

# **Cryotransfer Scanning Electron Microscopy on Cementitious Systems: Applications and Examples**

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## **1 Introduction**

The Scanning Electron Microscope (SEM) is used for investigations on cementitious materials for a long time [1-3]. It is possible to analyze hardened cement, mortar or concrete as well as cement powders or polished clinker grains with very different methods of SEM investigations. Problems arise if we want to study the early hydration processes especially within the first 24 hours of reaction. Because of the high water content it is of course not possible to analyse these not hardened samples without a formation of artefacts at normal SEM conditions. Previously hardened cementitious specimens also can show high vacuum or electron beam heat sensitivity. For example, the dehydration of water-containing hydration products might occur [4].

With the cryotransfer technique it is possible to set liquid, beam and vacuum sensitive specimens into a stable state by shock freezing. Thus this method enables an adequate preparation of cement pastes with high water content and hardened cement, mortar or concrete with vacuum sensitive phases. This preparation method in combination with high resolving SEM enables high-resolution images of hydrating cement pastes and also an extensive characterisation of the microstructure within the samples. Therefore cryotransfer SEM (also called low-temperature SEM) is an alternative or additional method to the established environmental SEM (ESEM) investigations [4-14].

This article describes possibilities, gives examples of ongoing investigations and discusses and summarizes advantages and disadvantages of the advanced cryotransfer preparation.

## **2 Methods and Samples**

All SEM analyses were done with a Leo 1530VP from Carl Zeiss SMT with a field emission gun. The SEM enabled high resolution imaging and the variable-pressure mode (VP) allowed a variation of the chamber N<sub>2</sub> gas pressure between high vacuum and 100 Pa. The SEM was equipped with an EDS, type PHOENIX from EDAX Microanalyses and with a Gatan Alto 2500 cryotransfer-unit.

Further investigations were necessary for the exact identification of several hydration products. These analyses were done by in-situ X-ray diffraction (XRD) with a PANalytical X-Pert Pro system with X'Celerator high speed detector.

All samples were hydrating cement pastes from 1 minute to 24 hours hydration time. They were prepared with water-cement ratios between 0,35 and 0,40. Temperature and relative humidity during the hydration reactions were between 20 °C and 22 °C and between 93 % and 97 %. Two different kinds of cements were used for the investigations. The first group consisted of some ordinary Portland cements (OPCs). The second group consisted of two different rapidly hardening cements. They were Portland cement based special cements with low quantity of additives (<2%) and are used for special spraying methods. The first was a rapidly hardening cement (SC), the second was a high sulphate resistant rapidly hardening cement (HSSC).

#### Cryo-Transfer-Technique:

First step of the cryo preparation is the placement of a well mixed cement paste specimen on a special sample holder. To guarantee a fast and homogenous freezing process small samples have to be taken. Rivets with 0.5 mm to 2 mm diameter enable a good and reproducible preparation.

Next step is the storage of the samples under defined conditions. These free selectable hydration conditions are one of the main advantages of this method. Each kind of hydration condition, e. g. high temperature or high pressure, and each hydration time down to 20 s can be realized with quite simple technical equipment. It is also possible to prepare the samples after the storage but this procedure might destroy the formed microstructure and cause artefacts.

The shock freezing terminates the storage period and stops all reactions within the cement paste. Therefore sample holder and specimen have to be brought into a cryogen very quickly. The process is called Plunge-freezing because of plunging the sample manually or mechanically into the cryogen. Other methods like Spray-freezing, Jet-freezing or High-pressure-freezing should be mentioned here also [15]. To get a high heat transfer by using the Plunge freezing it is necessary to use subcooled or melting cryogens for the freezing process. Possible are e. g. Ethanol, Propane or Nitrogen [15]. The shock freezing is necessary to avoid the crystallisation of water and the orientation of particles.

