Microstructural Studies of Early Age Hydration of OPC Using TEM

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Abstract

Early age hydration of Portland cement was studied using Scanning Transmission Electron Microscopy to better understand the development of hydrates at early age, particularly in regard to the formation of a hydrate shell and to the effect of interstitial phases on hydration. Along with the imaging of microstructural development, another aim was to obtain accurate chemical information at high spatial resolution. OPC cement pastes with W/C=0.4 were studied at 2,6,10,12,18,24 and 48 hours of hydration. At 6 hours, a shell of C-S-H can already be seen around cement grains, containing a 'low density' product with virtual continuity between the reacting grain and the shell. The shell formation seems to be independent of the grain size. After one day of hydration, the shell gets more prominent presenting a larger gap in between, with the formation of distinct ettringite needles growing from the shell into the gap. This gap is almost fully filled by 48 hours by inner product and monsulfate plates. From a chemical point of view, at early ages, a significant amount of sulfate is absorbed on the C-S-H gel. Around 18-24 hours a renewed growth of ettringite occurs and this results in a depletion of sulfate associated with the shell. At 12 hours no iron is detected in the analysis of the hydrated phases. At later ages, low levels of iron are observed in ettringite but these are always much lower than the levels of aluminium in Afm and Aft phases.

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1. Introduction

Hydration of Portland cement is known to be a complex phenomenon. Although the broad pattern of reactions and microstructural development are known, a number of important questions remain unanswered. A major issue concerns the interactions between the different clinker minerals present in Portland cement. The hydration reactions with water are dominated by C_3S, which generally constitutes the majority of the cement. However, there are significant differences between the hydration of cement and pure C_3S and understanding these differences is fundamental to predicting the performance and durability of cementitious systems. Such understanding is also crucial to improving the sustainability of cementitious materials, which are the most widely used materials in the world, with an annual production of 1.7 billion tonnes, accounting for 3-5% of man made CO_2 emissions.

From a microstructural point of view, the most obvious difference in the early reactions of cement pastes and pastes of C_3S is the formation of a “shell” of hydration product, separated from the underlying reacting grains [1]. For small grains, this leads to the formation of hollow hydrate shells or “Hadley grains” [2], which persist in mature materials and are present even in pastes and concretes of very low water to cement ratio. This mode of hydration is important because it determines the distribution of hydration products. The deposition of the products away from the reacting grains, rather than directly on them is more effective in blocking porosity which improves the development of mechanical and transport properties.

Previous results [3] have indicated that the formation of separated shells was related to the presence of the aluminate phase and suggested that at early ages an amorphous “gel” rich in calcium and alumina, but probably also containing silica and sulphate formed on the surface of the cement grains, from the initial reaction of calcium sulphate with the aluminate phase. In specimens observed in conventional TEM or SEM, the gap between shells and grain appeared to be empty, which was attributed to the shrinkage of the “gel” during drying. Recently Kjellsen [4] has suggested that separated shells are also formed during the hydration of alite (impure C_3S). However this study indicates that the separated shells are much less marked than in cement paste and mostly disappear, by the age of about 1 day. Furthermore the alite used in this study was stabilised with Al_2O_3, so, even through present at low levels, the presence of alumina, may be related to the formation of separated shells.

In this study, samples less than 1 day old (up to 2 hours) were successfully prepared and studied in a STEM. For the first time, images have been acquired in the dark field mode which has improved the image quality in terms of resolution and contrast, even at higher magnifications. It gives a clearer view of the fine intermixing of hydration products. This has been complimented with highly accurate chemical analysis, giving interesting insights into the early age microstructure.

