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Microstructure of tricalcium silicate and Portland cement systems at middle periods of hydration-development of Hadley grains

K.O. Kjellsen [a,*], B. Lagerblad [b]

[a] Norcem A.S, Heidelberg Cement Group, N-3950 Brevik, Norway
[b] Swedish Cement and Concrete Research Institute, S-100 44 Stockholm, Sweden

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Abstract

The development of the microstructure of C_3S paste and a Portland cement paste was studied between 7 and 24 h by means of backscattered electrons in a field-emission SEM. The course of hydration was measured by isothermal calorimetry. While the abundant occurrence of Hadley grains (hollow-shells) in Portland cement systems is well documented from a number of SEM and other microscopy studies, some earlier reports have noted that Hadley grains do not form in C_3S or alite paste alone. This report shows evidence of Hadley grains in C_3S paste, and follows their development from middle to late hydration stages. At around 10 h the microstructure with respect to Hadley grains were seen to develop in a very similar manner in C_3S and cement. In both systems, a narrow gap often developed between the receding anhydrous cores and layer of reaction product enveloping the cores. By 1 day, Hadley grains had continued to develop only in the cement paste, where they became a prominent feature. Only small 'hollowed-out' hydration shells were observed in the C_3S paste by 1 day. These were presumably reminiscences of the small gapped Hadley grains seen at the earlier hydration stages.

Keywords: Hydration; Backscattered Electron Imaging; SEM; Ca_3SiO_5; Cement Paste

1. Introduction

Tricalcium silicate (C_3S) is the most abundant phase in Portland cement. As its reaction with water is much simpler than the reaction between Portland cement and water, it has commonly been used as a model system for the hydration of Portland cement. In-situ microscope studies [e.g. 1–4] of the first few hours of microstructural development of Portland cement and C_3S have shown the formation of a very thin surface layer of reaction product covering the anhydrous particles. Upon the continued reaction with water, the anhydrous grains gradually recede beneath the hydrate layer enveloping the grains, and the layer grows in thickness. The question then is whether the layer grows inwards (towards the cement core), or outwards (into the capillary pore space), or in both directions simultaneously.

The latter option, i.e. simultaneous inward and outward growth was early postulated. Taplin [5] termed products deposited on the inside of the original cement grain boundary 'inner' products, while he termed hydrates formed on the outside 'outer' products. By actually observing concrete microstructures Hadley [6] revealed 'hollowed-out' hydration shells, and sometimes gaps between remnant cement cores and shell of reaction products. The observation of these hollow-shells, which later often were termed Hadley grains, led him to the conclusion that hydration takes place through solution and subsequent deposition at sites relatively far away from the cement grain. In other words, distantly-deposited outer products form instead of inner products, and consequently a void develops between the receding cement core and the layer of reaction product that formed around the initial cement grain surface. Later, Hadley's observations of this specific type of microstructure have not only been fully confirmed, but the microstructure he observed have indeed been found to constitute a common and very significant feature of mature Portland cement and concrete microstructure [e.g. 2,7–

* Corresponding author. Tel.: +47 35 572357; fax: +47 35 570400.
E-mail address: knut.kjellsen@norcem.no (K.O. Kjellsen).

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13]. Scrivener and Pratt [14] reported the formation of hollow-shell separations as early as 5 h in a Portland cement paste. It thus seems that the early or middle product also can be separated from the cement grain.

While Hadley grains are a characteristic feature of Portland cement systems, it has been suggested that Hadley grains do not form in pure C_3S systems [15–17]. However, as no experimental results were presented to support this statement the basis for it is not clear. Considering the common methodology used up to the early 1980s, at the time Pratt and Ghose [15] and Taylor et al. [16] published their papers, it seems likely that the statement cited above were based on studies of fractured specimens in the secondary electron mode of the SEM. Fractographic studies may not be particularly suitable for detection of Hadley grains as will be discussed later. Scrivener and Pratt [18] suggested that the presence of C_3A and a source of sulfate must be a necessary precursor for the formation of Hadley grains. However, two recent articles do report the occurrence of Hadley grains in C_3S pastes alone [13,19]. Observations by Kjellsen and Justnes [19] of pure C_3S or alite pastes hydrated for 24 h revealed small hollowed-out hydration shells, analogous to those observed in Portland cement, and very likely developing as a result of a rapid 'hollowing-out' hydration process of small C_3S grains. It seemed that the small C_3S grains had fully reacted by one day, and left only the hollow hydration shells. There appeared to be contact between the larger C_3S grains and shell of reaction product. In accordance with the findings of Scrivener and Pratt [18], who studied a mixture of monomineralic C_3S and C_3A particles (plus hemihydrate) at 24 h. These findings are in distinct contrast to the usual findings with Portland cement, where at 24 h there is a clear separation up to a few micrometers wide between the receding alite cores and the shell of reaction product enveloping the cores. It thus appears that at about one day Hadley grains are a much more common feature in Portland cement paste than they are in C_3S paste, but nevertheless the small hollowed-out hydration shell variant of Hadley grains are common in C_3S paste at this age. This type of small hollowed-out Hadley grain seen at one day will hardly be revealed from fractographic studies of C_3S paste, since the fracture path will ordinarily be between particles, and thus will seldom pass through the small hollowed-out hydration shells, and thereby reveal their existence. This appears to be a likely reason why Hadley grains have not been noted in C_3S paste in the past.