Afterwards the frozen sample has to be transferred to the cryo preparation unit, which is directly connected to SEM chamber by a valve. After this action, time is no longer a critical factor because preparation unit as well as SEM stage are cooled to about -170°C and stand at high vacuum. So the cement paste specimen stays in a stable state and no water loss, dehydration effects or further hydration occur [4].

The equipment of the preparation unit enables a brittle fracture of the frozen cement paste to eliminate disturbing surface effects or contaminations and to lay open the internal structure of the specimen. The sublimation process is necessary to uncover the cement grains and hydration products which are surrounded by frozen water. The sample has to be transferred into the SEM chamber. To start the sublimation conditions of 10 Pa to 50 Pa N<sub>2</sub> gas pressure and -80 °C to -120 °C temperature are required. The already mentioned VP mode and the low-temperature-stage of the SEM enable these settings. The whole process could be controlled online with the MPSE-SEM (multiple pressure secondary electron) image. A sputter coating at the preparation unit finishes the preparation.

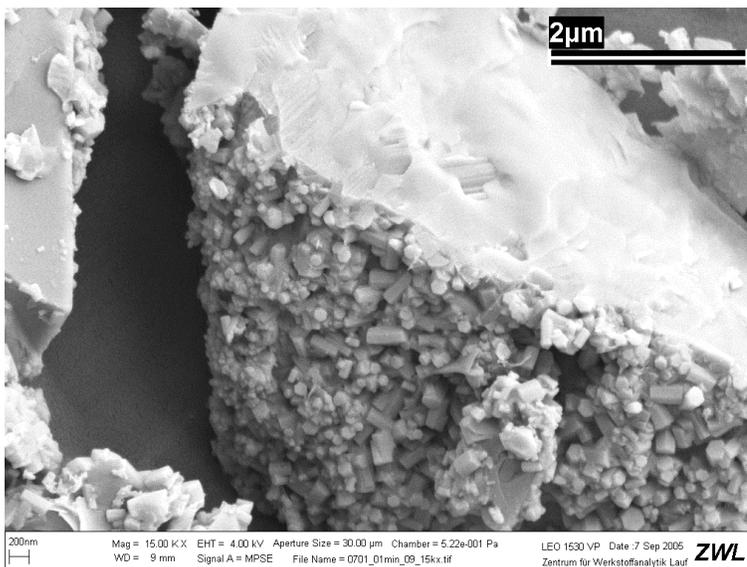
Au, Pt, Cr and different Au/Pd alloys were tested as sputter targets. Finally best results and image quality were received with the Au/Pd alloys. Especially the brittle fracture and the sublimation process require practical experience and depend on the skills of the operator. In every case the parameters of the sublimation process (temperature, pressure, time) need to be adapted to the attributes of the sample (e.g. w/c ratio, specific surface).

Further information about the cryotransfer procedure, the freezing process and possible artefacts are given in references [4,15,27].

