

Application of TEM to characterize fly ash- and slag cements

Hans S. Pietersen

Delft University of Technology, Faculty of Civil Engineering and Geo-Sciences, Materials Science Engineering Section, Stevinweg 1, 2628 CN Delft, The Netherlands.

E-mail: H.Pietersen@CT.TUDELFT.NL

A Portland fly ash cement containing 20 % of a fine fly ash and a blast furnace slag cement of approximately 290 days old were examined with analytical transmission electron microscopy, in order to examine the (local) microstructure in these cements in detail. In the Portland fly ash cement the fly ash reacted with CH resulting from the cement hydration. Due to this pozzolanic reaction, initially a dense C-S-H reaction rim precipitates around the fly ash glass spheres. In course of time, a radially fibrillar and more porous zone of C-S-H is formed in between the dense C-S-H zone and the fly ash surface. The dense C-S-H notably contains aluminium and potassium, elements which are likely to originate from the fly ash.

The microstructure of the blast furnace slag cement is also marked by a local chemical differentiation; a zoned structure is formed surrounding the original slag grain. Chemical analyses and element maps indicate that notably Si and Ca, and also some of the Al, is transported out of the slag grain interior. The driving force for this element transport is accounted for by a postulated gel-layer, creating a chemical potential gradient for water. Hydrophillic elements, such as Si and Ca will migrate out of the slag, and will cause a gradual paste densification, responsible for the low permeability in blast furnace slag cements. Within the gel-layer, a water poor region is formed in which a hydrotalcite-like phase precipitates, possibly together with minor amounts of C-S-H like material at its inner edge.

Key words: Transmission Electron Microscopy, fly ash, slag, microstructure, pozzolanic reaction, element distribution, chemical gradient

1 Introduction

Transmission electron microscopic (TEM) studies of fly ash- and slag composite cements have so far been limited to only a few studies. This is somewhat surprising, because in principle, chemical analysis with TEM may provide very detailed chemical and microstructural information on the microstructure (and possible reaction products) of blended cements. It is inherent to TEM that only local microstructural information can be obtained.

The first transmission microscope study of the hydration of Portland cement (or C_3S) was reported in [1];[2], using paste, dispersed in a solvent. Replicated specimens were studied by Ciach et al. [3]. "In situ" hydration has been studied by Double et al. [4] and Jennings and Pratt [5]. Dalglish and

Ibe applied ion-milling in their TEM study of Portland cement [6], which resulted in an increased detail of the microstructure. During the last decade the TEM technique was linked to analytical tools, enabling both spot chemical analysis as well as chemical maps by using pixel based imaging techniques [7];[8].

Using the analytical TEM, Mohan and Taylor [9];[10] found that the C-S-H in fly ash composite cement pastes displayed a somewhat decreased Ca/Si ratio; Rodger and Groves [11] studied a C₃S-PFA paste by TEM and found that the fly ash particles react; initially, regions of dense C-S-H were formed surrounding the fly ash spheres. In course of time, between this rim and the (new) fly ash glass surface areas of low density consisting of radially fibrillar C-S-H were formed. Occasionally, denser regions of silicium-hydrogarnet (experimentally shown to be C₁₂A₃FS₄H₁₆) were observed. Studies of a 180 to 885 day old granulated blast furnace slag cement with analytical electron microscopy revealed that both a cement hydration product (CHP), other than C-S-H, and an "inner slag hydrate" (ISH), resembling a hydrotalcite-like phase, were formed [12];[13]. Other studies also indicated the presence of low- or non-calcium bearing magnesium-aluminium hydroxide, similar to the naturally occurring mineral hydrotalcite, but of variable composition [14];[15].

It is the aim of this study to use analytical transmission electron microscopy in order to obtain insight in the microstructure, and possible associated chemical differences, of fly ash- and slag composite cements.

