CHARACTERISATION OF THE REACTIVITY OF CEMENT CONSTITUENTS

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The properties of a cement derive from the totality of its constituents and their interaction. With the introduction of the new European cement standard EN 197-1, 27 cement types are now standardised and hence the use of new constituents has become possible.

The main components of cement are classified as follows:

- Hydraulic constituents such as for example Portland cement clinker
- Latent hydraulic constituents such as for example granulated blast furnace slag
- Pozzolanic constituents such as for example coal fly ash, lignite fly ash and silica dust and also
- Inert constituents such as for example limestone

In view of the increasing share of composite cements in the overall sales volume, the effect of the constituents apart from the clinker is becoming ever more important. However, the user requires a product that is not only of high quality, but also very homogeneous, hence a reliable assessment of the individual components and of their interplay becomes essential.

By way of example, the following contribution concentrates on various possible methods for the characterisation of the performance of clinker and of granulated slag. In this, particular attention is paid to microscopic assessment.

Portland Cement Clinker

Portland cement clinker still remains the essential component of all standardised cements. Its properties have a decisive influence on the behaviour of the cement. Its workability, setting and 28-day compressive strength are essentially influenced by the phase composition of the clinker and the morphology of the individual clinker phases. These parameters are controlled both by the composition of the feed materials, i.e. raw material and fuels, and also by the combustion and cooling conditions during the clinker burning process. The properties of the fuels determine the temperature profile and thus the formation of the sintering and precooling zone. Together with the oxygen availability there, they decisively influence the reactivity of the clinker. The phases alite (C_3S) and C_3A in particular are responsible for the strength and working properties of the resulting cement. With its high reactivity, the C_3S mainly determines the strength development, while the C_3A is responsible for the stiffening and setting of the cement and thus for its workability.

The calculation of the particular clinker phases from the Bogue chemical analysis is carried out solely on the basis of the oxide composition and thus does not take account of possible process influences. Hence these figures do not provide an adequate assessment basis, in order for example to be able to make a statement concerning the reactivity of the clinker analysed. The Rietveld assessment of X-ray diffraction measurements makes it possible to estimate the reactivity on the basis of the quantitative phase composition.

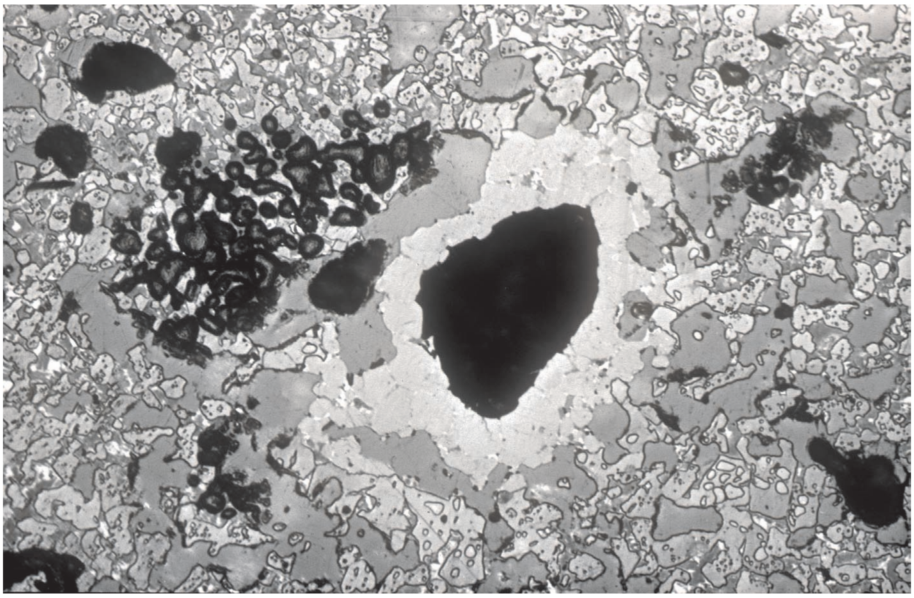


Figure 1: Influence of an excessively coarse raw material on the clinker composition. Around a pore which originally contained a quartz grain, as structural inhomogeneities, concentrations of belite and free lime can be clearly discerned as the cause of an excessively large limestone particle.