It appeared that studying the microstructure of C_3S paste at early and middle hydration stages would provide more information on the nature of Hadley grain formation of C_3S. Such information can be helpful in establishing models for Hadley grain development, which we currently are working on. This is the background for the experimental study undertaken here. We separately mixed a Portland cement paste and a pure C_3S paste, and preserved the microstructures of each at predetermined ages by quenching the specimens in liquid nitrogen. The specimens were then freeze-dried, impregnated with epoxy resin, polished flat, and examined by backscattered electrons in a field-emission SEM (FE-SEM). In order to relate the microstructure observed to the extent of reaction, the hydration heat developed at each stage was obtained by isothermal calorimetry.

2. Experimental

2.1. Materials

Triclinic tricalcium silicate (C_3S, or $3CaO{\cdot}SiO_2$), and a Portland cement were used in this study. The C_3S was supplied by Dr P B West, Construction Technology Laboratories, Illinois. The Portland cement was a Swedish low-alkali sulfate-resistant Portland cement, which corresponds to ASTM Type V cement. The characteristics of the materials used are given in Table 1. All the pastes were made of de-ionized water and the specified anhydrous materials at water/solids ratio of 0.40. The pastes were mixed by hand for 5 min. After mixing, the pastes for microscopy were cast into very small conical shaped polyethylene tubes, and the open ends of the tubes were sealed with laboratory film (Parafilm®). The tubes were designed to accommodate paste samples of about 0.15 g. Mixing and storage took place at 20 °C.

2.2. Calorimetry

Isothermal heat development at 20 °C was measured in a conduction calorimeter. A sample of the hand mixed paste, containing 43.4 g of anhydrous material, were weighed into a plastic beaker and immediately placed in the calorimeter. The time elapsed from first contact between water and anhydrous material to the start of measurement was about 10 min; thus the first major heat peak (S_I, according to [20]) is not correctly revealed in the measurements. The heat evolution was measured for 30 h.

2.3. Microscopy

At predetermined times, the laboratory film was removed from the tube forms and the small paste samples were carefully released from their forms by compressed air, and were then directly quenched in liquid nitrogen (−196 °C). The small sample size was used to ensure very rapid freezing and thereby minimize the formation of ice crystals and volume increase. The frozen water was then removed through sublimation by freeze-drying.

Table 1
Characteristics of the materials

	C_3S	Cement
SiO_2	26.2%	22.2%
CaO	73.6%	64.9%
Al_2O_3	0.29%	3.4%
Fe_2O_3	–	4.8%
MgO	0.10%	0.91%
SO_3	–	2.0%
K_2O	–	0.56%
Na_2O	–	0.04%
Free lime	0.31%	0.70%
Loss-on-ignition	–	0.63%
Specific surface area (Blaine)	332 m^2/kg	302 m^2/kg
Specific weight*	3110 kg/m^3	3220 kg/m^3

Percentage by mass.
*Determined by Helium Pycknometry.

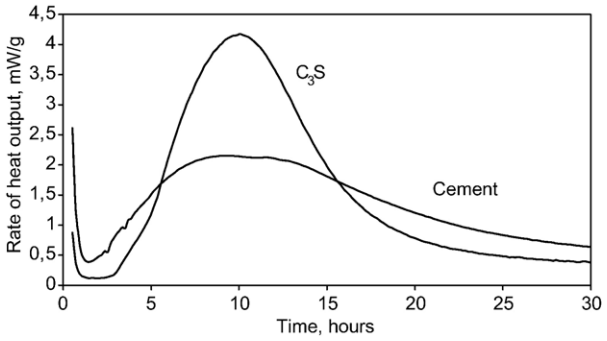

Fig. 1. Rate of heat evolution of the C_3S paste and the Portland cement paste.

It is interesting to note that the particulate structure of the fresh cement paste apparently was retained after freeze-drying. The fresh or young cement paste specimens did not collapse after removal of the water, but retained their original shape and size. They were naturally extremely fragile at this point due to the modest extent of hydration that occurred during the first few hours, and had to be handled with great care. Varieties of this method for stopping the hydration and preserving the structure of fresh or young cement paste, mortar and concrete for microscopy examination have been presented earlier [1,21–23].

