Nanoscale Characterization of Hydration Processes by means of High Resolution Scanning Electron Microscopy Imaging Techniques

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Abstract: In order to characterize nanoscale structures which develop through dissolution-precipitation processes as well as through nucleation and growth of hydrates various high-resolution scanning electron microscopy imaging techniques were used. The investigations were carried out on pure C_3S and OPC. Furthermore, ultra-high performance concrete (UHPC) was investigated. In the early state of hydration the ESEM-FEG was used. By optimizing the system Peltier cooling stage/ sample holder the imaging deficiencies in the ESEM-WET mode that occurred in the past could mostly be eliminated. The achievable resolution is now 2 nm at 30 kV accelerating voltage and even better as far as fully hydrated samples are concerned. In order to be able to achieve a detailed image in very dense microstructures (e.g. UHPC) an optimizing of contrast becomes necessary. For this purpose a FEG-SEM with low vacuum imaging capabilities was deployed. High resolution (e.g. 1.8 nm at 3 kV) in low voltage mode (between 1 to 4 kV) and low vacuum water vapor atmosphere without partial charge build-up can be achieved with a helix detector when the magnetic immersion lens technology is connected with the ESEM technology. ESEM investigations show that syngenite is formed as an intermediate phase during the early hydration of cements which have a high content o f alkali sulfates (water soluble K_2O). This was confirmed by cryo-SEM investigations.

1. Introduction

The properties of cementitious binders such as workability, setting behavior, regification, strength and durability depend directly on the hydration process. In order to understand the relations between material properties and material formation processes one has to understand the multiscale heterogeneous structure which is created. Water does not only play an important role in the hydration process but also with respect to the durability of cement-based and other materials. Furthermore, water or pore solution are essential components within the microstructure of cementitious systems being the materialistic bracket over all observation levels – from the centimeter size grain down to the mesogel pore range of a few nanometers.

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By means of high resolution scanning electron microscopy this range can be imaged and investigated continuously (7 magnitudes in the length scale). In this context ESEM technology in connection with high resolution electron microscopy is especially important since water vapor can be used as gas in the sample chamber (ESEM-WET mode). Thus, water containing structures and phases can be investigated without sophisticated preparation i. e. in the native state which allows the observation of dynamic processes such as crystallization, dissolution, hydration etc., as well as in-situ investigations on samples which are exposed to micro mechanical stresses. In contrast to investigations in high vacuum SEM only marginal sample preparation is required for ESEM-WET mode investigations. This leads to only little formation of artifacts.

In applied electron microscopy artifacts are defined as image information which is not caused by the object properties but by preparation or imaging processes. With the number of preparation steps increasing the number of possible artifacts increases, too. Artifacts like the formation of artificial structures, the modification of the morphology and chemical composition of individual phases as well as the destruction of the lattice structure may lead to serious misinterpretation of the results when are considered to be part of the object [1].

But not only artifacts caused by preparation can lead to object modifications and thus to misinterpretation but also beam damages can be responsible for characteristical changes. Those changes are either primarily caused by interaction of the electrons with the molecules (radiation damage) or heat generation through interactions of the electrons with the sample atoms (thermally induced damage) or both. Special contrast phenomena as well as inadequate imaging and analysis conditions can produce errors, which result from the interaction of the electron beam with the sample.

In ESEM-WET mode in which wet samples are investigated there is a danger that precipitates in amorphous and/or crystalline form remain on the surface. These precipitates are created from the liquid phase in which different ions are solved. Therefore it is also important to produce a fresh fractured surface by means of a micromanipulator during the examination of the samples in the microscope.

The following sections illustrated by means of some selected examples how it becomes possible to increase the information depth by the combining the different electron microscopic techniques and other physical methods The method combination described here makes it possible to link morphological, chemical and structural material characteristics to each other. Considering those experimental and physical characteristics of the individual methods makes it possible to make clear statements. Artifacts and beam damages which particularly occur in aqueous samples become obvious and measures to avoid them are described.