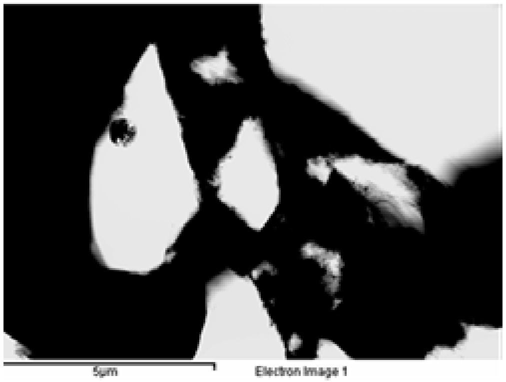
2. Experimental

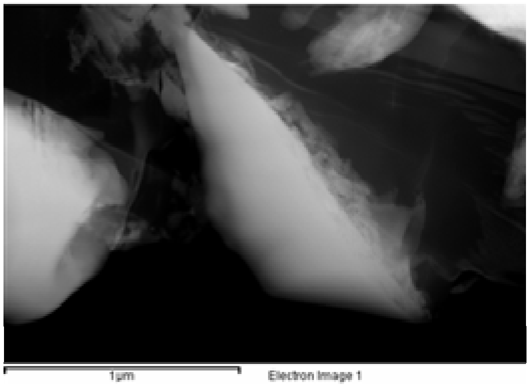
Cement pastes were made using a CEM I 52.5 at a water to cement ratio of 0.4. Hydration was stopped by freeze drying at 2-4-6-8-10-12-18-24 and 48 hours. Samples were then epoxy impregnated, mechanically polished (tripod) and then refine by ion milling. TEM imaging was done in dark field mode on a HAADF-STEM. EDS spot analysis and elemental mappings were done on a conventional TEM

3. Results and discussion

3.1. Microstructural development at early ages - formation of separated hydration shells

By two hours (Figure 1) most of the grains look unreacted (alite surface is not etched, almost no detectable hydrates on grain surface). Occasionally, a few diffuse hydration products are observed. EDS elemental mapping shows that those are mainly made of calcium, sulphur and aluminium (figure 1 - bottom). This association of elements is attributed to the presence of Aft and is the only evidence of reaction product at this age.





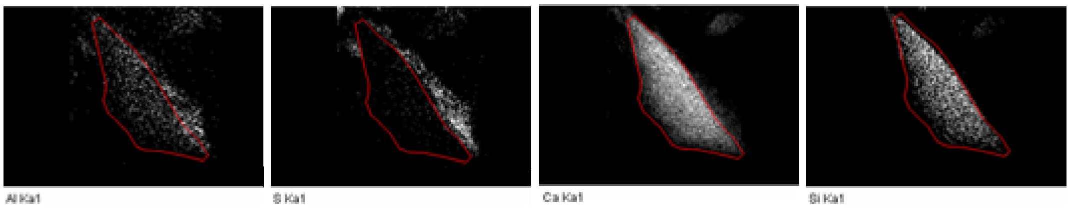


Figure 1. 2 hours of hydration - totally unreacted cement grains (left) and beginning of surface hydration (right) with corresponding EDS mapping

After 6 hours of hydration a thin shell of hydration product is visible around cement grains. The shell is usually connected with the grain by a well spread out foil like material. The phenomenon of shell formation does not seem to depend on grain size. Not all parts of a grain react at the same rate, thus there appears to be a preferential reactivity of the grains