2 Experimental

Samples of Portland fly ash cement (containing the 20 % m/m EFA fly ash) and a CEMIJ blast furnace slag cement (type A, containing approximately 65 % slag) were cast, and quickly transferred to sealed bottles and cured at approximately 20 °C. In both cases the water / solids factor was 0.40. Chemical analyses of the fly ash, the blastfurnace slag and the Portland cement were published previously[16]. After approximately 290 days the samples were demoulded and any remaining (free) water was removed by freeze drying. Further sample preparation consisted of impregnating the sample with "Araldite D", attaching the sample to a glass plate (using a resin which melts upon heating), and carefully polishing it to a thickness between 50-100 µm. Essentially, routine geological techniques were applied, except that non-aqueous media were used as polishing aid. Upon heating the glass plate the samples were cut loose with a razor blade and mounted on a TEM grid. Additional sample thinning was performed by ion-beam milling using argon ions accelerated to 5 KeV, with an ion-current of 50µA. The material removal rate was approximately 1 µm/hour. During the ion-milling the specimens were rotated continuously and were tilted at low angles (10–15 °) to the ion-beam; N₂ cooling was applied to prevent excessive heat build-up. Ion-milling was stopped whenever a hole was formed within the centre of the sample. Prior to the TEM operation, the samples were coated with a thin carbon layer. The TEM study of the fly ash cement paste was performed on a Phillips EM-30, which was linked to an energy dispersive spectrometer, in order to be able to provide an impression of the sample (or spot) composition. The slag cement was studied on a JEOL 200EX microscope with a LINK AN10/855 EDS analysis system, at the University of Aberdeen, Department of Chemistry.

3 Results and discussion

3.1 Portland fly ash cement

In the Portland fly ash cement a large variety of particles may be detected. Chemically, most particles reflect the major element chemistry of the fly ash (EFA), which is marked by relatively high potassium contents and a 1:2 aluminium-silicium ratio in its glass. Also some particles consisting primarily of silica glass or (unreactive) iron oxides were detected. Some of the particles did not appear to have reacted at all, although the local sample thickness could have been too high. Those fly ash particles that could be detected in transmission generally displayed very specific reaction patterns, similar to those reported by Rodger and Groves [11].

Prior to a detailed discussion, it should be made clear that (all) the C-S-H immediately surrounding the fly ash spheres results from the pozzolanic reaction of CH and the fly ash glass. However, in the TEM micrographs no CH surrounding the fly ash could be detected. Two explanations are possible. The first and most likely one, is that it is only possible to examine a few fly ash spheres *in transmission* in a single TEM sample (others parts of the sample are usually just too thick). The second is that the blended cement pastes are already 290 days old, so hydration- and pozzolanic reactions will be in an advanced stage and most of the CH deposited on the fly ash spheres may have been consumed.

A typical transmission electron micrograph of a PFA particle immediately surrounded by a clearly visible reaction zone, primarily consisting of radially fibrillar C-S-H, is displayed in figure 1. The calcium-silicate hydrate appears to be quite porous, as compared to the C-S-H deposited further away from the fly ash sphere. More difficult to recognize on the micrograph is a second layer (it “sticks out” on the lower right in figure 1), which is significantly more dense. This phenomenon has been reported earlier in studies of a C₃S- fly ash pastes [11]. Efforts to produce diffraction patterns of both the porous and the dense regions did not indicate the presence of crystalline phases; an example of the diffraction “halo”, representing amorphous material, is shown in figure 2. A detail of the radially fibrillar C-S-H surrounding the fly ash particle from figure 1 is presented in figure 3. Here, a much clearer indication of the presence of the two C-S-H “shells” surrounding the PFA particle (top of the figure) is provided; a relatively porous region of fibrillar C-S-H (middle), surrounded by a much denser C-S-H region (below). A detail of this fibrillar region is presented in figure 4.

The uniformity of the microstructure surrounding the PFA particles is confirmed in the figures 5, 6, 7 and 8. In figure 5, the little dark block-like material in the dense outer shell of C-S-H represents possibly hydrogarnet or strätlingite, since the elemental spot-analysis points, besides at Si (from the PFA) and Ca (from the CH), at Al (from the PFA) and some iron (most likely also from the PFA); unfortunately, the analysis was only qualitative, since no stoichiometric “matching” analysis could be obtained. The material is in any case not amorphous. Rodger and Groves [17] were able to obtain diffraction patterns and quantitative microanalysis of similar material. Their results pointed at a silicious hydrogarnet phase with an approximate composition of C₁₂A₃FS₄H₁₆. It is important to note that both in this study, as well in the studies of Rodger and Groves [11];[16] the hydrogarnet regions are found within the original fly ash particle boundaries.