2. Is high resolution imaging in the ESEM-WET mode possible ?

It is often said during congresses or in publications dealing with electron microscopy and especially ESEM technology that it is not possible to achieve high resolution imaging in ESEM-WET mode: “The ESEM is not a high resolution machine …” [2]. Contrary to this statement our investigations show that the resolution of 2 nm for ideal test samples (gold on carbon specified by the microscope manufacturer [FEI Company]) can also be achieved with non-ideal specimens such as samples in completely hydrated state. This high resolution can even be achieved using an analytical working distance of 10 mm at a pressure of 13.6 mbar in a water vapor atmosphere.
In order to investigate samples in the ESEM-WET mode at a relative humidity close to 100 % a Peltier stage must be used to cool the samples. Using the Peltier cooling stage makes the microscope more vulnerable to mechanical vibrations and acoustical noise, so that the high resolution imaging is negatively affected. These imaging problems already occur at a magnification factor of 25,000. The flow of the water which is required to cool the Peltier stage for low temperature investigations (< 10 °C) intensifies the vibrations even more.

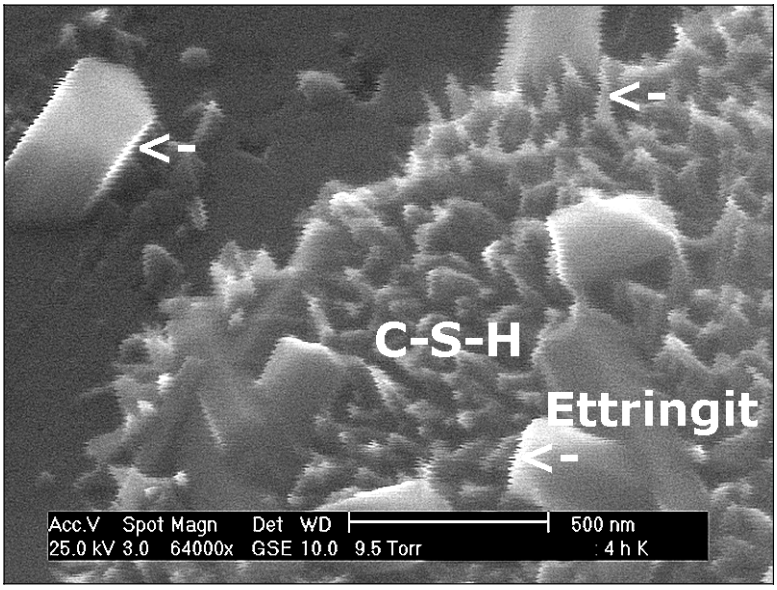

Fig. 1:

ESEM-WET mode: OPC after 4h hydration time, visible vibrations when Peltier cooling stage is used, oscillation amplitude approx. 15 nm

In Figure 1 showing a cement paste sample in the early hydration state the vibrations become visible especially strongly at the crystal edges (see arrow in Fig. 1). The oscillation amplitude of the vibrations is approximately 15 nm. The use of free magnification factors beyond 100,000 without such deficiencies is a must in order to investigate phenomena such as nucleation, dissolution and precipitation processes in detail. These processes are taking place during hydration, carbonatization and phase transformation of hydrate phases.
By optimizing the Peltier cooling stage and the sample holder we succeeded in minimizing the vibration problem. Thus, a significant

improvement in the image quality could be achieved and it is now possible to image samples in their native state in completely hydrated conditions at a working distance of 10 mm (water vapor atmosphere near 100 % relative humidity).
The comparison of Fig. 1 and Fig. 2 at the same magnification factor on a similar sample proves that by means of the above mentioned measure the vibrations on the crystal edges could be minimized or even eliminated.

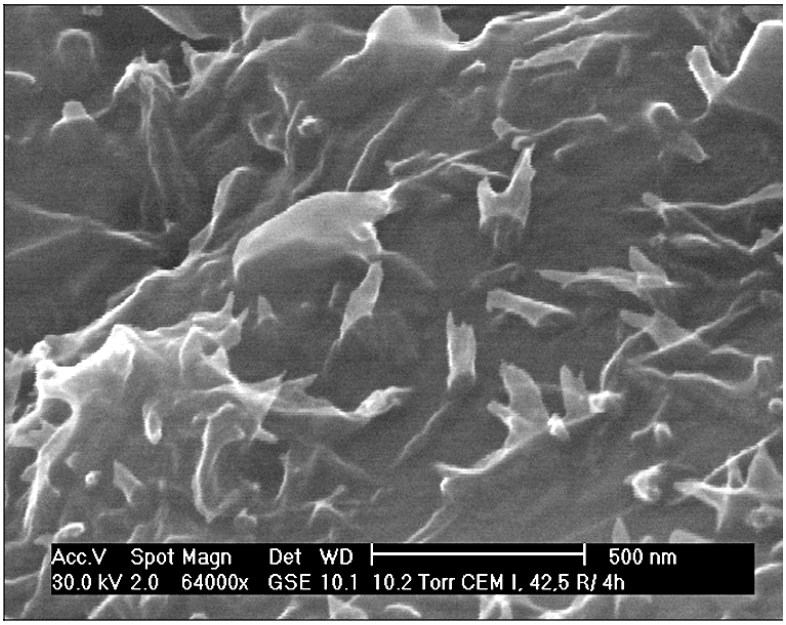

Fig. 2:

ESEM-WET mode: OPC after 4h hydration time, minimizing the vibrations by modification of the sample holder in connection with the Peltier cooling stage (compare Fig. 1), the oscillation amplitude is now smaller than 1.5 nm

The electron micrographs in Fig. 3 and 4 show details using a higher magnification factor of the same sample area shown in Fig. 2. Up to a magnification factor of 100,000 no vibrations on the crystal edges are evident. Only with an enlargement factor of 200,000 and above vibrations on the crystal edges become visible in the form of "indentations" with an amplitude of approximately 1.5 nm (see Fig. 4).
During the early hydration process of cementitious materials it is possible to image the microstructure in detail at high accelerating voltages. With the hydration process progressing it becomes clear, however, that the formed hydrate phases which have a comparably low density (1.7 g/cm^3 for ettringite and approximately 2.2 g/cm^3 for C-S-H phases) are strongly penetrated by the incident electrons at high accelerating voltages between 20 and 30 kV which are necessary for high gas pressures in the sample chamber of the ESEM. Through crystal formation and growth during the hydration process the microstructure becomes more and more dense. In the ESEM-WET mode the high gas pressure in the sample chamber causes a significant scattering of the primary electron beam. The gas atoms scatter the electrons away from the high resolution focus. The scattering phenomenon has been labeled “beam skirting”. Furthermore, the amount of beam electrons that are scattered depends largely on the type of gas, the beam gas path length and the accelerating voltage. By

increasing the beam energy the scattering effect becomes smaller (ceteris paribus) and the signal to noise ratio and thus the resolution improves.

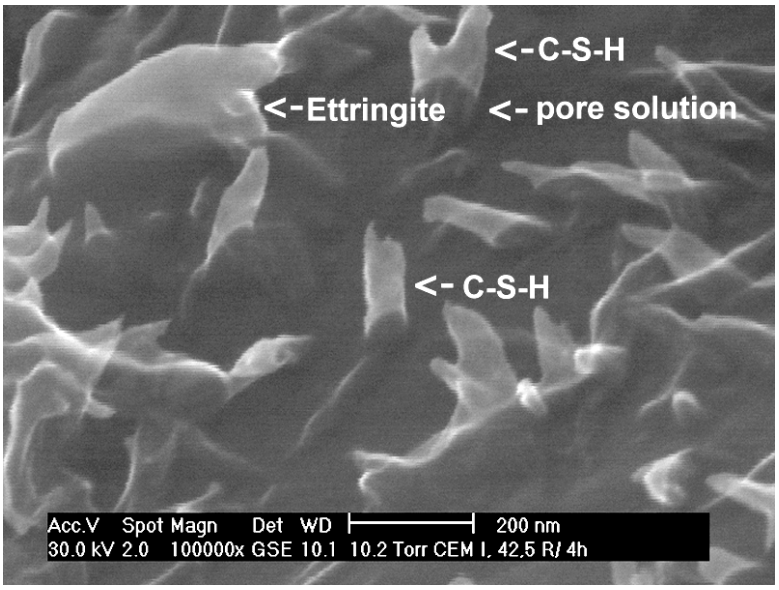

Fig. 3:

ESEM-WET mode: OPC after 4h hydration time, high resolution image by means of modified sample holder: C-S-H – nucleation process, Ettringit (200 nm) and pore solution