Thus for example through the differentiation of the modifications of the C_3A (cubic or orthorhombic) a broad statement as to the reactivity to be expected can be made. However, as always, polished section microscopy in particular offers an outstanding basis for assessment of the process conditions under which a clinker was formed, and of the performance to be expected of it. In Figure 1 the influence of an excessively coarse raw material can be discerned, which prevented the reactions leading to the clinker phases from proceeding to completion. This resulted in two remnant zones, one of which can be seen as a dark pore which previously contained a quartz grain, and the other as an adjacent free lime agglomeration. Indications of a possible extended sinter zone or overburning are severely coarsened alites, which lead to markedly worse clinker grindability and reactivity.

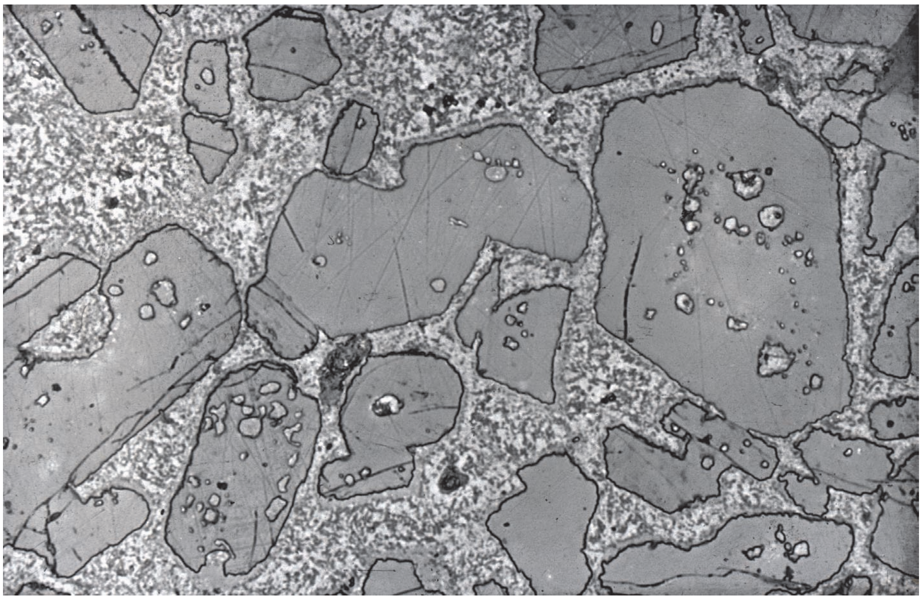


Figure 2: Rapidly cooled clinker with a finely divided matrix of the base compound phases C_3A and C_4AF

Again, the morphology of the C_3A permits various statements. For example, on the basis of the differentiation of the base compound phases C_3A and C_4AF the efficiency of the pre-cooling can be assessed. If they are clearly present as light and dark distinguishable phases finely divided in small crystals, as discernible in Figure 2, then this clinker has undergone rapid precooling. In contrast to this, Figure 3, in addition to clear differentiation with coarse grain structuring of the two base compound phases, which points to slower precooling, also shows a rod-like structuring of the C_3A. This orthorhombic modification of the C_3A is formed when the sulphatisation level is below 100% and hence alkalis are available for incorporation into the C_3A.