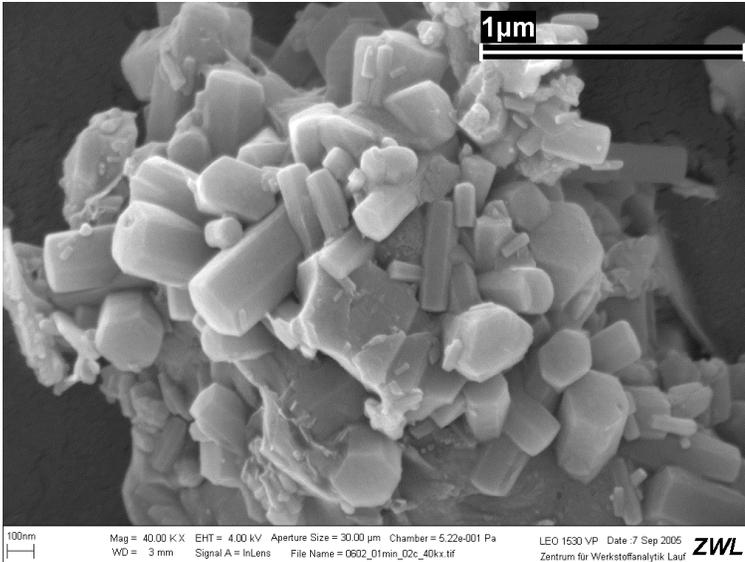
### 3 Results and Discussion

#### 3.1 Early hydration products

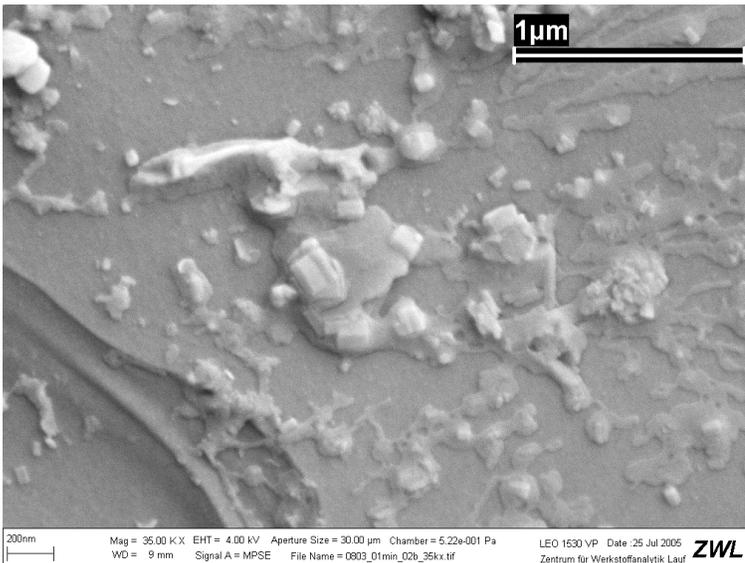
One of the challenges of this work was the imaging of the very early hydration products which form within the first seconds after mixing the cement paste. Figures 1a/b/c show some examples of different OPCs (all CEM I 52.5 R) after 1 min hydration time.



*Figure 1a:  
Cryotransfer-SEM  
image of OPC  
after 1 min  
hydration time;  
broken cement  
clinker grain;  
surface covered  
with ettringite  
crystals*



*Figure 1b:  
Cryo-transfer-SEM  
image of OPC  
after 1 min  
hydration time;  
dense layer of  
ettringite covering  
a clinker grain*



*Figure 1c:  
Cryo-transfer-SEM  
image of OPC  
after 1 min  
hydration time;  
surface of a clinker  
grain; growth of  
the first ettringite  
crystals*

All investigated cements showed spontaneous ettringite formation already after 1 min hydration time. Figure 1a shows a broken clinker grain with its fractured surface at the upper side. It is an important indication for well done preparation work, that this surface generated by brittle fracture shows no kind of contamination. By contrast the non broken surface shows a dense layer of ettringite covering big parts of the grain. At the background the lowered water surface is recognisable. Figure 1b shows a covered area at high magnification. All crystals built up short prismatic, hexagonal morphology with varying length to diameter ratios. Crystal sizes were between 50 nm and 500 nm diameter. Other grains showed almost blank surfaces or very small ettringite crystals, with particle sizes down to about 20 nm. If Fig 1c shows a kind of precursor or gel-like phase around the ettringite crystals or an artefact has to be clarified with further investigations [1-3,16-19].