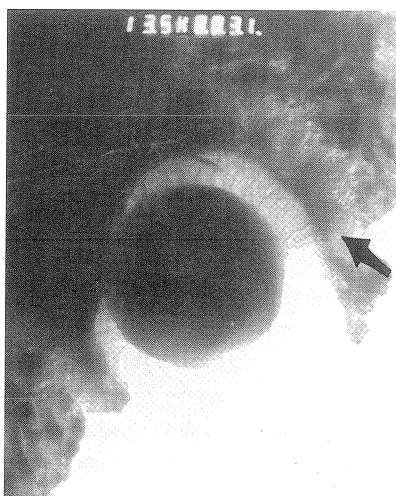


Fig. 1. Transmission electron micrograph showing a PFA particle surrounded by a reaction zone, consisting of radially fibrillar C-S-H, and a second dense rim of C-S-H (see arrow). Scale: 1 cm = 1 μ m.

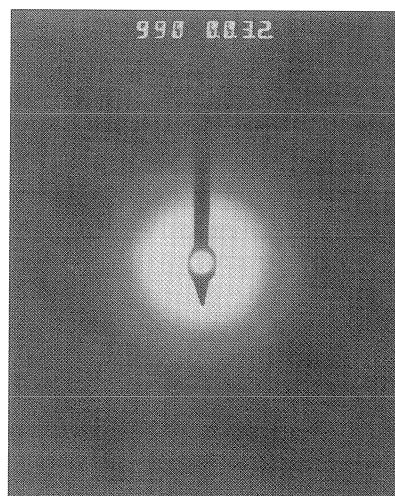


Fig. 2. Diffraction pattern of the fibrillar C-S-H. The material appears to be amorphous.

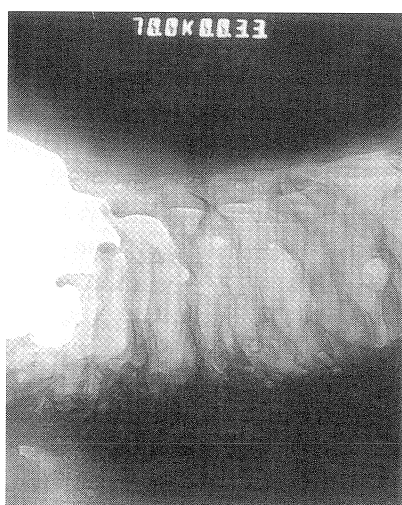


Fig. 3. Detail of figure 1, clearly indicating the presence of two "shells" surrounding the PFA particle (above); a relatively porous region of fibrillar C-S-H, surrounded by a much denser region. Scale: 1 cm = 200 nm.

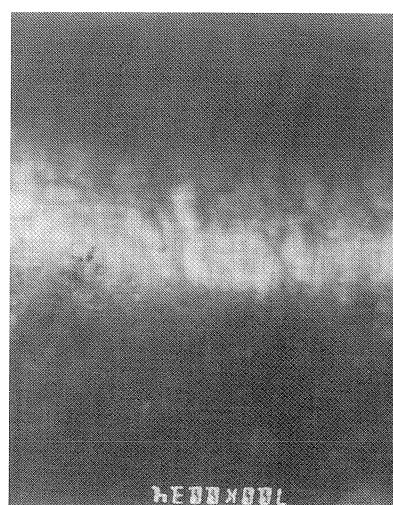


Fig. 4. Detail of the porous fibrillar C-S-H region of the PFA particle in figure 1. Scale: 1 cm = 200 nm.



Fig. 5. Detail of a large PFA particle (right) with a rim of porous C-S-H, and another denser rim, containing mainly C-S-H, but also two areas consisting of Ca, Si, Al and Fe (possibly hydrogarnet; see arrows). Scale: 1 cm = 600 nm.

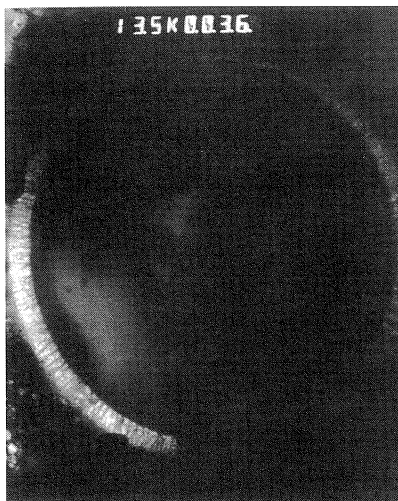


Fig. 6. Fibrillar zone surrounding fly ash particle. Scale: 1 cm = 1 μ m.