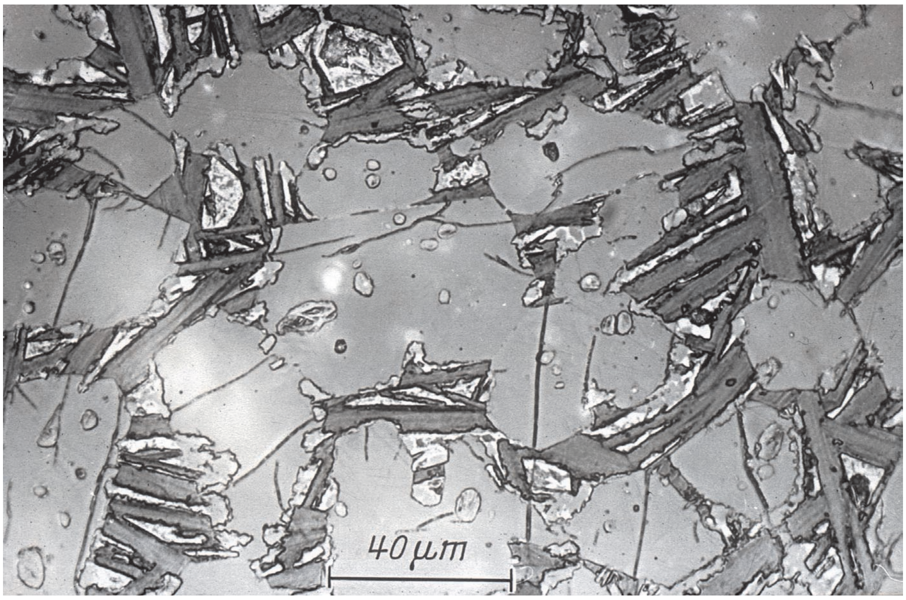


Figure 3: Slowly cooled clinker with a well differentiated matrix of the base compound phases C_3A and C_4AF. The rod-shaped C_3A is indicative of the orthorhombic modification.

A clinker can only be as homogeneous as were the conditions under which it was produced. This means that the composition of the raw material, the kiln atmosphere and the kiln operation must be kept as constant as possible. The microscopic assessment of clinkers vividly reveals that it is above all the clinker combustion and cooling conditions, which are to a considerable extent influenced by the fuel composition, that are decisive for the clinker properties. Thus the clinker morphology provides a great variety of information, from the fuel composition and fineness right down to the combustion and cooling conditions. As a result, polished section microscopy provides an outstanding basis for assessing the combustion process and appropriately optimising it.

Granulated Slag

The use of granulated slag as a standardised cement constituent is a long-established practice, both in Germany and also in the rest of Europe. In the criteria for granulated slags, the requirements of EN 197-1 confine themselves to a glass content of more than 66.6 wt.% and the chemical composition in which only the elements calcium, magnesium and silicon are taken into account in terms of the ratio of calcium and magnesium to silicon being greater than 1. If these minimum criteria are fulfilled, it is at least ensured that the granulated slag possesses latent hydraulic properties.

EN 197-1	
Glass content	≥ 66.6 %
$CaO + MgO + SiO_2$	≥ 66.6 %
$(CaO + MgO) / SiO_2$	> 1.0

Table 1: EN 197-1 requirements for granulated slag

In decades of experience, it has however been found that performance in the sense of a contribution to strength during the cement hydration cannot be adequately characterised on the basis of these requirements. Thus further empirical parameters have been established, which depend on the production conditions as well as on the chemical composition.

Thus in general a high Al_2O_3 content is regarded as favourable with regard to the strength contribution, and in contrast a high titanium or manganese oxide content as more likely to be unfavourable. Beyond their chemical composition, granulated slags also differ in the micro-structure of their glass. Studies at the Cement Industry Research Institute have shown that particularly in granulated slags regarded as especially reactive small quantities of merwinite, a calcium magnesium silicate, could be observed.

If the devitrification behaviour of granulated slag in the temperature range between 800 and 1100 ° C is investigated, and in the process the formation of crystalline phases from the glass phase is followed crystallographically, then in a typical granulated slag of normal reactivity the phase melilite mainly arises. Figure 4 shows the projection of diffraction diagrams of a granulated slag meal in this temperature range. Beyond a temperature of about 750 ° C, the intense blackening in the region of 2 theta ca. 31 ° confirms the exclusive presence of melilite (Me).