As indicated earlier, after drying the dried paste specimens were vacuum-impregnated with epoxy resin; this procedure had to be very carefully performed in order not to disturb the fragile specimens. After hardening of the epoxy resin the impregnated specimens were ground and polished flat in accordance with [24], and then were coated with carbon. Examination was carried out in a Hitachi model S-4300 field-emission SEM with the accelerating voltage kept at 10 kV throughout. We examined a considerable number of sections of each of the various specimens to be certain that the images we present always are representative of the specimens.

3. Results and discussion

3.1. Hydration heat development

The results are presented as the rate of heat evolved per gram solid material in Fig. 1, and as the heat of hydration in Fig. 2. It

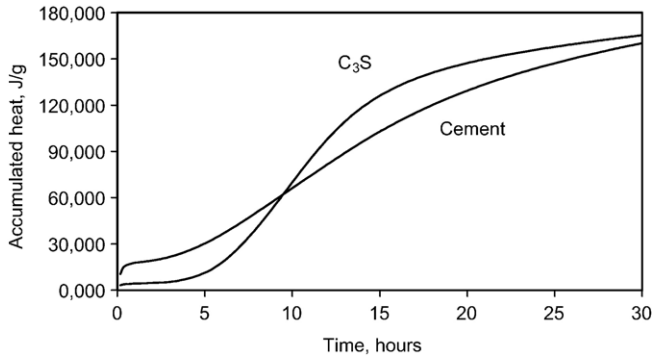

Fig. 2. Accumulated hydration heat of the C_3S paste and the Portland cement paste.

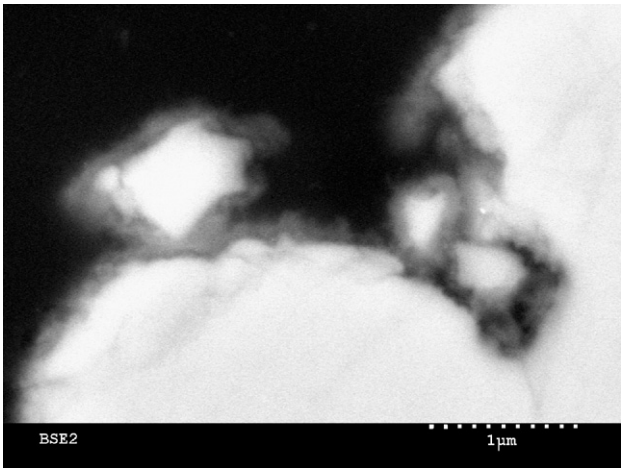

Fig. 3. Backscattered electron image of the C_3S paste hydrated for 7 h.

can be observed that the C_3S exhibits a more pronounced and longer dormant period (S_{II}, [20]) than the cement; nevertheless the maximum rate of heat occurs at around 10 h for both materials. At 7 h the C_3S hydration lags somewhat behind the cement hydration, however, after about 9 h the extent of C_3S hydration is higher than the cement. The pattern of hydration of the C_3S found in this study, with a maximum rate of hydration at around 10 h, well resembles those reported by others [1,25–27].

3.2. Microstructure

3.2.1. At 7 h

Seven hours is towards the end of the acceleration period (S_{III}, [20]), so relatively little hydration has occurred at this point (cf. Fig. 1). High-magnification backscattered electron images of the 7-hour old C_3S and cement pastes are provided in Figs. 3 and 4, respectively. The level of detail and the contrast between various phases is sufficiently good to reveal the thin layers of mainly C–S–H (gray), apparently about 100 nm thick, that cover the anhydrous particles (the bright phases). From a TEM study of ion-beam thinned C_3S paste, Jennings et al. [1]

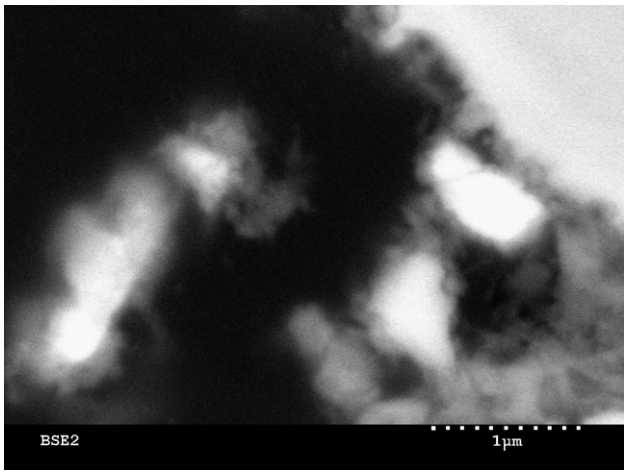

Fig. 4. Backscattered electron image of the cement paste hydrated for 7 h.