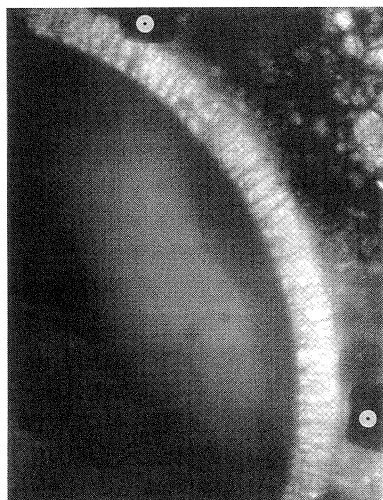


Fig. 7. Detail of the porous fibrillar C-S-H region of the PFA particle in figure 6. Note the denser region outside the fibrillar zone, containing clusters (hydrogarnet crystals) of Si, Ca, Al and Fe containing material (circles). Scale 1 cm = 700 nm.



Fig. 8. Detail of the reaction zone surrounding a PFA particle, clearly displaying a dense C-S-H outer zone (arrow), and a porous C-S-H inner zone. Scale: 1 cm = 500 nm.

The thickness of the fibrillar region(s) seems to vary between 300-1000 nm, t. The thickness of the denser outer region appears to be of the same order of magnitude, although this is more difficult to assess since this region (gradually ?) borders to the equally dense C-S-H from the Portland cement hydration. Figure 8, in which both the porous and the denser regions can be seen, provides an example. Ca/Si ratios in both reacted zones appeared to be similar to those found in ordinary Portland cement pastes, with ratios varying between 1.8 and 2. The outer zone contains somewhat more Al and especially K.

Rodger and Groves [11] discussed the observed “rhythmic precipitation” of C-S-H hydration products surrounding fly ash particles in cement paste. They argued that this effect is reminiscent of a “Liesegang ring phenomenon”. Such phenomena of rhythmic precipitation are observed in gels containing two diffusing species, which react if (locally) a specific critical supersaturation is reached [18].

In the case of reacting PFA glass particles, it may be assumed that upon “activation” of the fly ash the silicium concentration on or near the fly ash particle surface rises (the silicium originates from the fly ash). At the same time the calcium concentration in the cement paste pore solution will rise. Taken together, this will lead to a *local* supersaturation of Ca and Si resulting in the precipitation of (dense) C-S-H; such a process will occur when the pore water alkalinity will be sufficiently high in order to dissolve the fly ash glass. The C-S-H precipitation depletes the region immediately next to the precipitating C-S-H with Ca and Si. At some distance of the first precipitate a new (dense) C-S-H precipitate may be formed, provided that diffusion of Si and Ca has again provided local supersaturation (this process explains the observation of Rodger and Groves of rhythmic precipitation of dense C-S-H shells).

The observed “porous” fibrillar C-S-H is believed to be growing inward from the “dense” C-S-H in conditions of lower supersaturation, occupying the “empty” space between either the dense C-S-H and the fly ash surface or two dense C-S-H region. It is believed that such a process is indeed able to explain the observed local phenomena.

3.2 *Blast furnace slag cement*

The principal hydration products which are formed in blast furnace slag cements are essentially similar to those formed in Portland cement; C-S-H gel, CH, C_3AH_6 and AFt. Increasing slag contents will gradually result in the formation of C_2ASH_8 (incompatible with CH) and silicious hydrogarnets (see discussion in [19]).

It is well known that during the hydration of blast furnace slag cements, (a) layer(s) of in situ formed reaction product are deposited on the boundaries of the slag grains. Upon an initial rapid “burst” of reaction, a relatively dense rim of gel develops around the margins of slag grains. In course of time, the slag hydration reaction gradually slows down (the “dormant” period), and the rim will only gradually thicken.

Zonal structures may be formed within the rim, which may eventually crystallize. Electron-microscopy indicates that this progresses inward, towards the original slag centre [20]. In the near vicinity of the original slag grains, but outside its original contours, also reaction products may be formed. Cement hydration products, adjacent to slag, are usually readily distinguishable by their high Mg content, derived from slag. Feng et al. used the name cement hydration product (CHP) in order to distinguish the material from “ordinary” C-S-H [12]. The CHP appears to be relatively dense.