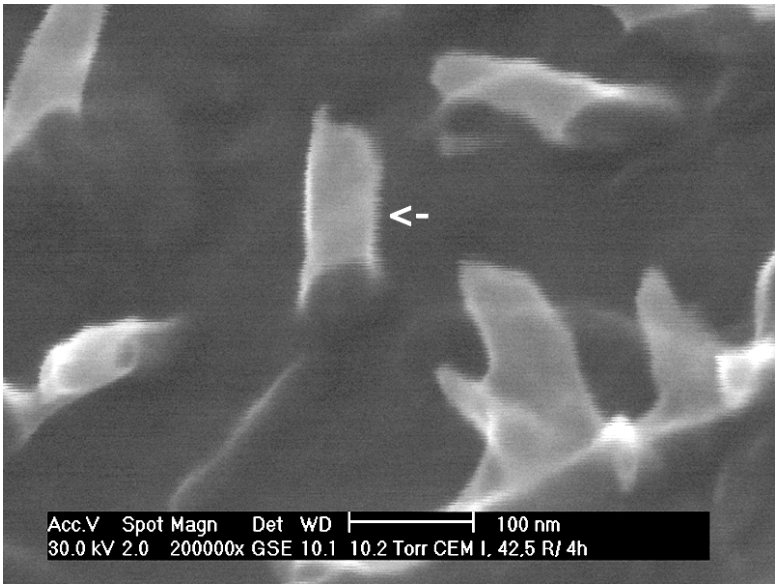

Fig. 4:

ESEM-WET mode: OPC after 4h hydration time, high resolution image by means of modified sample holder reduction of oscillation amplitude smaller than 1.5 nm, C-S-H nucleation process and pore solution

On the other hand the surface contrast gets almost completely lost and certain structure components cannot be imaged clearly although the resolution is high. As Fig. 5 shows the formed structure components appear “diffuse” and not very high in contrast at a high accelerating voltage. In this case a detailed visualization is only possible using high resolution imaging in low accelerating voltage mode (see the following section). Pore solution covers the needle-like C-S-H phases and creates very thin films (thickness smaller than 10 nm) in the cement stone structure. Only through optimization of the beam voltage (smaller than 1.5 kV) we can clearly distinguish between the C-S-H phases (approx. 50 nm)

and the pore solution in the cement stone structure. The scattering volume of the electron beam at an accelerating voltage of 1 kV is only 23 nm (e. g. in tobermorite). The C-S-H phases appear consequently dark and the very thin pore solution films in the C-S-H structure appear bright (see Fig. 6).

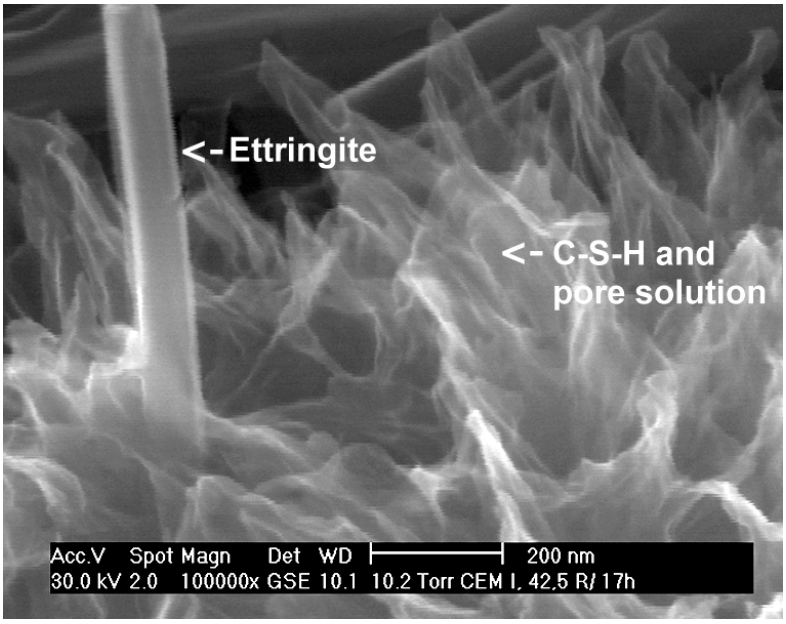

Fig. 5: microstructure of OPC hydration after 17 h, hydration progress is determined by the longitudinal growth of the ettringite (up to 2,5 µm) as well as the C-S-H phases loss of surface information due to high beam energy of 30 keV