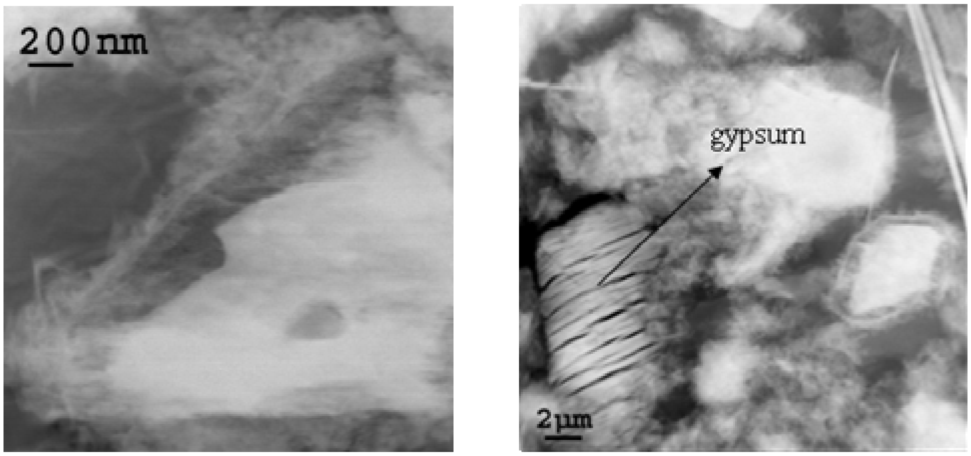


Figure 2. 6hrs hydration

By 12 hours, the shell gets denser and wider like a foil crumpled at the edge only. The low-density material has got relatively denser and well spread out within the shell. Also, at the edge of the grain, seen is the transition from the grain surface to C-S-H. The reaction with water has etched the alite surface and the original smooth edges of alite have become streaky.

Figure 3. 12hrs - Shell formation around alite with 'low-density' product in between

After 18 hours the gap in between the shell and the grain continues to increase with the material in between becoming almost like a thin carpet with long thick tubes of C-S-H embedded within.

By 24 hours the shell has taken its final shape and the gap in between is up to 2µm. The shell appears rather dense and is held in place by some still left over low-density material. Several ettringite needles are seen in between the shell and the grain, in places where the low-density material was.

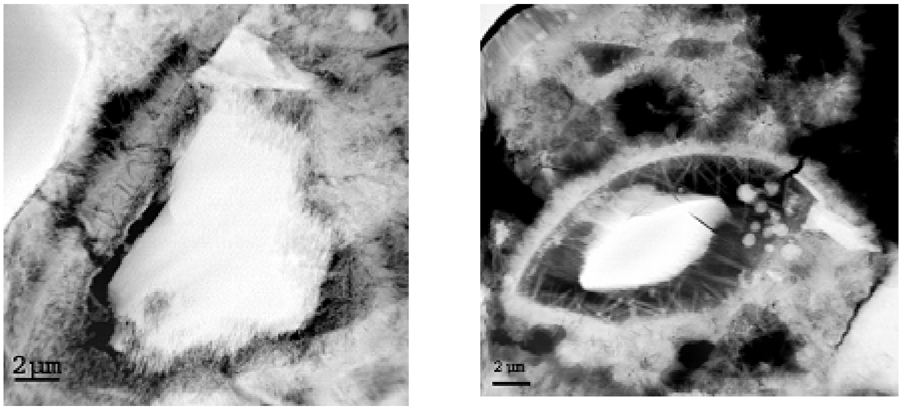


Figure 4. 24hrs - left : continuum between reacting alite grain and precipitating C-S-H / right : growth of ettringite needles from the schell towards the grain

As expected by 48 hours, clear inner and outer products have formed. The inner product is dense and compact. The low-density product within the shell develops into a dense and homogenous inner product having a well-defined interface with the outer product. The bonding between the inner and outer products seems to be excellent.

