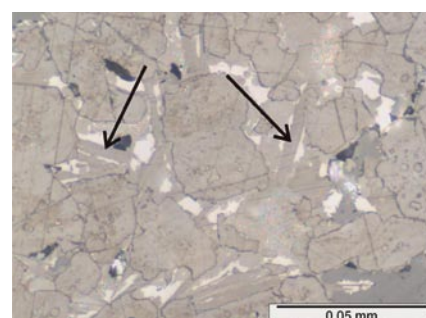


Fig. 2: Strongly elongated crystals of the orthorhombic modification of C_3A in the interstitial mass of clinker (black arrows), high reactivity

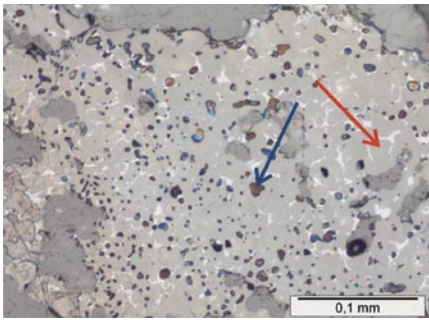


Fig. 3: Mixed cluster of belite (red arrow) and free lime (blue arrow) caused by phosphorus

Phosphate-content in fuels

Meat and bone meal as well as sewage sludge introduce phosphate compounds into the kiln. The phosphate is incorporated into the silicate phases of the clinker. High phosphate contents can stabilize belite and inhibit the formation of alite, resulting in clusters of belite and free lime which are clearly identifiable with optical microscopy (Fig. 3). The decrease of alite content in the clinker can lead to a loss of early strength in the cement.

Reducing burning conditions

The burning behaviour of fuel particles mainly depends on the size, the density and the surface of the respective fuel. Especially larger fuel particles with higher densities and small surfaces tend to fall out of the flame before burning out completely. Smouldering fuel particles in the kiln charge can locally cause reducing burning conditions. The insufficient supply of oxygen leads to the formation of ferrous iron (Fe^{2+}) which can be incorporated into the alite crystal structure. Once the iron is oxidised again during the cooling process it is incompatible with the crystal lattice of alite and causes its decomposition to a non-hydraulic modification of

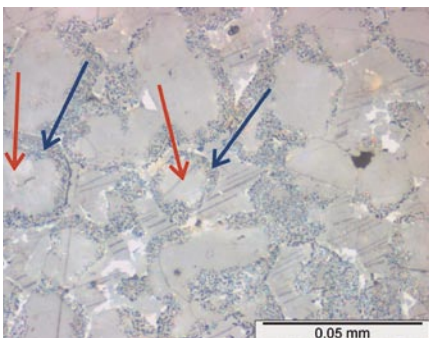


Fig. 4: Decomposition of alite crystals (red arrows) into fine grained belite and free lime (blue arrows); process starts at the crystal surfaces

belite and free lime (Fig. 4). This can lead to a loss of early strength in the cement. With clinker microscopy, even minor degrees of reducing burning conditions can be detected. Thus immediate counteractions would be possible before the product properties are affected.

Temperature profile of the kiln

The burning behaviour of fuel particles and their calorific value determine the flame shapes and the temperature profiles in the kiln. Varying burning characteristics of different fuels can change the sintering conditions significantly. Low sintering temperatures or a short sintering zone in combination with high kiln throughput can cause short residence times of the kiln charge at the maximum temperature. This can result in lower burning grades of the clinker and lower cement strengths.

Formation of coarse granules

The introduction of higher amounts of chloride or sulphur by alternative fuels via the calciner can cause the formation of coarse clinker granules due to mineralising and binding effects in the kiln meal. The cores of these large granules often show signs of a low burning grade like high amounts of clusters of free lime and belite clusters, high porosity or low alite contents (Fig. 5) although the rims of such granules are normally or even hard-burned. If the content of large clinker granules – and correspondingly the content of poorly burned material – is too high, the early strength as well as the soundness of the cement could be affected. XRD can only detect lower average burning grades while only microstructural investigations can reveal the simultaneous occurrence of different burning grades.

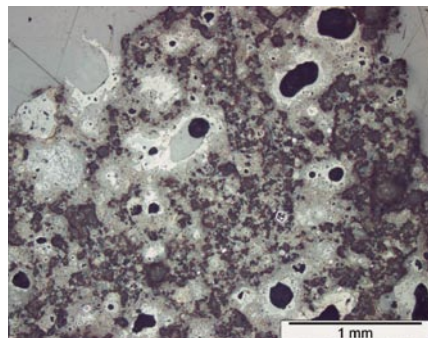


Fig. 5: Weakly burned clinker with high amounts of belite and free lime and very high porosity

New ECRA Website

Dear members,

Everything is subject to change. Combining well-established values with new ideas in order to form a synthesis (which is an art in itself) is essential to avoid stagnation.

We would like to take the opportunity to present our new website. You will notice that the structure of our website offers an easier flow of information which will invite you to dwell for a while. The new design offers more clarity and a brighter colouring. The menu navigation is self-explanatory which entails a shorter sequence of mouse clicks and a user-optimised handling.

You will also find a few modifications regarding the registration form layout. The registration form is structured in a clear and open way and we are convinced that it will facilitate future enrolments for our seminars. For your convenience we intend to offer registrations via Internet, only, as processing of information will take place on a faster level. In addition to this the probability of loss of information as well as misunderstandings will be reduced considerably. Furthermore, we will be given the possibility to react to your questions and feedback in a timely manner.

Another fine feature is the coloured bar sign which precedes the registration form. This bar sign quotes the availability of places according to the following colouring: From green (places available) over yellow (a few places left) to red (no places left).

We hope you enjoy the new design and we are looking forward to your suggestions.



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