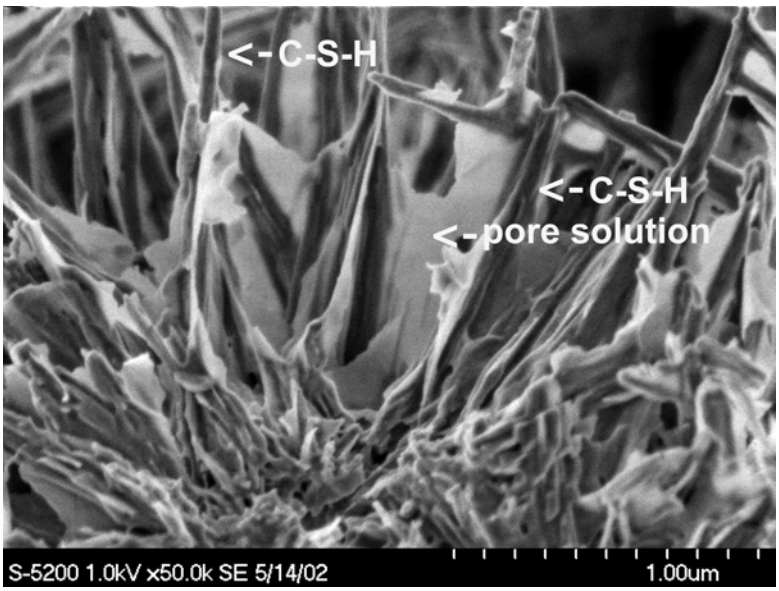

Fig. 6: The needle-like C-S-H phases are covered by pore solution (mainly KOH). The dried pore solution creates very thin films (< 10 nm), such microstructure is only visible by decreasing the beam energy to a value smaller than 1 keV

The indication that these thin films are pore solution indeed can only be given indirectly by comparison of the microstructures of C_3S hydrated with and without synthetic pore fluid (main component KOH). If one replaces such pore fluid with distilled water no such films occur [1]. These thin films have such a tiny dimension that they cannot be analyzed by means of energy dispersive X-ray spectrometry (EDS).

As with biological specimens in "Life Science" the achievable resolution dependents not only on the microscope properties but it is also limited by beam damages (radiation damage at high charge density) [1, 3 – 5]. The comparison between Fig. 7 and Fig. 8 shows that it is possible that the C-S-H phases are strongly damaged in ESEM-WET mode under high resolution conditions, especially when exposed to a high electron intensity (high probe current of 150 pA is equivalent to the charge density of 0.8 C/cm^2). It is clearly visible that the parallel aligned C-S-H phases with a thickness of sometimes only 20 nm show a formation of a “diffuse mass” caused by beam damage. The rise of the specimen temperature results in an irreversible thermally induced damage.

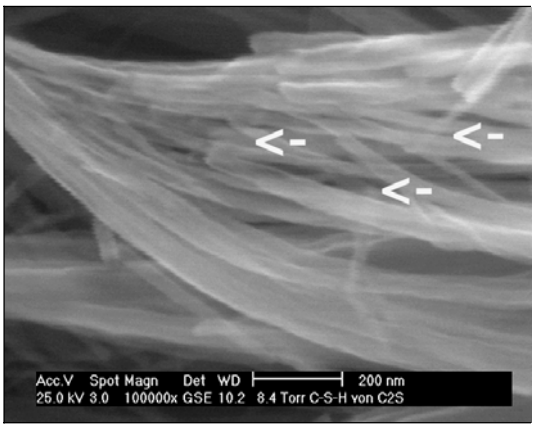

Fig. 7: high resolution image in ESEM-WET mode: bundles of C-S-H phases before radiation damage: diameter of the individual fibers between 20 - 50 nm

Fig.8: same sample area as Fig. 7: “melting” of the C-S-H nanofibers through exposure to an electron beam of 150 pA beam current (is equivalent to the charge density of 0.8 C/cm^2)

This phenomenon is well-known from our comparative investigations for the clearing-up of preparation artifacts which are necessary for imaging such samples with the conventional SEM. For example, the thermal radiation under vacuum conditions during evaporating carbon or heavy metal on the sample surface leads likewise to such melting phenomena [6]. Particularly endangered are high and thin burrs or phases with fibrous habit (e.g. C-S-H phases).