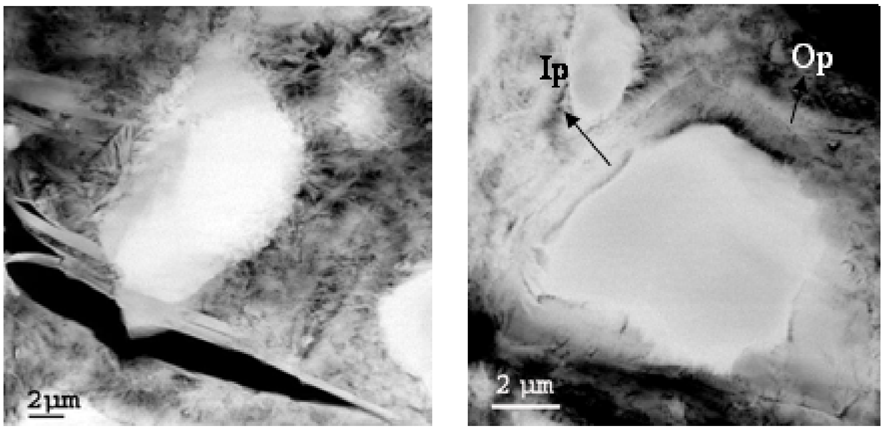


Figure 5. 48hrs – densification of the cementitious matrix / filling of the gaps with densifying inner product

3.2. EDS chemical analysis and chemical mappings

Beginning from 8 hours, a distribution of Ca/Si and S/Si ratios obtained from EDS analysis in TEM, over the observed ages, is presented below. It shows a wide distribution at all ages. A significant highlight of the chemical analysis has been the persistent presence of sulfur content in C-S-H in all the samples. It is assumed that the sulfur is present as $CaSO_4$ and, thus, to obtain the true value of Ca/Si of the C-S-H, sulfate content was subtracted from calcium and the remainder divided by silica.

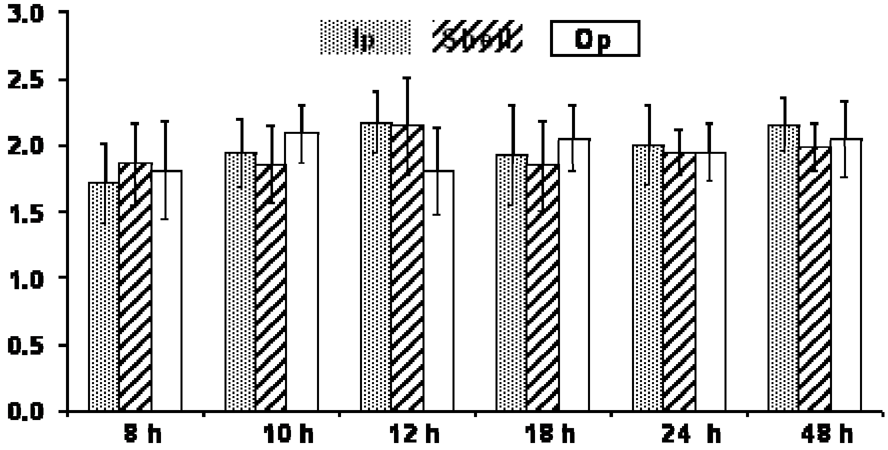


Figure 6. Analyses of Ca/Si ratio of product in shell, inside shell (Ip) and outside shell (Op) at different hydration times.

Table 1: S/Si atom ratios for all the regions and ages

	Ip		Shell		Op	
	Avg.±σ	n*	Avg.±σ	n	Avg.±σ	n
8	0.25±0.12	18	0.36±0.12	11	0.29±0.13	94
10	0.20±0.08	14	0.31±0.14	14	0.25±0.09	31
12	0.27±0.09	6	0.29±0.15	11	0.29±0.07	11
18	0.21±0.05	9	0.30±0.07	16	0.29±0.10	42
24	0.30±0.19	11	0.18±0.07	25	0.26±0.16	17
48	0.12±0.05	3	0.16±0	2	0.19±0.09	14

As seen in the Table above (S/Si) sulfur is present in a large number of analysis points in the low density product from the very beginning, indicating, beside the high solubility of gypsum in the pore solution, the high mobility of sulfate ions and the existence of through solution phenomenon at early stages of hydration. It is obvious that the ions released from alite will be calcium (Ca $^{2+}$) and silicate ($H_2SiO_4^{2-}$) but it would be rather inappropriate to image that the low-density material is only formed of pure C-S-H; indeed it also has a non-negligible presence of sulfure, as confirmed by the EDS chemical mapping below (figure 6)