As typical newly formed hydration product in (Mg-rich) blast furnace slag cements hydrotalcite like minerals ($M_{4-6}AH_{10-13}$) have been identified (see summary in [21], p.282–287). Hydrotalcite is related to $(Mg(OH)_2)$ (brucite), in which some Mg^{2+} is replaced by Al^{3+} or Fe^{3+} , and where the charge balance is maintained by anions which occupy the interlayer sites. The hydrotalcite found by Feng and Glasser [13], appeared to contain some Si; they argued that the phase they found consisted of $Mg_3(OH)_2Si_4O_{10}$, talc, which they supposed was interlayered with hydrotalcite.

In this study, slag reaction zones, at the boundary of the original slag contours with the cement paste, are commonly observed. In figure 9, a typical TEM micrograph of a (small) slag grain is displayed; the numbers in this micrograph correspond to the chemical analysis, presented as oxide ratios, in table 1. Since it is not clear which of the two (visible) layers in figure 9 (or both ?) represents the originally formed gel-layer at the slag edge, the expression “outside- and inside edge” of the slag grain is used intentionally in the following text. Compared to the unhydrated slag, the slag interior (spot 3) is “enriched” with MgO with a factor three, and it also contains less SiO_2 and CaO. The Al_2O_3 content is approximately similar. The analysis of the “inner edge” of the slag (spot 1) indicates the presence of significantly less silicon and aluminium, slightly increased MgO and an approximately similar CaO, as compared with the original slag. The “outer edge” (spot 2 and 4) indicate an increase in CaO content, an approximately similar MgO content, and a decrease in SiO_2 and Al_2O_3 . Just outside the slag boundary (spot 5), the paste is marked by a significantly higher CaO, an approximately similar SiO_2 and a significant decrease in MgO and Al_2O_3 content. Taken together, these data clearly point to a net transport of Ca, Si and Al from the slag centre; magnesium seems to act as a chemical “goalpost”, as has been suggested by Feng and Glasser [13]. It is also evident that chemically different zones are formed, approximately at the position of the original slag boundary; apparently, these zones remain, once they are formed, at their place, and may act as (chemical) barriers or membranes (this will be discussed later on). Figure 10 provides a detail of figure 9, clearly displaying the zoned edge of the slag grain.



Fig. 9. Reacted slag particle. The figures indicate the number of the spot analysis.



Fig. 10. Detail of figure 9 (lower right corner). The zonal structure surrounding the slag particle is clearly seen.

In figure 11 it may be seen that the inner slag hydrate (ISH) indeed seems to have crystallized to well-formed platelets, presumably a hydrotalcite-like phase; no detailed analysis or diffraction pattern could be obtained. The apparent high internal porosity is noteworthy. Hydrotalcite is a hydrate phase which is known to be capable to be formed in water-deficient regions.

Figure 12 displays the X-Ray microanalysis maps of respectively Mg, Al, Si, S, Ca, Ti and Mn, as well as the TEM image. The relative brightness in these maps indicates the presence (white) or absence (black) of each element. From these element maps, it can be seen that indeed Ca and Si are relatively concentrated just outside of-, and also (probably) just within the original slag boundary. In between, an area with a relatively high Mg and Al content is visible; especially Al seems concentrated in this area. This area is clearly depleted with respect to Si and Ca. The slag interior is clearly depleted from Si and Ca, and consist mainly of Mg and some of the Al.

The typical backscattered image from a slag grain in a blast furnace slag cement in figure 13, hydrated for 90 days, also clearly points at the presence a chemically different zones. Their presence is commonly observed in blast furnace slags; thicknesses of these gel layers range from barely detectable at a few days, to 10-20 μm after about 1 year.

It has already been noted by Feng, Lachowski and Glasser [12] and Feng and Glasser [13], that there is an element transport (mainly Ca and Si) from the slag outwards into the paste, which results in the precipitation of the, relatively dense, CHP. According to Feng et al. [12], the inner zone of the slag (inner slag hydrate, or ISH) crystallizes to a hydrotalcite-like phase. This ISH phase consists of well formed platelets, clearly visible as a result of the high intraparticle porosity within this ISH. In their view, the process of porosification and paste densification should be considered as complementary. The element transport results in relatively porous, but isolated, areas formerly occupied by the interior of the slag grains, and a densification of the slag-cement paste outside the slag grains, resulting in an overall lowered permeability; the total porosity of the blast furnace slag cement pastes changes only little in this process.