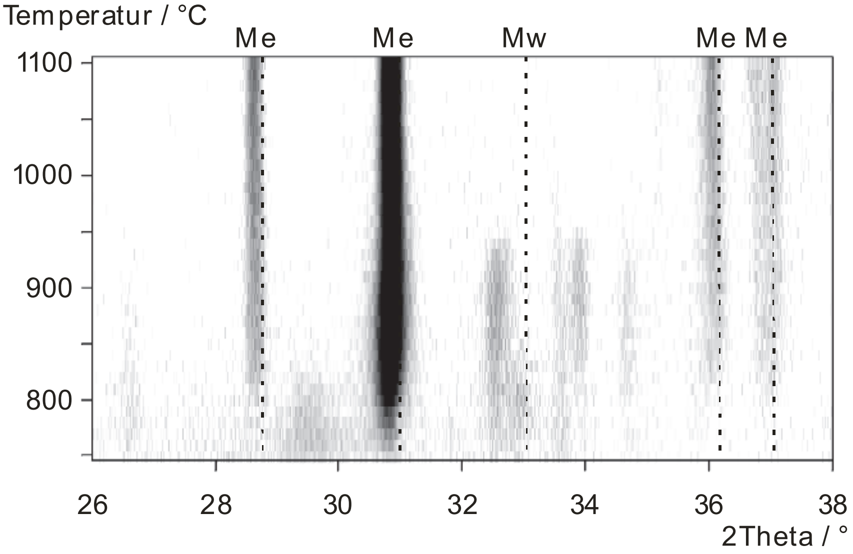


Figure 4: Temperature-dependent X-ray diffraction of granulated slag meal 1 in the temperature range from 750 to 1100°C in projection (degree of blackening = peak intensity). At 2 theta ca. 31° the phase melilite (Me) is clearly discernible.

In another granulated slag, which displays higher reactivity, in addition to the melilite phase already observed just now, the appearance of a phase which was not previously observed is discerned in the temperature range between 800 and 900°C at 2 theta 33°, Figure 5. This phase was identified as merwinite (Mw), an aluminium-free calcium magnesium silicate $Ca_3MgSi_2O_8$.

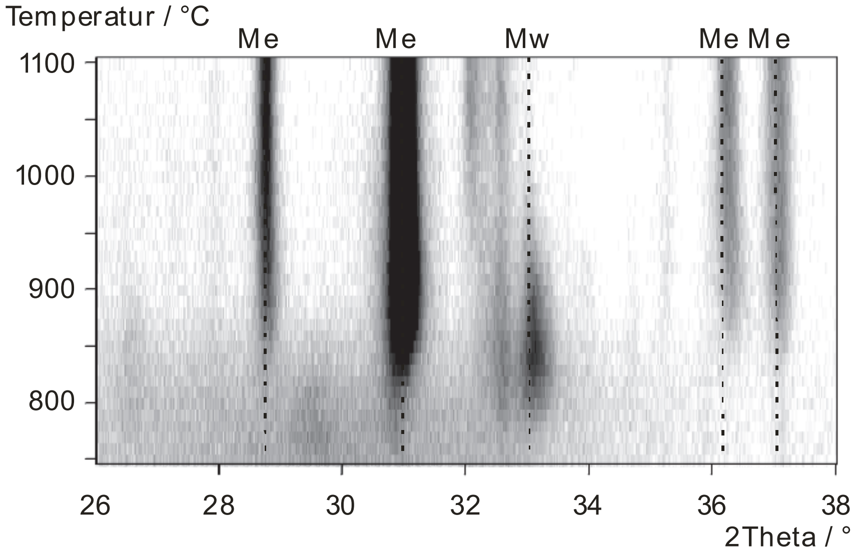


Figure 5: Temperature-dependent X-ray diffraction of granulated slag meal 2 in the temperature range from 750 to 1100°C in the two-dimensional projection. In the temperature range from 800 to 900°C, the peak of the phase merwinite (Mw) appears.

If now a thin section preparation of this granulated slag is examined in the scanning electron microscope using different detectors, then crystalline constituents can be discerned in the granulated slag glass. In the cathode luminescence mode, a luminous feature is observed, which on closer inspection proves to be a crystalline aberration of the glass structure Figure 6. Through the material contrast, the backscatter electron micrograph highlights the fact that regions of differing chemical composition have formed there Figure 7. Microanalysis of the respective zones confirms that these dendrites have the composition of merwinite, whereas the contact region displays an increase in the aluminium content in the adjacent glass phase. If the same place is examined using the secondary electrons Figure 8, a pronounced microporosity is observed in the region of these dendrites. This porosity arises through the crystallisation of the merwinite of density 3.15 g/cm³ from the granulated slag glass of density 2.90 g/cm³ .