3. High resolution at low beam voltage conditions in low-vacuum mode

Compared to the high beam energy investigations, low beam voltage conditions (low-kV mode) in a SEM or ESEM provide the following advantages: better secondary electron images (compare Fig. 5 with Fig. 6), higher electron spatial resolution, higher X-ray spatial resolution, less

penetration of the electron beam, better X-ray emission for light elements, less damage as well as less charging of the sample.
For the investigations in the low kV mode a FEG-SEM (Nova NanoSEM, FEI Company) with imaging capabilities in a water vapor pressure up to 1.3 mbar in the sample chamber was deployed. High resolution (e.g. 1.8 nm at 3 kV on ideal samples such as gold on carbon) in low voltage mode without partial charge build -up can be achieved by means of a helix detector when the magnetic immersion lens technology is connected with the ESEM technology. The combined effect enables ultra-high resolution, low-vacuum characterization capabilities. By means of this type of microscope it becomes possible to choose excitation conditions for non-coated and non-conductive samples in such a way that contrast rich imaging as well as spatial resolution in the microanalysis can be optimized. This method enables us to see structures in ultra-high-resolution which are not evident using conventional SEM or ESEM. As the micrographs in Fig. 9 and Fig. 10 show microscopy with optimized electron energy is especially helpful when extremely dense structures for example ultra-high performance concrete (UHPC) is to be imaged.
Furthermore, the imaging in low vacuum mode is not hindered by charge build-up as occurring in high vacuum conditions even at very low accelerating voltages of several hundred volts. Figs. 11 and 12 show the same object area showing a C_3S grain with hydration rim. Fig. 11 shows it in high vacuum at very low voltage of 800 volts whereas Fig. 12 shows it in low vacuum mode at 4 kV imaged by means of a helix detector with the Nova NanoSEM. In direct comparison (see arrows) it becomes clear that relevant structure details get lost because of partial charge build-up in high vacuum especially in the interface area between the grain and the hydration rim. Generally there is a loss of depth of focus to be noted in high vacuum.

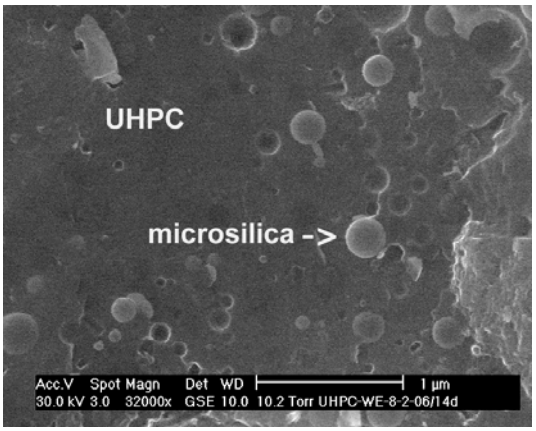

Fig. 9: ESEM-WET mode: micro-graph of the dense microstructure of UHPC at U_0 = 30 kV: loss of surface contrast

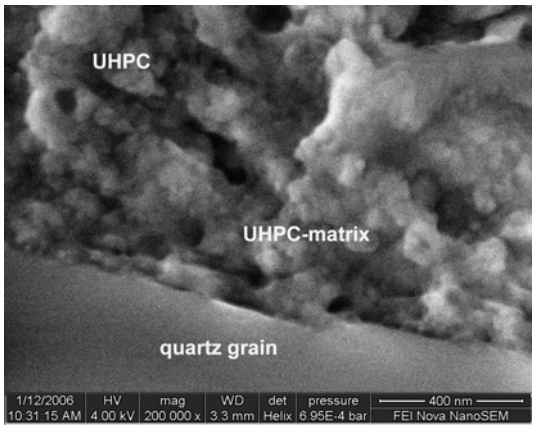

Fig.10: same sample but not the same area as Fig. 9: Nova NanoSEM with helix detector at U_0 = 4 kV, high resolution in low vacuum

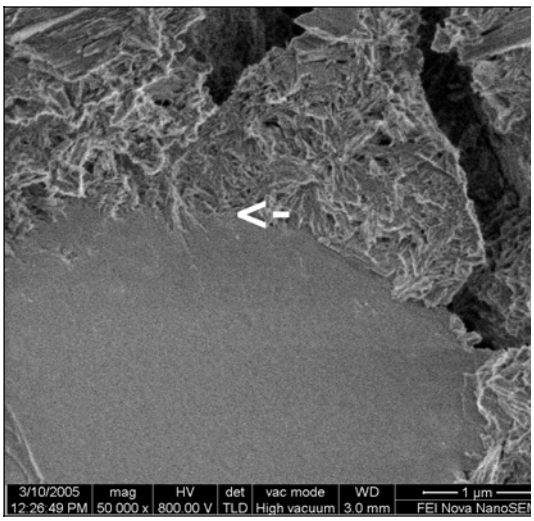

Fig. 11: C_3S grain with hydration rim: low voltage mode, U_0 = 800 V in high vacuum, partial charge build-up, loss of depth of focus (see arrow)