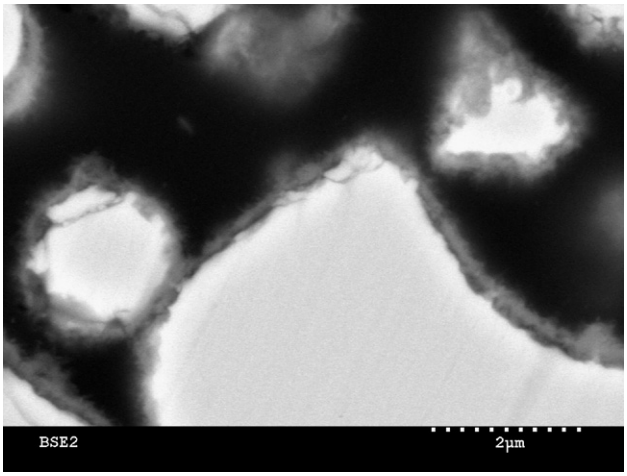

Fig. 5. Backscattered electron image of the C_3S paste hydrated for 9 h.

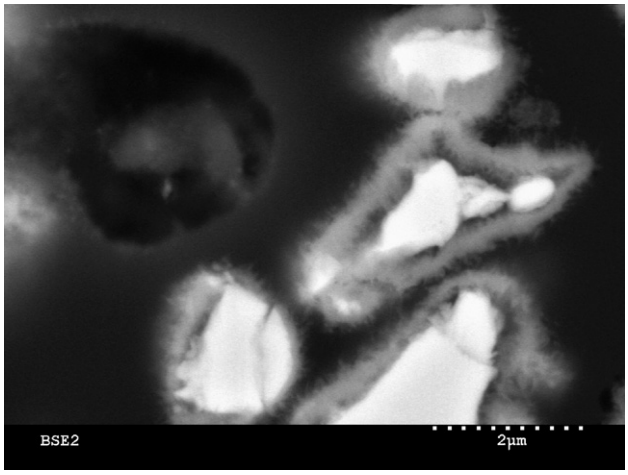

Fig. 7. Backscattered electron image of the C_3S paste hydrated for 11 h.

reported a layer thickness of about 50 nm after 6 h. They reported that the layer appeared viscous gelatinous, and that both flaky and needle shaped products formed on the substrate of the gelatinous product, possibly as a result of drying of the specimen. Henderson and Bailey [28] provided detailed TEM images of C_3S paste hydrated for 7 h showing fibril-like 'outgrowths'. Again, the influence of drying on these observations can probably not be ruled out. Sujata et al. [3] used ESEM, and under wet conditions reported the formation of an amorphous coating of C–S–H on the surface of C_3S grains at 8 h. They did not report a needle-like morphology until a later stage. The relatively featureless structure of the hydrate layer previously reported is also perceived from the FE-SEM images in Figs. 3 and 4. The resolution is not sufficiently good to clearly reveal any possible fibrous product at this stage. As will be shown, the fibrous structure does appear later.

The epoxy resin used to impregnate the pore space appears black in backscattered electron images. The absence of such a layer between the anhydrous grains and the layer of product covering them in both the C_3S paste and the cement paste indicates that they are in contact, at least within the limit of the resolution achieved.

3.2.2. At 9 h

A backscattered electron image of the C_3S paste hydrated for 9 h is revealed in Fig. 5. The apparent thickness of the shell has increased and appears now to be about 150 nm. The microstructure of the cement paste hydrated for 9 h is shown in the backscattered electron image in Fig. 6. The thickness of the hydration layers covering the cement grains appears to vary very much, which can be due to different reactivity of different portions of the particles.

Close examination of Figs. 5 and 6 reveal a narrow physical separation, viewed as a dark layer, at the interface between the phase of product and several of the anhydrous grains. This separation very likely represents an early stage of Hadley grain formation. From a STEM study of cement paste thin-foils, Scrivener and Pratt [14] observed a definite 'shell' structure with a narrow gap between cement core and product as early as 5 h. Scrivener [2] later associated this separation to a 'hollow-shell' hydration mode. The 'shell structure', with its separation,

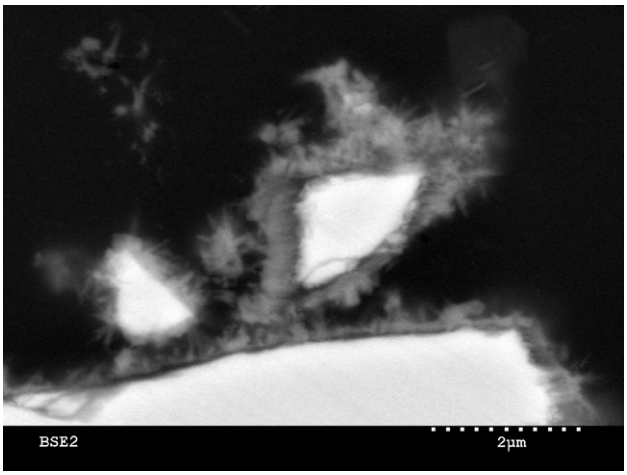

Fig. 6. Backscattered electron image of the cement paste hydrated for 9 h.

