Cryotransfer Scanning Electron Microscopy for the Study of Cementitious Systems

M. Fylak1, J. Göske1, W. Kachler1, R. Wenda2, H. Pöllmann3 1. Zentrum für Werkstoffanalytik, Lauf a.d. Pegnitz, Germany 2. Georg-Simon-Ohm Fachhochschule, Nuremberg, Germany 3. Martin-Luther University, Halle, Germany

INTRODUCTION

Scanning electron microscopy (SEM) has been used for a long time for the investigation of cementitious materials. It is possible to analyze hardened cement, mortar or concrete. However, problems arise if we want to study the earlier hydration processes especially those occurring within the first 24 hours of reaction. Because of the high water content it is impossible to analyze these non-hardened samples without the formation of artifacts under normal SEM conditions. Previously hardened cementitious specimens can also show high-vacuum or electron-beam sensitivity. For example, the dehydration of water-containing hydration products might occur [1].

But with an SEM cryotransfer technique it is now possible to set liquid, beam- and vacuum-sensitive specimens into a stable state by quick-freezing. Thus this method enables the 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 resolution 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 method to the well-established environmental (E) or variable pressure (VP) SEM methods [1-3]. The advantages and disadvantages of cryotransfer SEM, ESEM and VPSEM in the study of cementitious systems are summarized in ref [1].

This article describes the possibilities that cryotransfer SEM offers for the investigation of hydrating cement pastes, especially during the first 24 hours of reaction.

MATERIALS AND METHODS

Scanning electron microscopy

All SEM analyses were done with a Leo 1530VP SEM (Carl Zeiss SMT) with a field-emission gun. The SEM enabled high-resolution imaging and the variable-pressure (VP) mode allowed a variation of the chamber N2 gas pressure between 1 and 100 Pa. The SEM was equipped with an EDAX energy-dispersive spectroscopy (EDS) system and a Gatan Alto 2500 cryotransfer unit.

X-ray diffraction

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

Cement samples

All samples were hydrating cement pastes with 1 minute to 24 hours hydration time. They were prepared with water-cement ratios of between 0.35 and 0.4. For the cryoSEM investigations the temperature and relative humidity during the hydration reactions were 20-22°C and 93-97%, respectively.

Two different groups of cements were used in this study. The first group consisted of some ordinary Portland cements (OPC). The second group consisted of two different rapidly hardening cements. They were Portland-based special cements with a low quantity of additives (<2%) and are used for some special spraying methods. The first was a rapidly hardening cement (SC), the second was a high sulphate-resistant rapidly hardening cement (HSSC).

ACKNOWLEDGEMENTS

All analyses were done at the laboratories of the Zentrum für Werkstoffanalytik Lauf GmbH. Thanks are due to Dr H.-G. Pankau, Dr R. Rieß (both of Gatan GmbH), S. Kuhn (Carl Zeiss SMT AG) and Dr R. Meier (PANalytical B.V.) for technical support.

BIOGRAPHY

Marc Fylak worked for his diploma at the Georg-Simon-Ohm University of applied science at Nuremberg in the field of hydrating special cements. He is now working on his PhD at the Martin-Luther University Halle-Wittenberg and at the Zentrum für Werkstoffanalytik Lauf GmbH. His research is on SEM and X-ray analyses of hydrating cements. It is supported and supervised by Prof. Wenda and Prof. Pöllmann.

AUTHOR DETAILS

Marc Fylak, Zentrum für Werkstoffanalytik Lauf GmbH, Hardstrasse 39b, 91207 Lauf a. d. Pegnitz, Germany
Tel: +49 91 23 99 80 02
Email: marc.fylak@werkstoffanalytik.de
Microscopy and Analysis 20(4):9-12 (UK), 2006

2μm

Figure 1a: Cryotransfer SEM image of ordinary Portland cement after 1 minute hydration. (a) Broken cement clinker grain showing surface covered with ettringite crystals.
There is general interest in the morphologies of the reaction products, the starting point of formation, and their influence on the setting and hardening of the cement. Important phases are ettringite (calcium aluminium sulphate hydroxide hydrate: \( \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} \)), C-S-H (calcium silicate hydrate: \( \text{2CaO} \cdot \text{SiO}_2 \cdot 1-3\text{H}_2\text{O} \)), portlandite (calcium hydroxide: \( \text{Ca(OH)}_2 \)) and several so-called AFm phases such as monosulphate (calcium aluminium sulphate hydrate; \( \text{Ca}_4\text{Al}_2[\text{SO}_4]_2(12-16\text{H}_2\text{O}) \)).

