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European Cement Research Academy



## Newsletter 2/2004

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- CO<sub>2</sub> Reduction Provided by Project Based Mechanisms under the  
Kyoto Protocol and Future European Legislation  
June 7, 2004
- Emission Monitoring  
June 23 - 24, 2004

# Microscopy – Still a Strong Method for Clinker Assessment

## Microstructures of clinker phases reveal important information on both burning conditions and product properties

Microscopical methods are known as important and powerful tools for the examination of Portland cement clinker. Although the required sample preparation time is too long for an implementation of microscopy into online quality control systems of cement plants, a lot of process engineering issues can be solved. In addition a rough forecast of product properties is possible by means of optical microscopy.

In recent years, the aim of cost 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 of primary fuels while maintaining the level of clinker performance in cement applications. In addition, the given geochemical conditions of any cement plant location 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 visualised by microscopical techniques. In the following, some examples are given.

### Use of secondary fuels

A common way of reducing the specific amount of primary fuels is their replacement by secondary energy sources. Depending on their burning behaviour, their calorific value and their specific gravity, the temperature profile of rotary kilns can be affected significantly. Thus, a prolonged sintering zone can lead to a growth of alite grain sizes in conjunction with a decrease of clinker porosity (**fig. 1**). Both effects are known to influence technical properties. A possible way to modify the burning characteristics for a given fuel composition would be to change the ratio of axial and swirl burner air.

### Phosphate-bearing fuels

Since the extended prohibition of the use of animal meal for feeding cattle by the European Union in the year 2001, an increased amount of animal meal has been used as al-

ternative fuel in the cement industry. The bone fractions of animal meal consist of phosphate compounds which can be incorporated into the silicate phases of Portland cement clinker. High phosphate contents can inhibit the formation of alite in favour of belite (**fig. 2**). This is proven for industrial clinkers as well as for artificial clinkers burnt under laboratory conditions. The decrease of alite contents can lead to a loss of early strength of cement and can be observed similarly, if sewage sludges are used as secondary fuels.

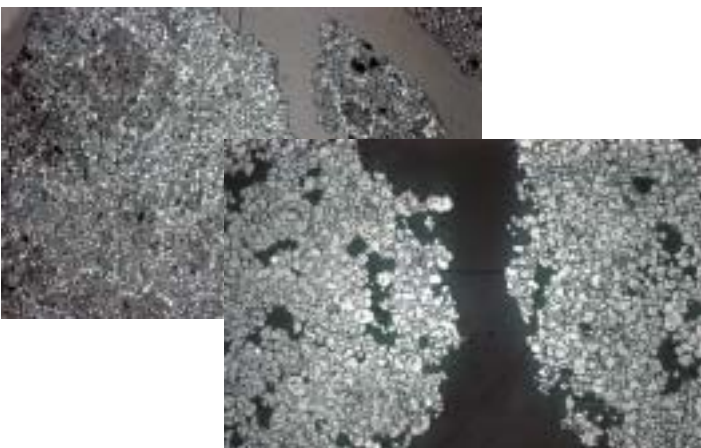
### Incorporation of alkalis

The geological conditions of the limestone or marl deposit used in clinker production can determine the alkali content. This can be of importance for the clinker reactivity. Depending on the degree of sulphatisation, high amounts of alkalis can be incorporated into  $C_3A$  and may lead to a change of its

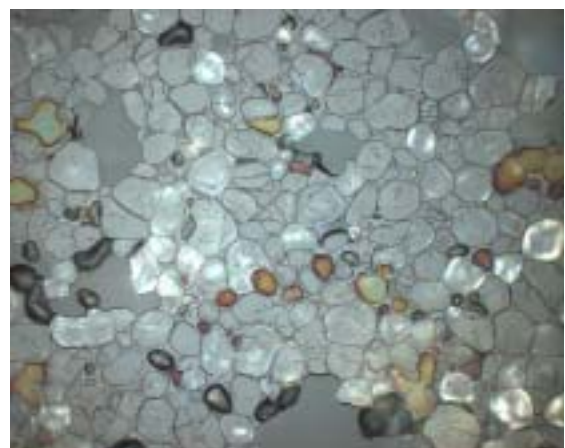
crystal structure (**fig. 3**). It is well known that alkali bearing  $C_3A$  modifications are more reactive than the alkali free modification, especially if the clinker cooling rate is low.

### Effects of clinker cooling rate

The cement performance with respect to setting and hardening behaviour can be affected to a high degree by the reactions during clinker cooling. Even in the precooling zone inside the kiln an exchange of material between the calcium silicates and the liquid matrix takes place. Particularly clinkers with high alumina contents show a tendency towards alite corrosion due to an increased calcium demand of the crystallising matrix together with a raised incorporation of aluminum and iron oxide into the silicates (**fig. 4**). Whereas the alite corrosion may affect the strength development of cement, its setting behaviour is mainly a result of the  $C_3A$ -characteristics. A slow cooling rate associated with an extended



**Fig. 1:** Micrographs of clinker with high and low porosity. The left clinker contains an increased amount of open pores. The right clinker is more dense and exhibits enlarged alite crystals due to prolonged sintering.