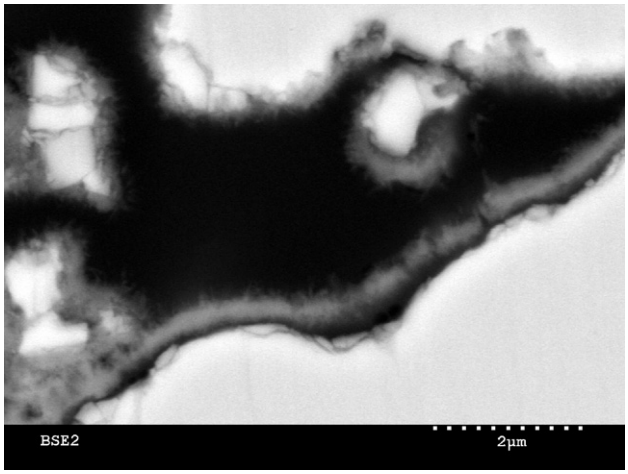

Fig. 8. Backscattered electron image of the C_3S paste hydrated for 11 h.

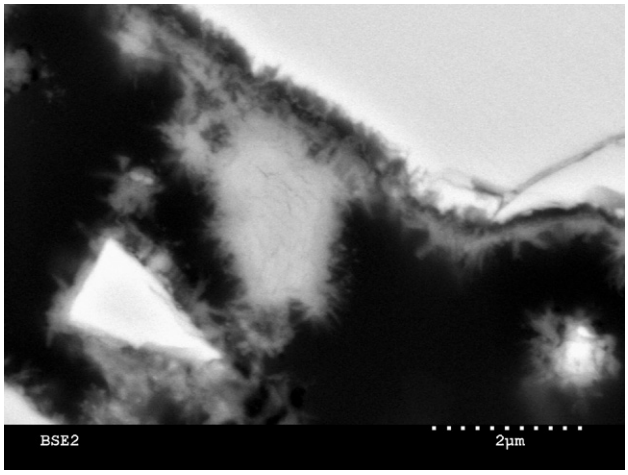

Fig. 9. Backscattered electron image of the cement paste hydrated for 11 h.

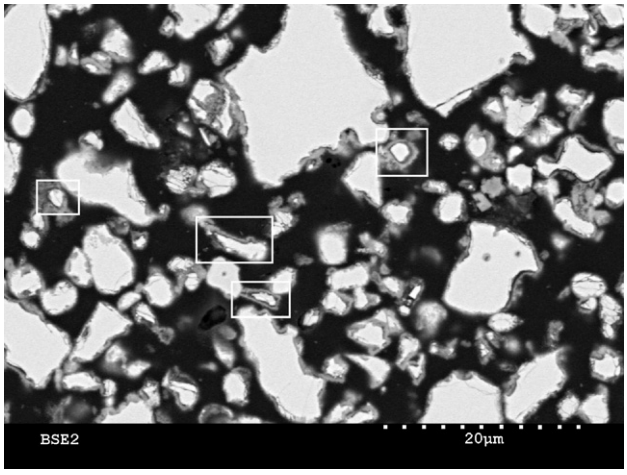

Fig. 11. Backscattered electron image of the C_3S paste hydrated for 13 h.

observed in Fig. 5 resembles very well the 'shell' structure of the 5-hour old cement paste (Fig. 8 in [14]). In other words, it appears from Fig. 5 that the early development of hollow-shell formation in Portland cement first noted in [2,14] also takes place in C_3S paste.

The 'separated shell-structure' were seen in association to many grains, in both the C_3S and Portland cement pastes; but they were most frequently observed in the cement paste. There were also many other particles in both pastes where there appeared to be contact between product layer and anhydrous particle. Still other grains in both pastes revealed both characters i.e. contact around parts of the grains and separations around other parts.

3.2.3. At 11 h

As revealed in Figs. 7 and 8, from 9 to 11 h the layers of hydrates enveloping the hydrating C_3S grains have developed a step further. Figs. 9 and 10 show two different areas of the cement paste hydrated for 11 h. At this age also, the microstructures of the C_3S and cement systems appear similar. There is contact between the outer layer of product and the interior of many grains, but there are also many grains were the layer of product is separated from the core. As at 9 h, the intra-shell voids were relatively more abundant in the cement paste than in the C_3S paste, but they do occur frequently in the C_3S paste. The intra-shell gaps appear to have widened from 9 to 11 h in both the C_3S (cf. Figs. 5, 7 and 8) and in the cement paste (Figs. 6, 9 and 10). A quite distinct Hadley grain nature is now quite often displayed, as observed from Fig. 10.

The hydrate layer covering the C_3S grains appear thicker and more uniform than does the layer of reaction product enveloping the cement grains. The apparent thickness of the hydration layers enveloping the C_3S grains is about 250 nm at 11 h. The fibrous character of the C–S–H surrounding the shell is now exhibited more clearly (cf. Fig. 7). The 'fibers' appear shorter and thinner with C_3S than in the cement paste. Fibrous C–S–H has generally not been noted from backscattered electron images previously due to limited resolution of many standard SEM instruments, as discussed in [29]. With the FE-SEM adopted the fibrous nature of the outer C–S–H becomes clearly visible.