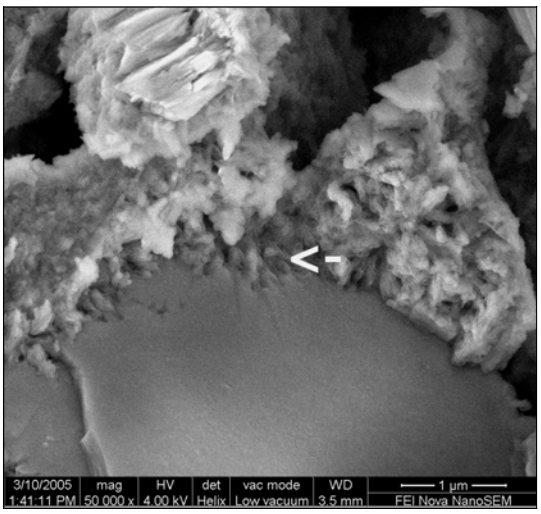

Fig.12: same area as Fig. 11: but imaging in low vacuum mode by means of helix detector, U_0 = 4 kV, clear separation of compact hydration rim and dissolution structure

4. Syngenite formation during the early OPC hydration - Only an ESEM artifact? - Investigations by means of cryo-SEM

ESEM investigations of alkali-rich OPC, i.e. cement with a high portion of arcanite, in the early hydration stage show syngenite crystals with long prismatic habit. Because in the past the XRD Rietveld analysis was not so developed syngenite could not be measured since it is often near the detection limit. It was therefore assumed that the formation of syngenite during early hydration process could be an artifact, which is caused by the local super saturation of the highly concentrated pore solution in the ESEM investigations.

The cryo-SEM technique is well established in "Life Science" investigations of water containing samples in high vacuum. The highly concentrated pore solution of the OPC can be freezed by the cryo preparation (shock freezing in liquid nitrogen at approx. –200 °C), so that the formation of amorphous and/or crystalline precipitates is excluded which can appear in the ESEM-WET mode as an artifact. The following freezing fracture permits the direct view on the structure of the frozen object. By this preparation method a subsequent crystallizing of syngenite can be excluded. A comparison with ESEM images shows that the same long prismatic crystals (lath-like habit) are formed which can be identified by means of EDS as syngenite [7]. The visualisation of the double salt syngenite can therefore be taken as a direct proof for the actual occurrence of this phase. Fig. 13 shows the freezing fracture of an alkali-rich OPC after a hydration time of 10 minutes before the sublimation process and without sputtering at a temperature of -120°C. The following

phases in the deep frozen microstructure are clearly visible: ice, ettringite (short prismatic habit) and syngenite (long prismatic habit).

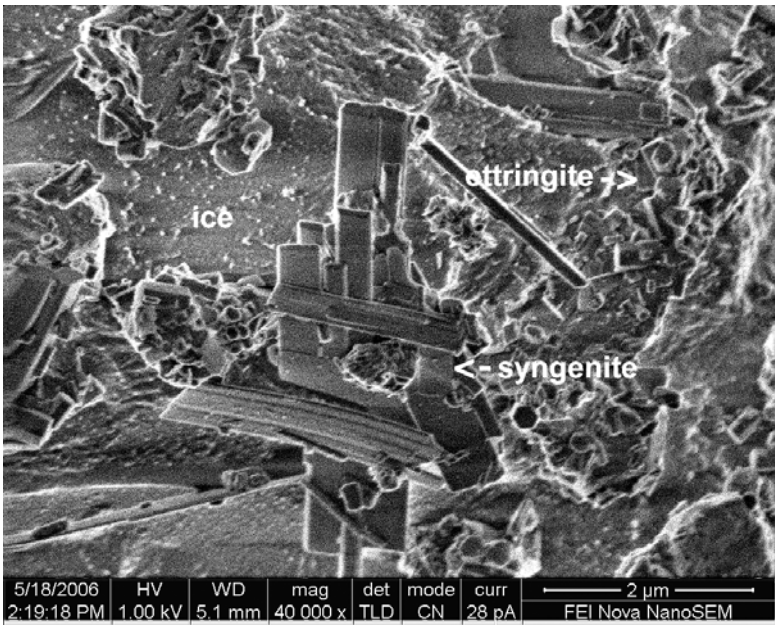

Fig. 13: Inner surface of an high-alkali OPC (10 min hydration time) after mechanical breaking of the deep frozen sample before the sublimation procedure (ice, syngenite and ettringite are clearly visible), without sputtering, in low voltage mode – 1 kV