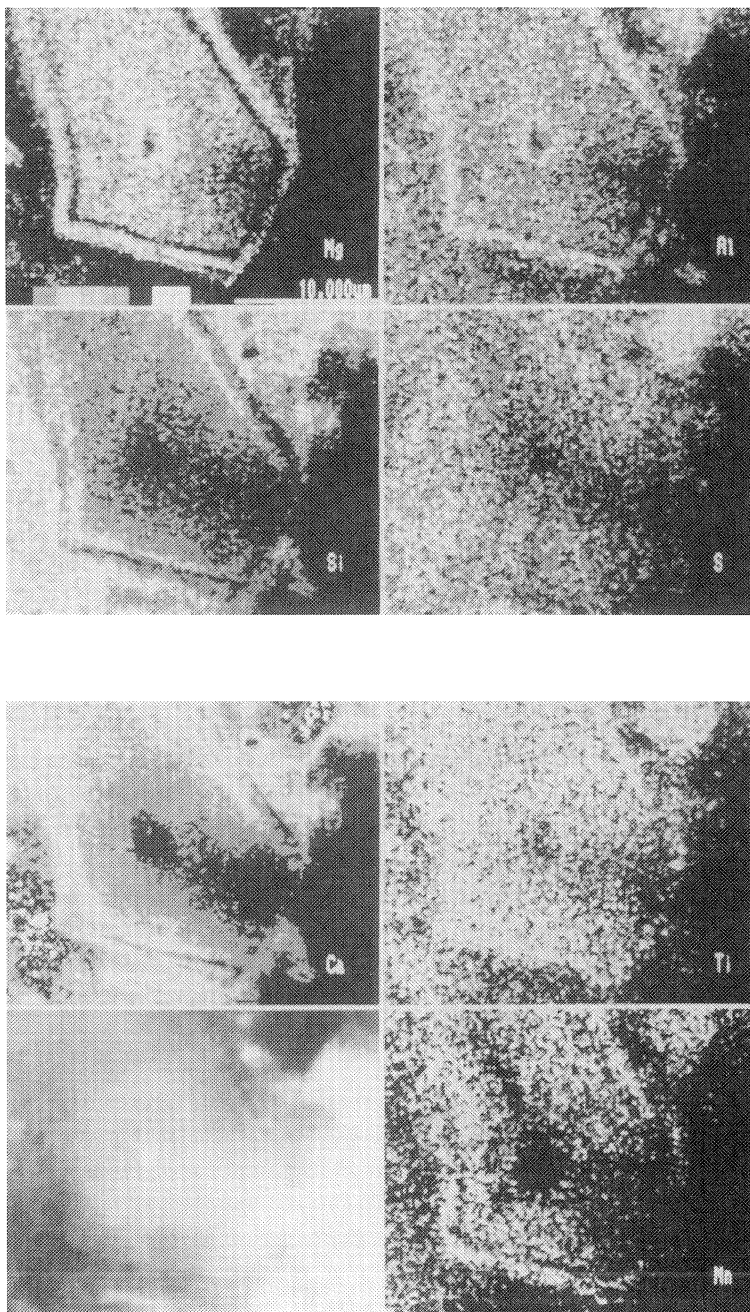


Fig. 11. Element map of the slag particle and rims, shown in figure 9. The zonal structure consists of rims of varying composition, with Mg, Al concentrated in an outside edge, and Si and Ca outside of the slag grain, as well as within an inner zone.

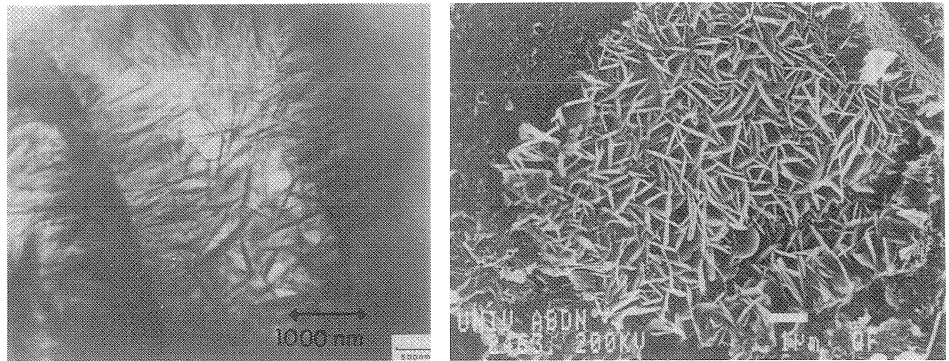


Fig. 12. Scanning Transmission Electron Microscopy micrograph of a well crystallized, hydrotalcite like phase, which has been developed within the original contours of a fully hydrated slag particle (ISH).