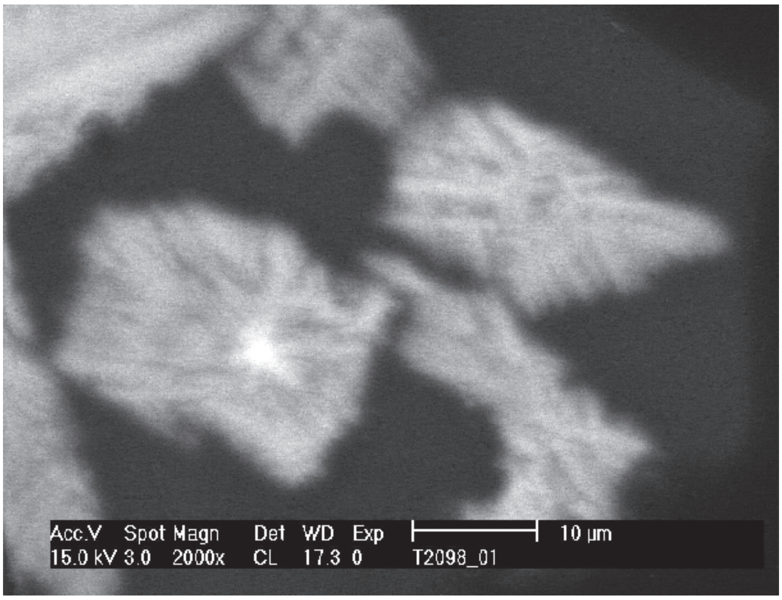


Figure 6: Cathode luminescence picture of a section of granulated slag 2 in the SEM. The crystalline regions in the granulated slag glass display a clear luminous feature (luminescence)

The observed high strength contribution of such merwinite-containing granulated slag glasses can be understood in terms of two overlapping effects. Because of the increase in the aluminium content in the adjacent glass matrix, an especially reactive glass phase is present here, whose surface area is moreover markedly increased by the high porosity and a rough pronounced crystalline surface structure in this region.

Besides the reactivity of the cement constituents as an active contribution for a compact and resilient structure, interest is focused on the durability and environmental compatibility of cement-based building materials and building components produced from them. In recent years, many studies concerned with the effectiveness of various cement constituents in the avoidance of damaging ASR have been carried out at the Research Institute.

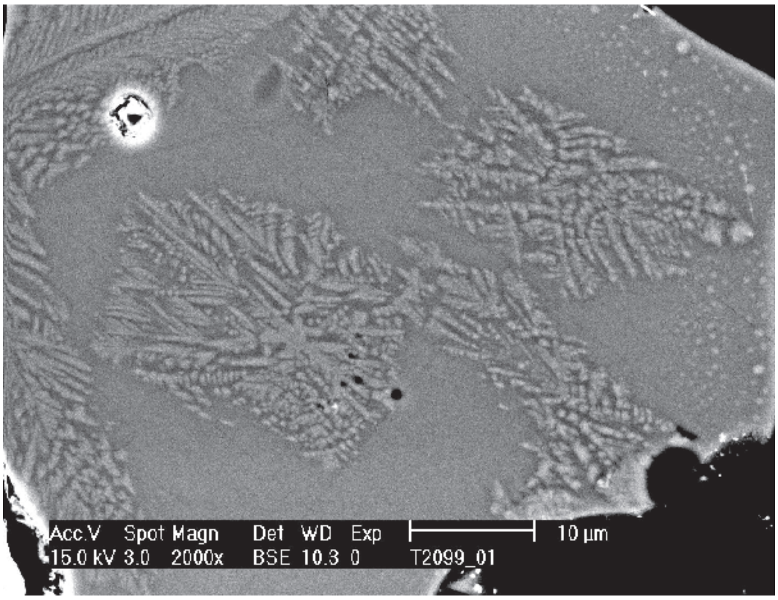


Figure 7: Backscatter electron micrograph of a granulated slag 2 section in the SEM. The crystalline regions in the granulated slag glass, the edge zones and the glass matrix itself are of differing chemical composition