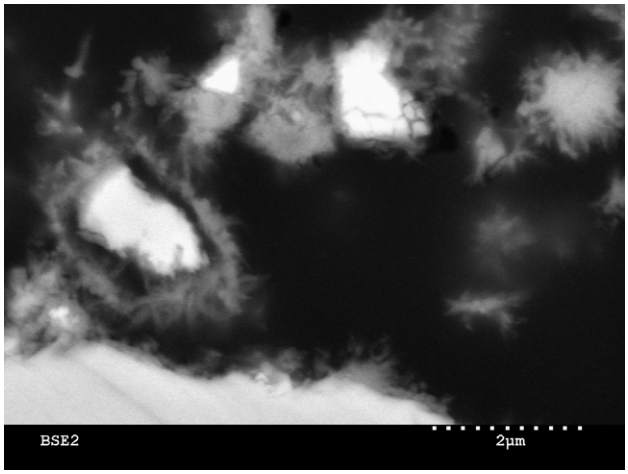

Fig. 10. Backscattered electron image of the cement paste hydrated for 11 h.

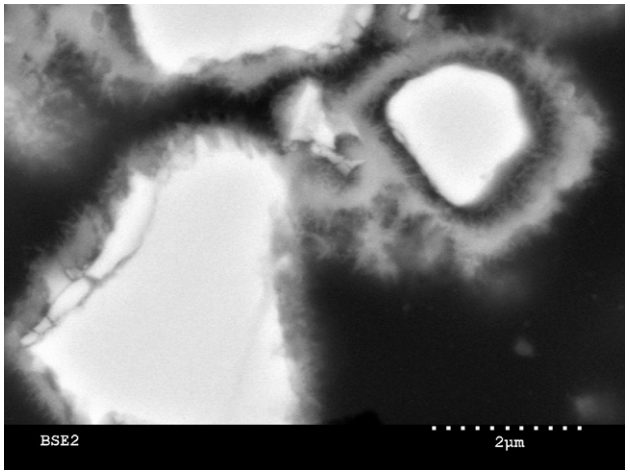

Fig. 12. Backscattered electron image of the C_3S paste hydrated for 13 h. Close-up of one of the framed areas in Fig. 11.

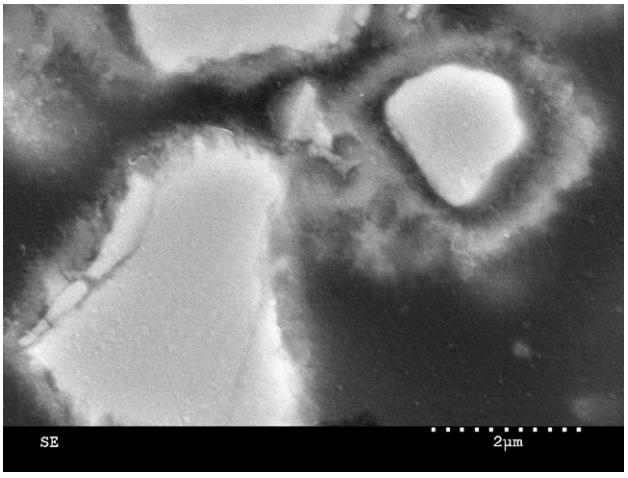

Fig. 13. FE-SEM image of the field from Fig. 12 obtained using a secondary detector.

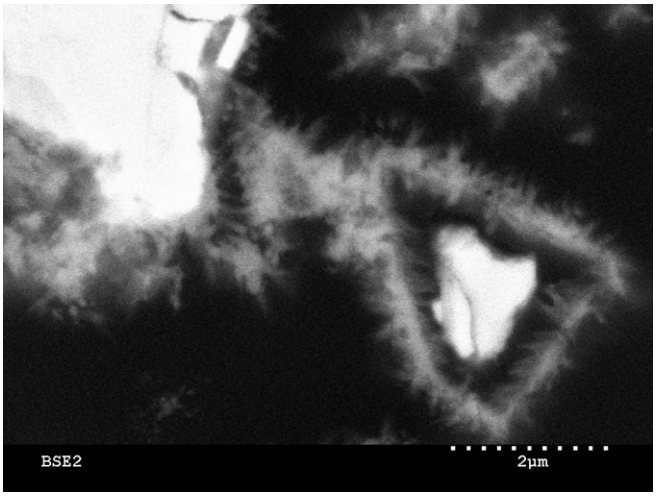

Fig. 15. Backscattered electron image of the cement paste hydrated for 13 h. Close-up of a portion of the area shown in Fig. 14.