The transport of silicium into the cement matrix is not so surprising, since slags contain about twice as much silica as cement. The diffusion of calcium (and aluminium) from the slag into the cement matrix, however, requires a different mechanism, since both elements are already more concentrated in the cement paste, and their diffusion then appears to run contrary to thermodynamic expectations. Feng and Glasser [13] suggested a "driving force" as follows. In the early stages of hydration, water and hydroxyl ions diffuse into the slag glass, break the metal-oxygen bonds (e.g. Si-O-Si) and replace them by more complex (hydrogen) bonds resulting from hydrolysis (Si-OH...OH-Si). As a result, a relatively dense gel layer develops around the slag grain, with a thickness of possibly only 0.1 μm . Once this layer is established, any reaction can only continue by transport of water through the gel layer; it starts to act as a "membrane"¹. Across the membrane, a water potential gradient will be created: a high potential at the cement hydrate and pore water side, and a low potential at the side of the anhydrous slag. In order to lower the free energy of the system, ions will begin to migrate through the membrane into an area where they can form stable hydrates. So, Ca, Si and Al will begin to migrate outwards, while any water migrating inwards will be consumed directly for the formation of a hydrotalcite-like phase.

The presence of a "membrane" gel-layer may be used to explain the occurrence of chemically zoned areas at the slag edges. In this case it may be assumed that the Mg and Al rich layer (outside edge) represents the remnants of the original gel-layer, formed on the original slag-cement paste boundary. The Ca and Si rich layer just within this layer (inside edge) then represents an area in which some C-S-H like hydration products are formed, since it is likely that the water passing the membrane will also find some Ca and Si migrating from the slag centre. Once formed, this C-S-H will remain, and may function as a second barrier.

¹ The presence of a "membrane" points to an osmotic process, according to the normal definition. However, since (liquid) water is believed to be absent on the "dry" slag interior side, there will be no question of an osmotic driving force. Only the chemical potential of all species, including water, in the system will act as driving force.