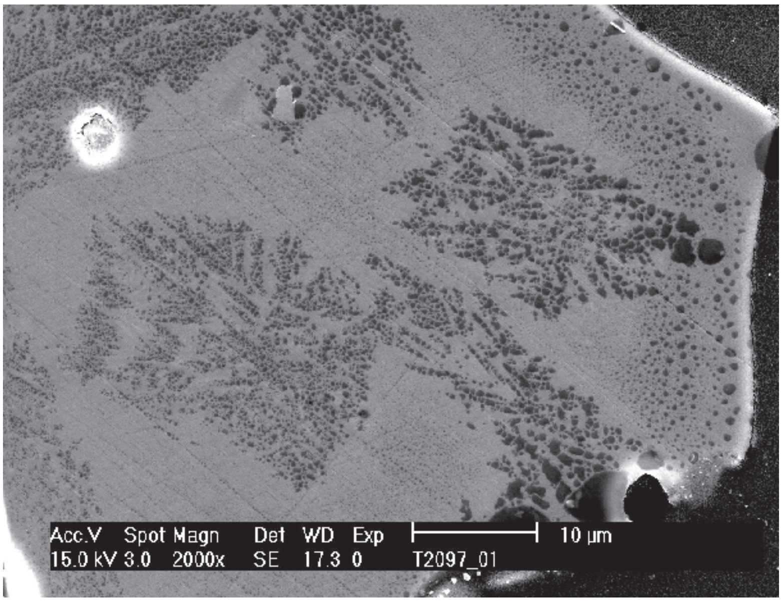


Figure 8: The picture using secondary electrons reveals the surface structure clearly. In the crystalline edge zones, an increased porosity becomes discernible.

One of the preconditions for the triggering of a damaging ASR is the effective alkali content of the cement. This results from the release of alkalis from the cement constituents and the binding processes taking place in parallel to this in the reaction products, which depending on their composition can take up differing quantities of alkalis.

In comprehensive studies, the influence of granulated slags on the alkali balance was considered. For this, the pore solutions of cements with different granulated slag contents were studied in relation to the hydration age. The balance assessment shows that granulated slag lastingly lowers the available alkali content almost proportionately to the content of the replaced clinker. The dissolved alkali content of granulated slag-containing cements roughly corresponds to the total alkali content of the clinker contained in the cement. This apparently inert action of the granulated slag can only be attributable to a superimposition of dissolution and binding processes.

In order to understand the processes responsible for the alkali release and binding, the reactions of the various cement constituents must be followed. Crystallographically, only the degradation of the clinker phases is detectable. However, owing to their finely divided state and low crystallinity, the reaction products are not identifiable. One method of indirectly indicating the formation of new phases is the combination of backscatter electron micro-graphs of the hydrated cement and semi-quantitative element distribution pictures.

By way of example, Figure 9 shows the backscatter electron micrograph (BSE micrograph) of a 28-day old CEM III/A. In addition to some clinker remnants (K), granulated slag grains (H) can be discerned in the matrix. The reaction product from the granulated slag stands out clearly from the unreacted core as a dark border. The grey scale suggests that the cores and the edge region are of different composition. In the backscatter electron micrograph, zones appear lighter the higher their mean order number. Accordingly, the edge zones of the granulated slag have a lower mean order number than the unreacted cores.