Then the temperature of the frozen sample was increased to –90 °C and it was exposed to the in-situ sublimation procedure in the sample chamber of the microscope. The micrograph in Fig. 14 shows the microstructure after the sublimation process. Again you can see long prismatically formed syngenite crystals in the frozen microstructure.

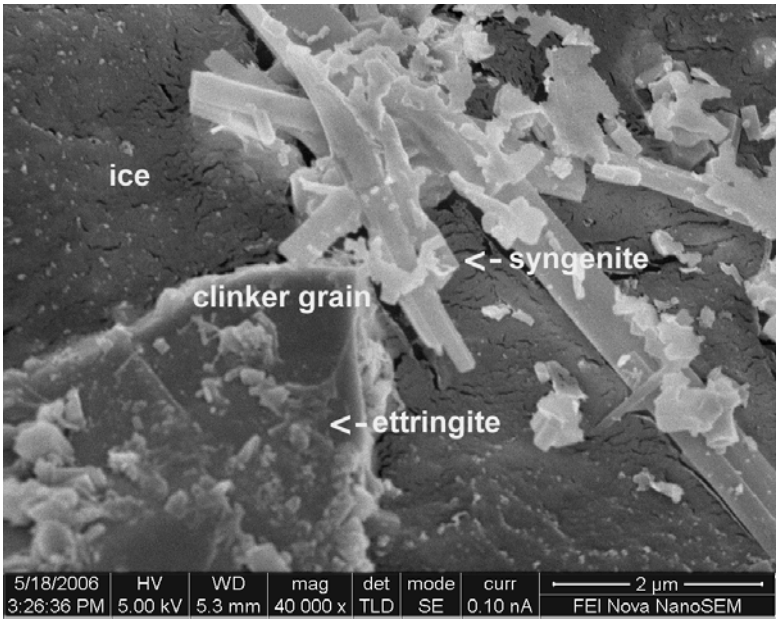

Fig. 14:

Inner surface of the deep frozen sample after the sublimation procedure in the SEM [direct observation of the sublimation process of ice]. Ice, syngenite and ettringite are clearly visible.

By means of cryo-SEM investigations it was revealed that syngenite is formed during the early hydration of an alkali-rich OPC. Thus, it can be

excluded that syngenite observed by ESEM is an artifact. Furthermore, temporary syngenite formation was proven by XRD Rietveld investigations and computation of saturation index in the aqueous phase of cement paste [8]. In addition it was shown that already minor contents of syngenite diminishes the fluidity of cement pastes and concretes significantly [9].

Conclusions

A considerable improvement of information depth in the field of cement-based materials could be achieved by combing different high resolution electron-optical techniques.
By optimizing the system Peltier cooling stage / sample holder we succeeded in minimizing the mechanical vibration problem in ESEM-WET mode. Thus, a significant improvement in the image quality could be achieved. Now it is possible to characterize “wet” samples in their “close to native” state in high resolution imaging mode.
The deployment of FEG-SEM with helix type detectors permits a detailed and high-contrast imaging of very dense microstructures e. g. ultra-high performance concrete. This microscope enables high resolution imaging capabilities in a low vacuum water vapor atmosphere at low acceleration voltages useful for charging and water containing material.
By means of cryo-SEM investigations it could be proved undoubtedly that the temporary syngenite formation during the early hydration of OPC with a high content of alkali sulfates (water soluble K_2O) is not an ESEM artifact.
From the ESEM investigations can be derived that the C-S-H phases occurring during the hydration process of OPC or C_3S in the outer hydration rim show always the same fibrous habit. These phases are very sensitive to electron radiation. Thus, the lattice structure, as well as the morphology, is destroyed when the charge density is too high. That means that phase “amorphisation” takes place through the measuring process. By means of electron diffraction pattern experiments in the cryo-TEM at very low electron doses the crystalline nature of these individual fibrous C-S-H phases could be proved undoubtedly [10].

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