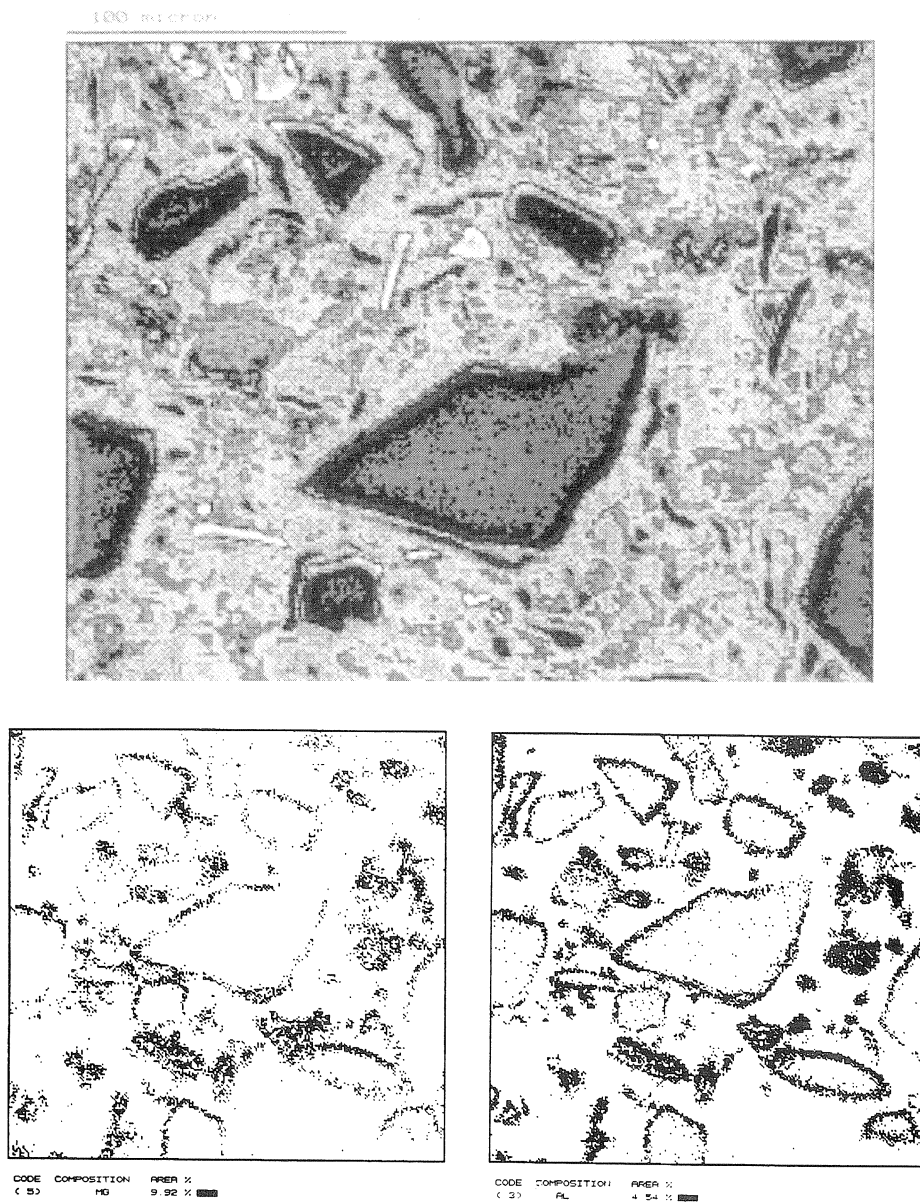


Fig. 13. Backscattered image of a reacted zone enveloping a slag grain in blastfurnace cement, hydrated for 90 days; differences in composition along the slag edge are clearly visible. The two smaller maps represent X-ray maps of respectively Mg and Al, and indicate the relative concentration of these elements at the slag edge, due to a diffusion of Ca and Si.

The most important question is of course the nature, chemically as well as physically, of this gel-layer. It is also not clear why such a layer is formed, and what conditions favour its formation. Which factors affect the diffusional characteristics; slag and / or cement composition, blend proportion, water content or curing regime ? And what microstructural changes may be expected in blast furnace slag cements with very high (or very low) slag contents ?

4 Conclusions

The following conclusions may be drawn:

- 1) With Transmission Electron Microscopy detailed information of the microstructure and the (crystal)chemistry of cement hydration products in blended cements may be obtained. Sample preparation procedures are essentially similar to those applied in geology, although the brittleness of the material prevents the use of very thin samples.
- 2) It has been shown that Portland fly ash cements C-S-H hydration products are being formed in concentric rims of low and high density around fly ash particles. In the dense region, tiny crystals, or crystal-clusters of phases containing significant amounts of alumina are present; it is likely that these represent hydrogarnet or strätlingite. The observed "porous" fibrillar C-S-H is believed to be growing inward from the "dense" C-S-H in conditions of lower supersaturation, occupying the "empty" space between either the dense C-S-H and the fly ash surface or two dense C-S-H region. The formation of the concentric C-S-H rings surrounding fly ash spheres may be explained as a Liesegang-type ring mechanism, due to precipitation of C-S-H in alternating periods of high respectively low Ca and Si supersaturation. The dense C-S-H appears to be somewhat enriched in Al and K, relatively to the fibrillar C-S-H.
- 3) Slag grains display a distinct outward elemental migration, notably of Si, Ca, and Al. The slag "centre" becomes enriched in magnesium and a hydrotalcite-like phase may develop as an inner slag hydrate. The driving force for this elemental migration is believed to be caused by a postulated gel-layer, which is formed during the initial slag hydration. This gel-layer will act as a membrane, which limits elemental transport, and which creates a water potential gradient between the "wet" cement paste and the "dry" slag interior. Si and Ca will precipitate outside (or possibly just within) this gel-layer, and form C-S-H (like) reaction products. Precipitation outside of the slag will cause a densification of the cement-paste, lowering the porosity, a common feature of blast furnace slag cements. Precipitation within this gel-layer may cause additional zoning, as observed in this study.
- 4) Transmission Electron Microscopy typically provides information from local areas within a cement. Obviously, more research with TEM is needed to investigate if the observed phenomena are common features, and if so, to relate the observed hydration mechanisms with data (and models) on blended cement performance, such as permeability.