**Fig. 2:** Micrograph of phosphorous bearing clinker. The formation of alite out of belite (round grey particles) and residual free lime (brown particles) is inhibited.

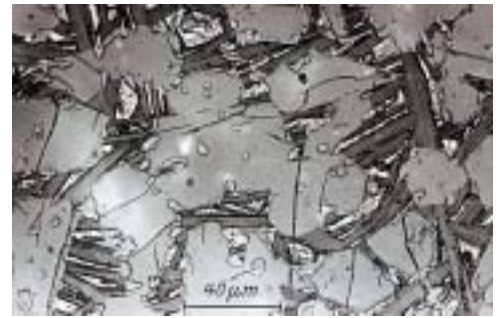
grain growth of the interstitial phases may lead to an increased  $C_3A$  reactivity. Eventually, the cement setting needs to be adjusted by changing the composition of sulphate agent additions if the clinker cooling rate is modified.

### Reducing kiln atmosphere

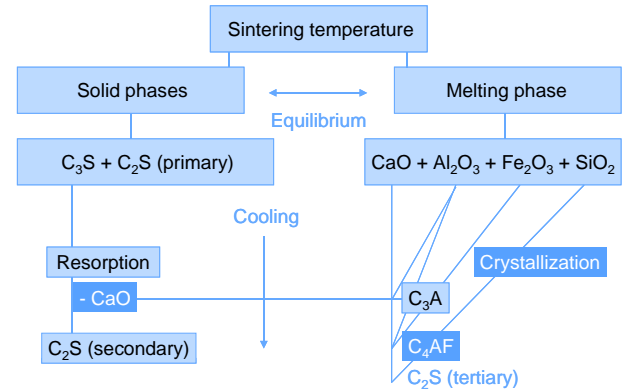
Reducing conditions can lead to a cement strength loss due to a decreased alite content in the clinker. Bivalent iron as a result of oxygen deficiency can be incorporated into the structure of alite. Once the iron is oxidised again during the cooling process, it becomes incommensurable with the crystal lattice of alite and causes a decomposition to a non-hydraulic modification of belite and free lime (fig. 5). By means of microscopy, reducing conditions can be recognised at an early stage, i. e. before any deteriorating effects on product properties are found.

In any case, optical microscopy is able to reach its full potential in combination with various other techniques like X-ray diffraction, chemical analysis and scanning electron microscopy.

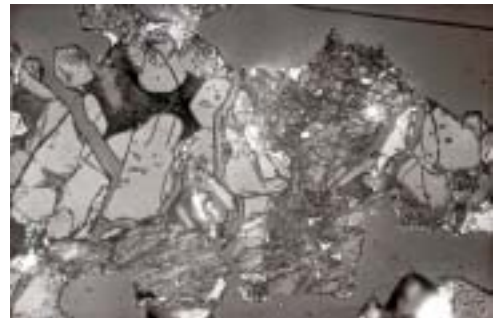
**Fig. 3:** Micrograph of clinker containing alkali-rich  $C_3A$ . The lath-like shape of  $C_3A$  aggregates (dark grey) indicates the alkali-bearing orthorhombic crystal structure.



**Fig. 4:** Interaction between silicate phases and interstitial matrix during clinker cooling.



**Fig. 5:** Micrograph of clinker burnt under reducing conditions showing a partial decay of alite (light grey crystals and decomposed areas, respectively).



## Can ASR Be Reliably Predicted through Performance Tests?

### Different test methods are available and can provide a deeper understanding of alkali-silica reaction

The alkali-silica reaction (ASR) is well known and its chemical and mineralogical reaction patterns are well understood. In many parts of the world very efficient regulations have been implemented to avoid harmful consequences of ASR in mortar and concrete. Each approach, however, is different, depending on the regional occurrence of reactive aggregates. On the other hand, alkali concentrations in cement depend on the individual raw material situation, limiting the potential for the production of low-alkali cement. Many attempts have been made to develop a performance test to predict ASR. These tests have proven to be very valuable, however, they all have their limitations and the test results must be interpreted very carefully.

Due to the availability of aggregates, ASR is always a regional phenomenon. In some regions, however, it is economically not viable to produce cement with a low effective alkali content or to substitute local aggregates by non-reactive ones. Effective test methods should be able to classify very clearly the sensitivity of aggregates. Furthermore, they should allow to evaluate the performance of concrete mixes and to predict their behaviour under field conditions. Efficient performance tests could thus optimize the use even of reactive aggregates. In many cases, ce-

ments with low alkali contents would not even be necessary.