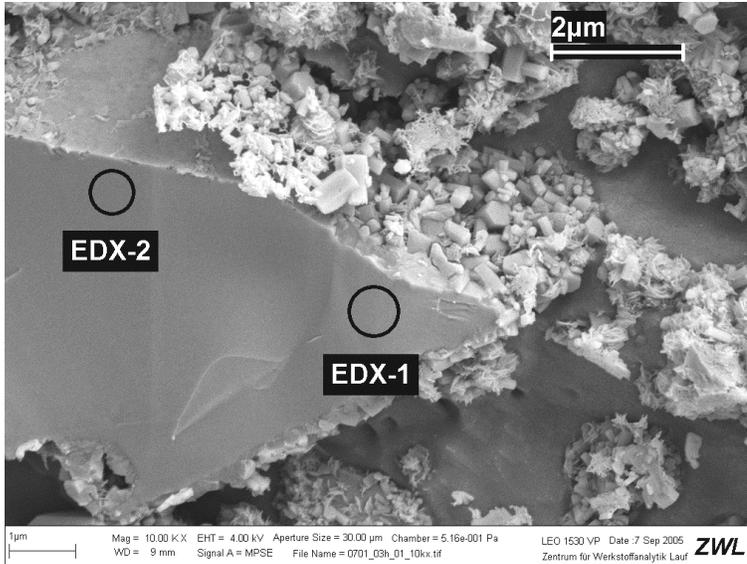


Figure 2a:  
Cryo-transfer-SEM  
image of OPC  
after 3 h hydration  
time; broken  
clinker grain,  
partially covered  
with Ettringite  
crystals

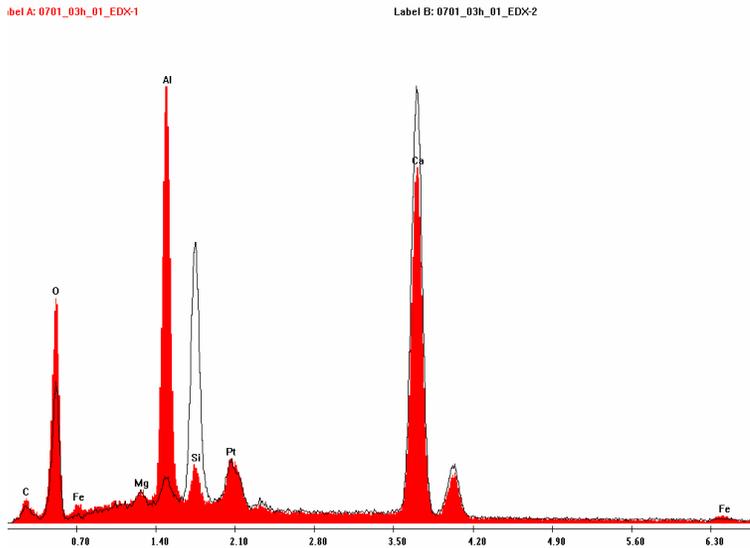
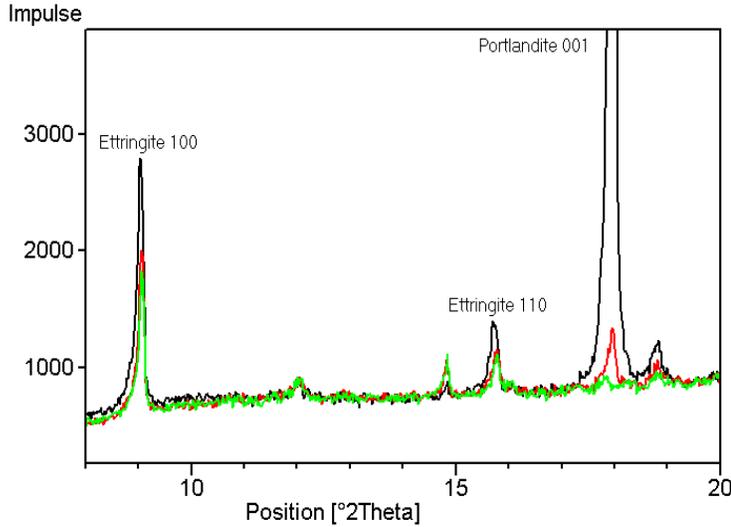


Figure 2b:  
EDX-spectra of the  
marked areas;  
EDX-1 (red),  
EDX-2 (black);  
scaling keV