Cryotransfer technique

The first step in the cryopreparation was the placement of a well-mixed cement paste specimen on a special sample holder. To guarantee a fast and homogenous freezing process small samples had to be taken. Rivets with a diameter of 0.5 to 2 mm normally enabled good and reproducible preparation.

The next step was the storage of the samples under defined conditions. These freely selectable hydration conditions were 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. Of course it is also possible to prepare the samples after storage but this procedure might cause some artifacts.

The quick freezing terminated the storage period and stopped all reactions within the cement paste. Therefore sample holder and specimen had to be introduced into a cryogen very quickly. This process is called plunge freezing because the sample is plunged manually or mechanically into the cryogen [4]. Other methods such as spray freezing, jet-freezing or high-pressure freezing are possible and should be mentioned here [4]. To get a high heat transfer by using plunge freezing it is necessary to use supercooled or melting cryogens for the freezing process. Standard cryogens are ethanol, propane or nitrogen [4]. The quick freezing is necessary to avoid the crystallisation of water and the orientation of particles.

After freezing, the frozen sample was transferred to the cryopreparation unit, which was directly connected to the SEM chamber by a valve. After this action, time was no longer a critical factor because the preparation unit as well as the SEM stage were cooled to about -170°C and were under high vacuum. So the cement paste specimen stayed in a stable state and no water loss, dehydration effects or further hydration occurred [1].

The accessory equipment in the cryopreparation unit enabled the brittle fracture of the frozen cement paste, to eliminate disturbing surface effects or contamination, and exposed the internal structure of the specimen [2].

After transfer into the SEM chamber a sublimation process was necessary to uncover the cement grains and hydration products which were surrounded by frozen water. To start the sublimation, a \( \text{N}_2 \) gas pressure of 10-50 Pa and a temperature of -80 to -110°C were used. The variable-pressure mode and the low-temperature stage of the SEM enabled these settings.

The whole process was controlled online using a multiple-pressure secondary electron (MPSE) image. At the end the sublimation process, the samples were sputter coated with a 4-8 nm layer of Pt or Au/Pd.

RESULTS AND DISCUSSION

Early hydration products

One of the challenges of this work was the imaging of the very early hydration products which formed within the first seconds after mixing the cement paste. Figure 1 shows some examples of different OPCs (all CEM I 52.5 R, EN 197-1) after 1 min hydration time. Ettringite is supposed to be the first crystal phase [5].

All investigated cements showed spontaneous ettringite formation already after 1 min hydration time. Figure 1a shows a broken cement paste...
Cryotransfer SEM image of OPC after 3 h hydration. Clinker grain with ettringite and the first C-S-H-phases. (b) Cryotransfer SEM image of OPC after 24 h hydration. C-S-H phases growing between clinker grains.

Figure 4: X-ray diffraction pattern analysis of OPC. 30 min hydration (red); 3 h hydration (blue); 24 h hydration (black).

Figure 3: X-ray diffraction pattern analysis of OPC. 30 min hydration (red); 3 h hydration (blue); 24 h hydration (black).

To determine the differences between covered and non-covered surfaces EDS analysis was necessary. The problem of surface effects was minimized by analysing only sections of broken clinker grains (Figure 2a). All EDS spectra showed similar results and confirmed our presumption that the Al-rich clinker phases (tricalcium aluminate, Brownmillerite) showed strong ettringite crystallisation on their surfaces and Si-rich (tricalcium silicate, dicalcium silicate) to a lesser extent or not at all. Figure 2b shows the different results of the analyses of the marked areas in Figure 2a; EDX-1 is the analysis of the region under the covered surface and EDX-2 the region under the non-covered surface.

X-ray diffraction analyses were done to prove the existence of the hydration product ettringite. A new generation of X-ray detectors enables high-speed X-ray diffraction with extremely short measurement times for XRD patterns. This allowed us to confirm the presence of ettringite after only 2 minutes by XRD. Further patterns obtained after 30 min, 3 h and 24 h confirmed the existence and showed increasing signal intensities (Figure 3).