### Alkali sensitivity of aggregates

The alkali sensitivity of most aggregates in concrete cannot be established by direct chemical and/or mineralogical testing of the aggregates. In order to get an idea of their reactivity susceptible aggregates are assessed by mortar or concrete test methods. A very quick test is the method designed by Oberholster even published with slight changes as ASTM C 1260 and RILEM AAR 2 test methods. The aggregate under test is

crushed to a grain size < 4 mm. Mortar prisms 4 cm x 4 cm x 16 cm or 2,5 cm x 2,5 cm x 28,5 cm are produced and stored in a 80 °C hot sodium hydroxide solution. The mean expansion of three mortar beams is calculated and the final value after 14 days storage is used as assessment criterion. The test method seems to overestimate the sensitivity of different aggregates. Concrete test methods are believed to be more reliable. In these test methods, e. g. published as ASTM C 1293 or RILEM AAR 3 method concrete beams with dimensions of 7,5 cm x 7,5 cm x 28 cm are stored

above water at about 40 °C. The concrete usually contains a portland cement with a high alkali content. As for the mortar test the length change is measured periodically. The expansion reached after a period of 12 or 24 month is used as assessment criterion. The long testing time is the main disadvantage of the concrete test methods.

### Performance test

A concrete performance test was created in France and taken over by RILEM. Prisms made from a concrete having the same composition as the concrete which, shall be used in certain structures, are taken for this test. The prisms are stored at 60 °C above water. The expansion of the prisms serves as a yardstick for assessing the risk of damage to concrete (fig. 1).

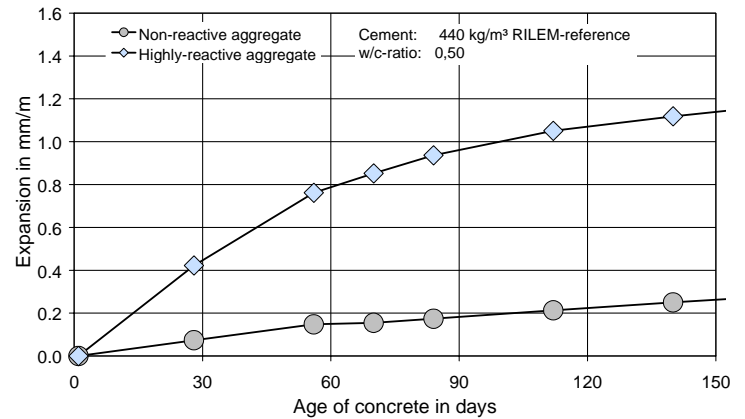
At the research institute the performance test will be developed further on changing the temperature and the humidity. Even a storage in sodium hydroxide solution is planned.

### Determination of the alkali concentration in pore solution

The alkali concentration of the pore solution is a major parameter in triggering a harmful alkali-silica reaction. It is dependent on the alkali release of cement components and concrete additions, the incorporation of alkalis by hydration products and the free water content.

The expression method constitutes one possible test of gaining the pore solutions from hardened cement paste. A test specimen is

**Fig. 1:** Expansion of concrete according to the RILEM performance test



placed into a high-pressure device. The pore solution is pressed out with a continuously increasing load up to 3 000 kN. As the method is very time-consuming and involves enormous effort in testing, it is not suitable for routine operational checks.

As alternative the so called solution method is investigated. In this method cement paste is manufactured with a water binder ratio of 1.0. After sedimentation of the cement, the excess water forms a water column, which is balanced with the liquid phase in the gel and capillary pores of the hardened cement paste.

Because of the higher water/cement ratio (1.0 vs 0.5), the alkali concentration determined with the solution method is markedly lower than that of the expressed pore solution.

Initial results suggested that for each cement type a base comparison between the solution process and the expressed pore solutions must be performed.

### Diagnostics of a harmful ASR

Extensive investigations are required to determine the causes of damage to structures when it is suspected, that an alkali-silica reaction is the cause.

#### Damage survey

All the available information on the structure and the concrete must be gathered before surveying the actual damage to the structure. For this purpose it is essential to obtain information from the consultants, clients, contractors and building materials suppliers.

#### Concrete samples

At the same time that the damage is being surveyed drill cores should be taken from the damaged and undamaged sections of the structure.

The bulk density and compressive strength have to be measured to assign the concrete to different classes. Storage of drill cores in a hot (e.g. 40 °C) and humid environment to initiate an accelerated reaction is absolutely essential for diagnosing an ASR. Microscopic investigations of ground sections and of thin sections are very helpful for identifying the alkali-silica reactions.

Individual results can be misleading and lead to false conclusions when assessing whether and, if appropriate, to what extent an ASR has been involved in the damage. All the investigations should therefore be combined and weighted (fig. 2).

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European Cement Research Academy  
Tannenstr. 2 · 40476 Düsseldorf  
P. O. Box 30 03 32 · 40403 Düsseldorf  
Germany  
Phone: +49 (0)211 2 39 83 8-0  
Fax: +49 (0)211 2 39 83 8-500  
info@ecra-online.org  
http://www.ecra-online.org

damage survey	cracking pattern splintering
starting materials	type and quantity of aggregate type and quantity of cement
humid storage at elevated temperature (e.g. 40 °C)	gel secretion cracking maximum expansion further increase
ground section and thin section	crack structure gel alkali-sensitive aggregates further observations <i>(e.g. secondary ettringite)</i>

**Fig. 2:** Evaluation criteria needed for establishing a harmful ASR