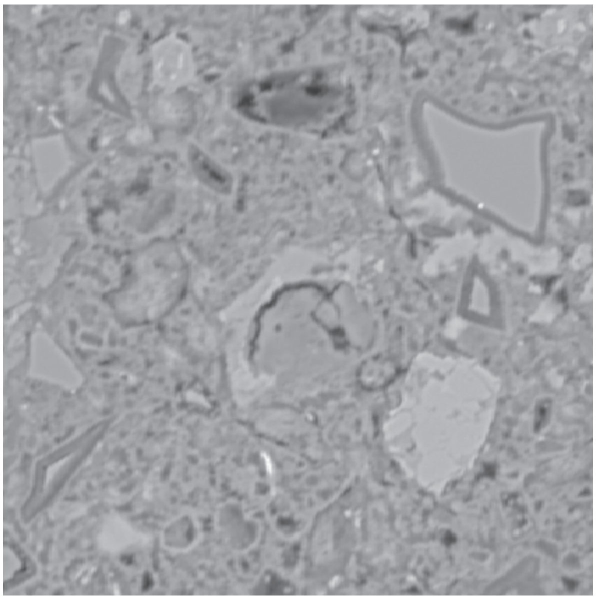
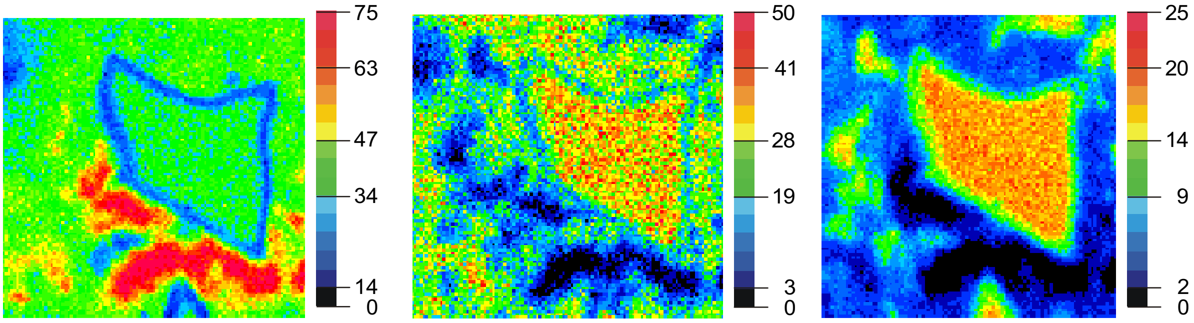


Figure 9: Backscatter electron micrograph of a 28-day hydrated CEM III/A, K: clinker remnant, H: granulated slag grain, picture edge length: 100 µm

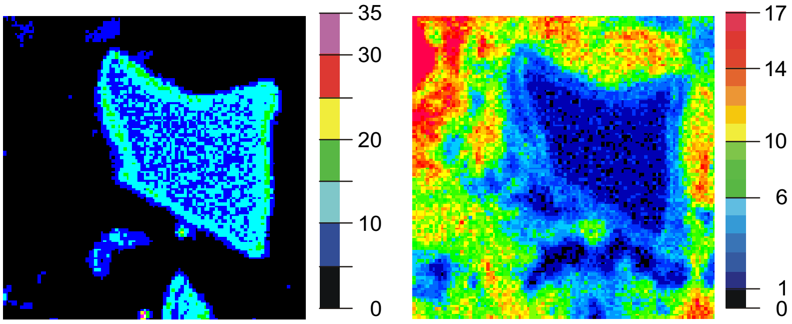
The change in the composition is confirmed by the element distribution pictures for the enlarged picture section A in Figure 9 shown in Figure 10. Compared to the core, the reaction border shows a markedly lower content of silicon and calcium, Figures 10 a and b. The aluminium content (Figure 10c) has also declined by about 5 wt.%. In contrast, a marked enrichment in magnesium in the reaction zone can be observed (Figure 10 d). The composition of the reaction border points to the formation of hydrotalcite-like phases, which are not able to take up alkalis. This also follows from the potassium distribution of the grain (Figure 10 e). At the boundary between the core and the border, a local enrichment in potassium can be observed. In contrast, the border is depleted in potassium in the direction of the matrix. Distribution pictures of older samples show that the potassium enrichment at the boundary decreases. Hence, no prolonged or intensified binding of alkalis at the reaction border of the granulated slag should be assumed.



a) Calcium

b) Silicon

c) Aluminium



d) Magnesium

e) Potassium

Figure 10: Element distribution pictures of the section A in Figure 9, contents in wt.%