3.2.4. At 13 h

Figs. 11, 12, and 13 depict the C_3S paste hydrated for 13 h. A number of C_3S grains with separations between the grain and shell of C–S–H can again be observed; examples are outlined in the overview image of Fig. 11. Fig. 12 reveals one of the outlined areas of Fig. 11 in detail. A small gapped Hadley grain can be observed towards the top right corner. The apparent diameter is about 2 microns. The apparent thickness of the hydrate layer covering the C_3S grains is typically about 300 µm at this stage. Fig. 13 is a secondary electron image of the area shown in backscatter in Fig. 12. The secondary electron image shows essentially the topography of the specimen surface, with the limited elemental contrast observed in Fig. 13 likely due to backscattered electrons impinging on the secondary detector. The surface appears smooth and practically without imperfections such as scratches or insufficient filling of epoxy resin. The epoxy resin has clearly filled all of the visible pore space, including the intra-shell separation of the Hadley grain. As impregnation with resin is performed prior to grinding and polishing [24], it is clear that the hollow-shells are real and not a result of material being pulled out during preparation. To detect artifacts caused by specimen preparation, such as incomplete filling of resin, and thereby avoid misinterpretation of the microstructure, in this work backscattered electron imaging were always preceded by secondary electron imaging.

The microstructural features observed in the cement paste at 13 h are shown in Figs. 14 and 15. Fig. 14 shows a lower magnification backscattered electron image; Fig. 15 reveals a portion of the area shown in Fig. 14 in greater detail. The intra-shell separations have widened further from 11 h, and are now more often separating the anhydrous grain and product along the entire perimeter of the alite grains. They are also seen in more of the grains. Note the similarity between the small gapped Hadley grains found in the C_3S paste (Fig. 12) and those found in the cement paste (Fig. 15). Small Hadley grains appear similar in C_3S paste and cement paste at this stage, though the hydrate layer covering the C_3S particles is thicker and has a less distinct fibrous appearance.

While the Hadley grain separations clearly have widened from 11 to 13 h in the cement paste, it appears that in the C_3S

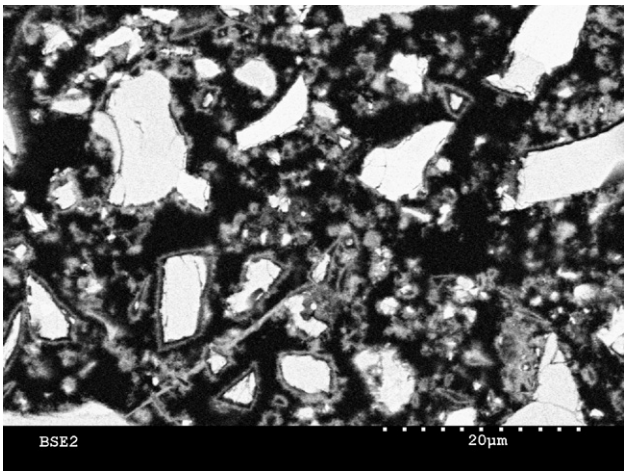

Fig. 14. Backscattered electron image of the cement paste hydrated for 13 h.

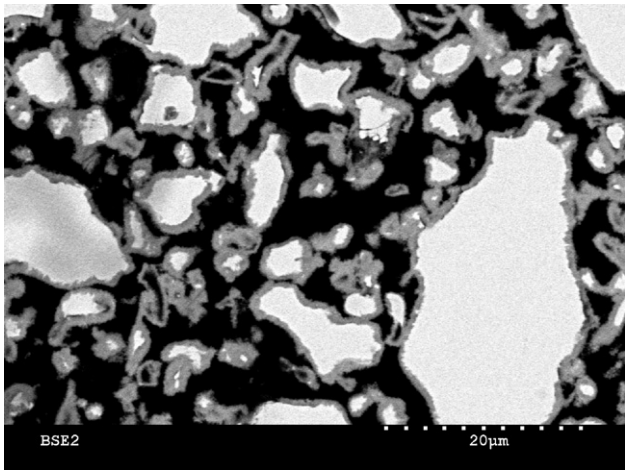

Fig. 16. Backscattered electron image of the C_3S paste hydrated for 24 h.

paste they have only done so for the smaller grains. The separation around parts of the larger C_3S particles at 13 h is not noticeably greater than they were at 11 h. There appear to be contact between the layer of product and the larger C_3S grains more often than there is separation between the two phases. While gapped Hadley grains are frequently observed in C_3S paste, they are not as common and as well developed as they are in the Portland cement paste.

3.2.5. At 24 h

Figs. 16 and 17 show backscattered electron images of the 24-hour old C_3S and cement pastes, respectively. The microstructure of these 1 day-old C_3S paste and cement paste were previously discussed in detail in [19], so we will here only point out a few points of particular interest.