Calcium silicate hydrate imaging
C-S-H and amorphous gels often show artifacts or dehydration effects under high vacuum or after normal SEM preparation procedures [1]. This also complicates the study of hydration products at later hydration times (a few days) making adequate interpretation of SEM images and conclusions concerning crystal morphology and microstructure extremely difficult.

Figures 4 and 5 demonstrate the possibilities of cryotransfer SEM and show OPCs and SCs after 3 and 24 h hydration times, respectively. After only 3 h the detection of the first C-S-H phases was possible (Figure 4a). Needle-shaped crystals with chains below 200 nm were formed principally on clinker surfaces but also on ettringite surfaces. There seemed to be no preferred positions (e.g. one kind of dinker phase) for the growth of the first crystals. Images showed only nucleation on surfaces, not in solution.

After 24 h a network of C-S-H dominated the images. Different morphologies are clearly recognizable in Figure 4b. A really dense structure had formed around dinker grains, where the first phases had also been found. These areas showed homogenous, extremely small meshed products with no preferred direction of growth. Particle and pore volume sizes were already too small for focused imaging and could be declared as really nano-sized. Completely different were the long, needle shaped structures growing into pore volumes between dinker 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. It is possible that Figure 4b and especially Figure 5a show a third kind of C-S-H morphology. The areas next to the dinker grains with ettringite surfaces showed meshed structures with low density.

Of course, portlandite - the hydration product which has to be formed with C-S-H - was also detectable. Typical layered structures are recognizable in Figure 4b. Because of the small crystal sizes or the semicrystalline or amorphous character of C-S-H, proving its presence by X-ray diffraction analysis was quite difficult. So the formation of portlandite had to used as indirect evidence of C-S-H formation. The X-ray analysis in Figure 3 shows portlandite was already present after 3 h and confirmed the cryoSEM results.

However, the results correlated partially with different hydration models and reports about the structure of C-S-H [5-7]. The variation in morphology relates to different Ca/Si ratios within the structures. Figure 5 shows hSSC after 24 h reaction time prepared with cryotransfer (Figure 5a) and normal SEM (Figure 5b), to point out the difference between the two methods. Artifacts 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.
Setting of rapidly hardening cements
Figure 6 shows a comparison between SC (Figure 6a) and HSSC (Figure 6b) after 3 min hydration time. Our aim was to find out the reasons for the completely different setting behaviour of these two special cements. The SC showed normal setting after ~1 min. The HSSC showed retarded setting after 8-15 min.

The main products of the SC were lamellar AFm phases. Ettringite was only 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 were bridging the pore volume and caused an interlocking of the microstructure during the first minute of reaction. The evidence for ettringite and monosulphate was made possible by X-ray diffraction analyses after 5 minutes.

By contrast, HSSC showed almost no formation of AFm. Ettringite with short prismatic morphology was detectable after 3 min (Figure 6b), although the number and length of the existing crystals did not suffice to cause an interlocking of the matrix and the setting of the cement. First a strong growth in length of the ettringite crystals between 5 min and 15 min reaction time effected a bridging of the pore volume and built up a stable network. X-ray diffraction confirmed the cryotransfer SEM results and showed increasing ettringite signals from 5-20 min and no AFm signal. These data clarify the reason for the different setting behaviour of SC and HSSC. SC setting is based on the growth in length of ettringite.

CONCLUSIONS
Advanced cryotransfer scanning electron microscopy opens new possibilities for the structural and chemical characterisation of short-term hydrating cementitious systems, with only a few seconds or minutes reaction time, as well as older specimens with some days of reaction time. Preparation methods were optimized and serious progress was made especially concerning high-magnification imaging, the reproducibility of results and the minimization of artifacts. Fast preparation, variable hydration conditions and the uncovering of internal structures are the most important advantages of this technique.

Of course there are critical aspects in the preparation process, such as the mechanical brittle fracture and the sublimation process. However, it is no problem to manage these aspects with qualified personnel and some practical experience. The advanced cryo-transfer preparation method can bring out some new interesting aspects concerning the investigation of ettringite formation, C-S-H phases and the overall hydration processes.

REFERENCES