To find out the difference between covered and non-covered surfaces EDS analyses were necessary. The problem of surface effects was minimized by analysing only sections of broken clinker grains (Fig 2a). All EDS spectra showed similar results and confirmed the presumption that Al-rich clinker phases ( $C_3A$ ,  $C_4AF$ ) show strong ettringite crystallisation on there surfaces and Si-rich ( $C_3S$ ,  $C_2S$ ) do less or not. Figure 2b shows the different results of the analyses of the marked areas at Fig 2a; EDX-1 (section under covered surface) and EDX-2 (section under non-covered surface). All investigated OPCs showed strong ettringite crystallisation but only very low quantities of gel-like or amorphous structures on Al-rich clinker surfaces after 1 min hydration time.

X-ray analyses were done to prove the existence of the hydration product ettringite [9,20,21]. A new generation of X-ray detectors enables high

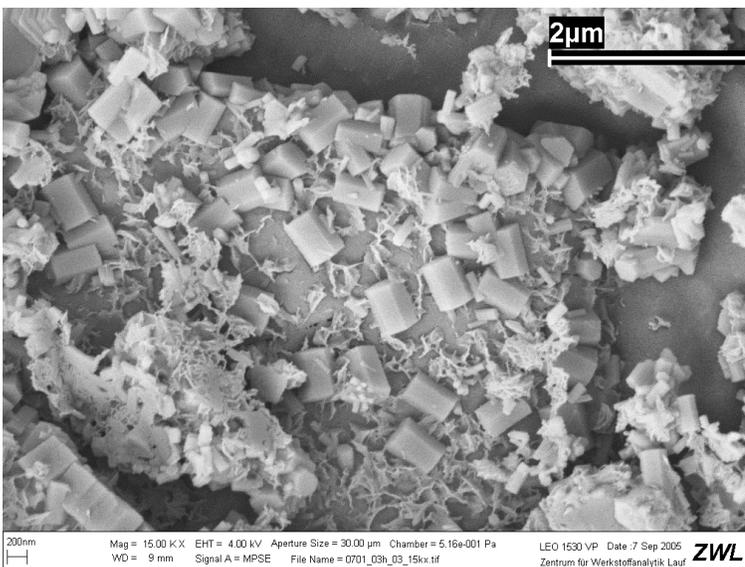
speed X-ray diffraction with extremely short measurement times for XRD patterns. So it was possible to evidence the presence of ettringite already after 2 min by XRD. Patterns after 30 min, 3 h and 24 h confirmed the existence and showed increasing signal intensities (Fig 3).



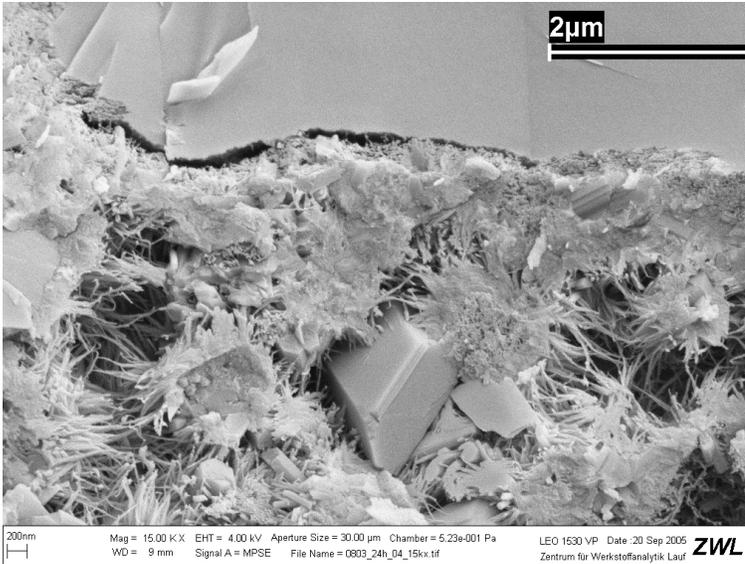
*Figure 3: X-ray diffraction pattern of OPC; 30 min hydration time (light green), 3 h hydration time (red), 24 h hydration time (black)*