The small gapped hydration shells with small remnant anhydrous cores frequently seen both in the C_3S and cement paste at 13 h, are not seen any longer at 1 day. Instead small fully 'hollowed-out' hydration shells are observed. This clearly indicates that the smaller grains showing gapped character at 13 h continue to dissolve rapidly and empty out their contents, so that hollowed-out hydration shells without much interior product are generally present by 24 h. This occurs in both the C_3S and cement systems. This type of Hadley grain appears to be smaller than about 5 μm across.

Around the larger remnant C_3S grains there generally appear to be contact between the hydration shell and the residual C_3S grain at 1 day (Fig. 16). It seems that sometime between 13 and 24 h the mode of reaction in the C_3S paste has changed, and deposition of C–S–H on the inside of the hydration shell became the prevailing scheme of hydration. The absence of gapped Hadley grains at 24 h is probably the main reason why Hadley grains have been claimed not to form in C_3S paste previously. The difference from the 1 day-old cement paste microstructure is striking, as gapped Hadley grains in the cement paste at this age are seen in association to practically all alite particles in the cement paste (Fig. 17). Actually, the gaps between anhydrous cores and product have widened significantly between 13 and 24 h in the cement paste, and the apparent width is now generally 1 to 2 μm. It does appear that a mode of hydration promoting the deposition of C–S–H on the outside of the hydrate layer have prevailed in the cement paste, at least up to 1 day. The degree of hydration between C_3S and cement paste appear different from Figs. 16 and 17, but is in fact similar as revealed from Figs. 1 and 2 and as discussed in [19].

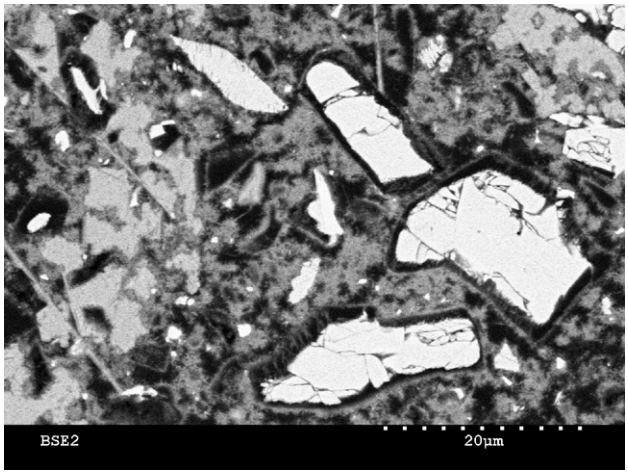

Fig. 17. Backscattered electron image of the cement paste hydrated for 24 h.

4. Conclusions

This FE-SEM backscattered electron mode study of flat-polished specimens shows the development of Hadley grains in pure C_3S paste as well as in Portland cement paste.

At 7 h, towards the end of the acceleration period, a layer of reaction product had formed on the anhydrous cement or C_3S particles. The apparent thickness of the hydrate layer was about 100 nm in the C_3S system. The hydrate layer appeared to be in contact with the underlying grain.

By 9 h, very narrow gaps were clearly observed at the interface between the shell of product and many anhydrous cores, very similar to the 'separated shell-structure' of young Portland cement paste found from STEM of thin-foils [14]. The character of these early-stage Hadley grains was similar in the C_3S and the cement systems.

At 11 and 13 h the 'intra-shell' separation appeared to have widened, and the thickness of the hydration shells had increased. A number of relatively distinct Hadley grains were seen both in C_3S and Portland cement. In particular, small gapped Hadley grains (<5 μm) were well developed, but a number of larger grains also revealed gaps between core and product. The character of the Hadley grains was similar in the C_3S and Portland cement systems, but such grains were more frequently observed in the Portland cement system. There were also many grains that did not display a Hadley grain nature at this stage in both systems.

The small gapped hydration shells (i.e. those Hadley grains with small remnant anhydrous cores) frequently seen both in the C_3S and cement paste at 13 h were not found at 24 h. Instead, small 'hollowed-out' hydration shells were observed. This indicates that the smaller grains showing gapped character at 13 h continued to rapidly dissolve and empty out their content so that hollow hydration shells without remnant cores or much interior product were established by 24 h. The small hollowed-out hydration shells were seen both in C_3S and cement at 24 h.

While small hollowed-out hydration shells were seen in both systems at 24 h to about the same extent, large gapped Hadley grains so typical for Portland cement at this age were not commonly observed in the C_3S paste. This variant of Hadley grains, with approximately 1 μm wide separation between the remnant cement particle and shell of product, was as expected a very significant and common feature in the Portland cement at this age. These gaps between the hydration product and the core were found in considerable numbers in the larger C_3S particles at 13 h, they were practically absent at 24 h. There generally appeared to be contact between shell and C_3S cores at 24 h.

While Hadley grains are a much less prominent feature in C_3S than in Portland cement at one day, this study has shown that they do form frequently in the middle hydration stages; and

specifically that the small 'hollowed-out' hydration shell variant of Hadley grains also may exist at later stages in C_3S paste.

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