### 3.2 C-S-H imaging

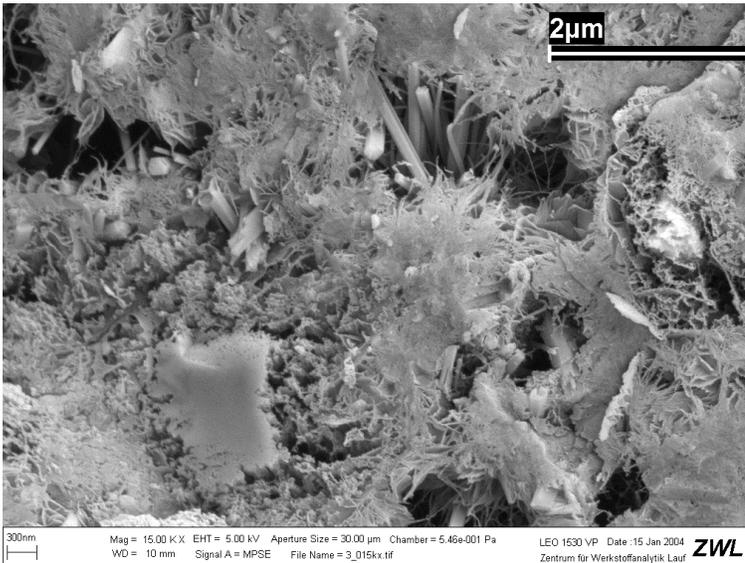
Especially C-S-H and amorphous gels often show artefacts or dehydration effects at high vacuum conditions or after normal SEM preparation procedures [4]. This also complicates the study of hydration products at later hydration times (a few days). Adequate interpretations of SEM images with conclusions concerning crystal morphology and microstructure are extremely difficult.



*Figure 4a: Cryotransfer-SEM image of OPC after 3 h hydration time; clinker grain with ettringite and the first C-S-H-phases*



*Figure 4b:  
Cryotransfer-SEM  
image of OPC  
after 24 h  
hydration time;  
different  
morphologies of  
C-S-H-phases,  
portlandite and  
gypsum*



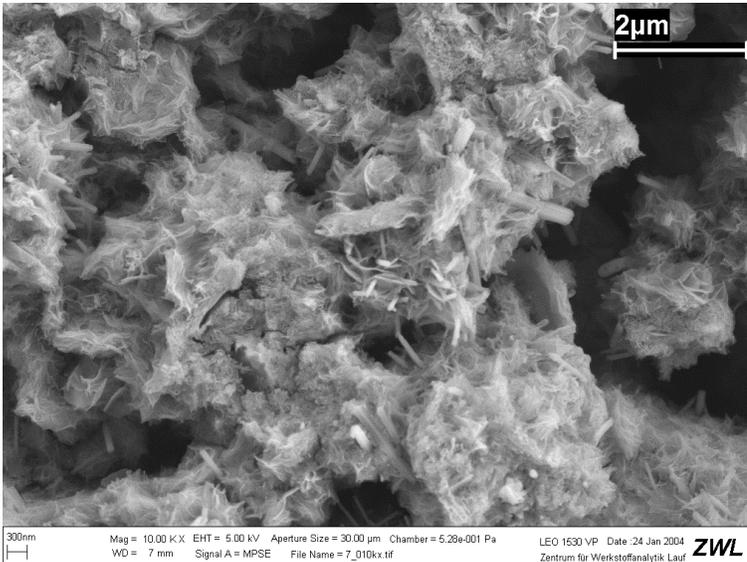
*Figure 5a:  
HSSC after 24 h  
hydration time.  
Cryotransfer  
preparation;  
different  
morphologies of  
C-S-H-phases and  
long needle  
shaped ettringite*

The Figures 4 and 5 show images of OPCs and SCs after 3 h hydration time and 24 h respectively. After 3 h the detection of the first C-S-H phases was possible (Fig 4a). Needle shaped crystals with chains below 200 nm were formed principally on clinker surfaces but also on ettringite and calcium carbonate surfaces. There seemed to be no preferred positions – e. g. one kind of clinker phase – for the growth of the first crystals. Images showed nucleation only on surfaces, and not in solution [13,14,22-25].

After 24 h a network of C-S-H dominated the images. Different morphologies are clearly recognisable at Fig 4b. A really dense structure has formed around clinker grains, where also the first phases had been found. These areas showed homogenous, extremely small meshed

products with no preferred direction of growth. Completely different, the long, needle shaped structures growing into pore volumes between clinker grains. These C-S-H phases seemed to build up from the dense areas mentioned before with defined growing directions. The needles showed diameters below 50 nm. Fig 4b and especially Fig 5a show a third kind of C-S-H morphology. The areas next to clinker grains with etched surfaces showed meshed structures with low density. Portlandite also was detectable. Typical layered structures are recognisable at Fig 4b. The X-ray evidence is given at the pattern at Fig 3. It shows portlandite already after 3 h and confirmed the cryo-SEM results.

However, results correlate with several hydration models and reports about the structure of C-S-H [22-25]. Especially with recent results of Gallucci et al. [25] who described the formation of a shell structure around hydrating alite grains by STEM analyses from 6 h to 24 h reaction time.



*Figure 5b:  
HSSC after 24 h  
hydration time.  
normal SEM-  
preparation*

Figure 5a/b shows the HSSC after 24 h reaction time prepared with cryotransfer (mag. 15.000) and normal SEM technique (mag. 10.000), to point out the enormous differences between both methods.

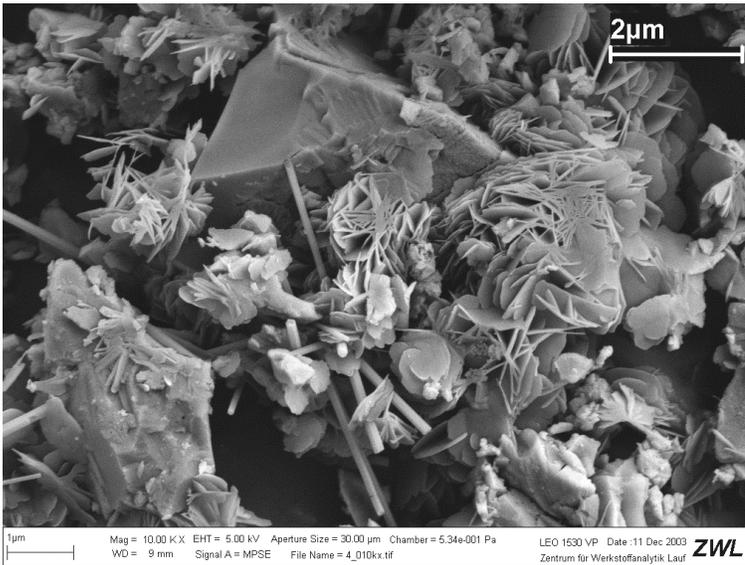
Hydration conditions were the same for both samples. The “normal SEM sample” was prepared out of bulk material. A cylinder (radius 2 cm, height 5 cm) was fractured and a piece of the middle of the sample was mounted on a conventional SEM sample holder. After 10 min of sample drying and a 2 sec carbon coating (5 nm to 10 nm) at high vacuum and room temperature the sample was set into the SEM chamber directly. Images were taken at high vacuum conditions. Tests with Au and Pt sputter coatings showed worse results than the carbon coating. Cryo samples were prepared as mentioned at chapter 2.

Artefacts could be seen clearly in the conventional SEM preparation. The voluminous C-S-H structure was no longer detectable and fuzzy layers of

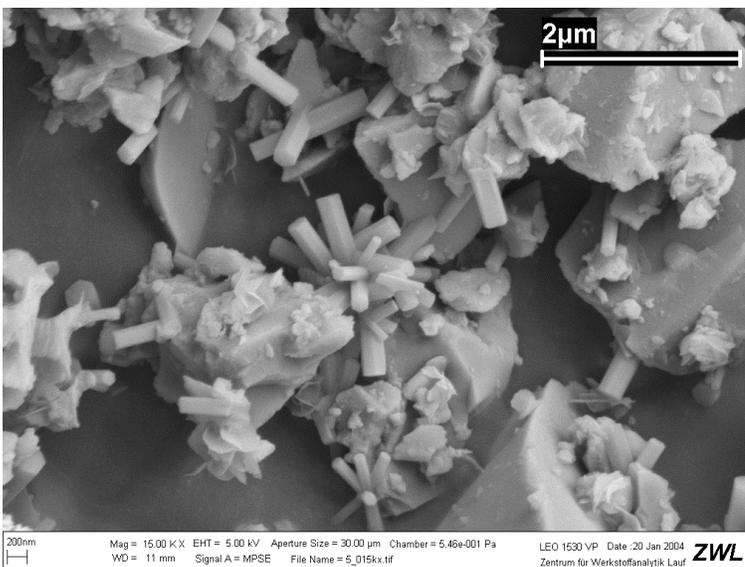
dehydrated reaction products covered the surface. It was not possible to draw proper conclusions about the microstructure and the building of C-S-H-phases.

### 3.3 Setting of rapidly hardening cements

Figure 6a/b shows a comparison between SC and HSSC after 3 min hydration time. The aim was to find out the reasons for the completely different setting behaviour of these two special cements. The SC showed 'normal' setting after about 1 min. The HSSC showed retarded setting after 8 min to 15 min.



*Figure 6a:  
Cryotransfer-SEM  
images,  
SC after 3 min  
hydration time;  
clinker grains,  
AFm-phases and  
ettringite*



*Figure 6b:  
Cryotransfer-SEM  
images,  
HSSC after 3 min  
hydration time;  
clinker grains and  
ettringite*

The main products of the SC were lamellar AFm-phases. Ettringite only was detectable in very low quantity and with long needle-shaped morphology. Thus, the setting process depends on the rapid formation and growing of the AFm-phases. They are bridging the pore volume and cause an interlocking of the microstructure during the first minute of reaction. The evidence of ettringite and monosulphate was possible by X-ray analyses after 10 min.

The HSSC showed rather no formation of AFm. Ettringite with short prismatic morphology was detectable after 3 min (Fig 6b). Though, number and length of the existing crystals did not suffice to cause an interlocking of the matrix and a setting of cement. First a strong length growth of the ettringite crystals between 5 min and 15 min reaction time effectuated a bridging of the pore volume and built up a stable network. X-ray analyses confirmed the cryotransfer SEM results and showed increasing ettringite signals from 5 min to 20 min but no AFm signal. These data clarify the reasons for the different setting behaviours of SC and HSSC. SC setting is caused by a rapid formation of many lamellar AFm-phases whereas the setting of HSSC is based on the growth in length of ettringite [16-19,26].

#### **4 Conclusion**

Advanced cryotransfer SEM opens new possibilities in structural and chemical characterisation of short-term hydrating cementitious systems, with only a few minutes or seconds reaction time, as well as older specimens with some days reaction time. Preparation methods were optimized and serious progress especially was made concerning the high magnification imaging, the reproducibility of results and the minimization of artefacts. Fast preparation, variable hydration conditions and the uncovering of internal structures are the most important advantages. Of course there are critical aspects at the preparation process, like the mechanical brittle fracture or the sublimation process. However, it is no problem to manage these aspects with qualified personal and some practical experience. The advanced cryotransfer preparation method more than ever is a powerful tool for microscopic investigations of hydrating cementitious systems and can bring out some new interesting aspects concerning the investigation of ettringite formation, C-S-H phases and the overall hydration processes.

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