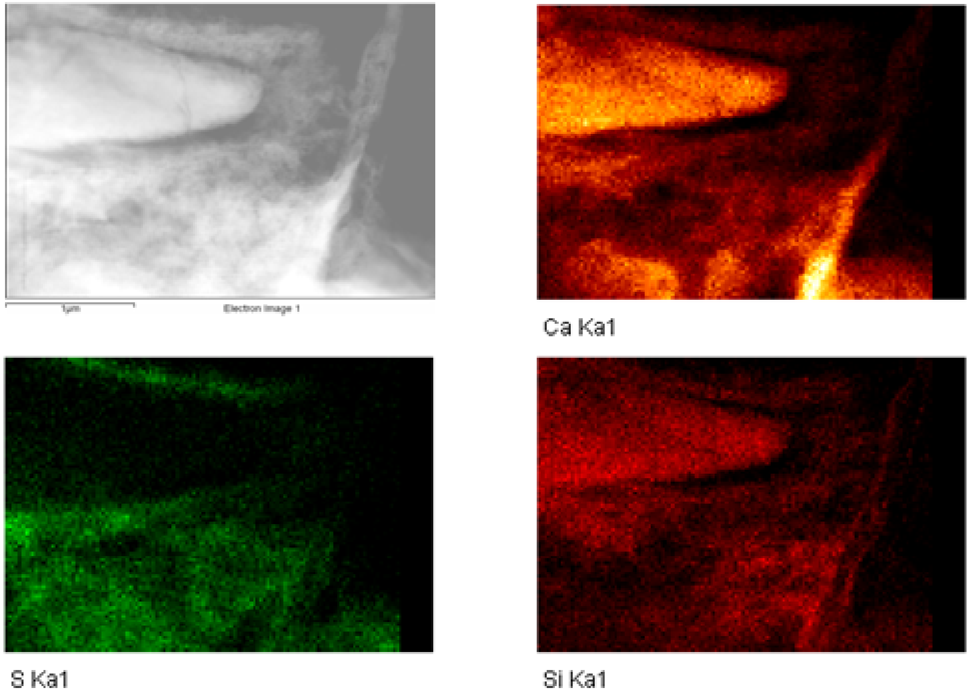


Figure 7. EDS chemical mapping - The S Ka1 map clearly shows the large amounts of sulfur present in C-S-H around the reacting grain

4. Conclusions

In the present work we have managed to prepare samples down to the age of 2 hours. Already at this age the shell is clearly present, while the separation between the shell and the underlying grain increases over the period 6-12 hours, with the less destructive specimen preparation techniques available, and the use of dark filed imaging it has been seen that the gap between shell and product is not in fact empty, but filled with a flimsy product. Furthermore, the reacting interface of the anhydrous grain is not sharp but, shows a layer of partial reaction about 100 nm thick. Despite considerable difficulties and the need to repeat the analyses several times we have now been able to analyse the composition of the product inside and outside the shell. It appears that the composition of the products is very similar and changes very little over time. The Ca/Si ratios are typical for calcium silicate hydrate (C-S-H) and significant quantities of aluminium are only seen in a few analyses.

This study has given the following main results:

- With careful specimen preparation it is found that what was previously thought to be a gap between the shell and the reacting grain is in fact filled with a flimsy, diffuse product
- The grains themselves do not react evenly, but the surfaces become heavily etched to a depth of about 500 nm already after 6 hours
- The different product morphologies – compact product forming the shell; fibrilar product on the outside of the shell and the flimsy diffuse product within the shell, do not seem to show any significant difference in chemical composition
- Between 24 and 48 hours the area between the shell and the grain becomes in filled with a denser deposition of product, which appears to form evenly throughout the space, rather than depositing progressively on the inside of the shell or the surface of the grain.
- Analyses of the sulfate content of the different C-S-H products forming the shell indicate that this is initially high and later drops between 18 and 24 hours when renewed growth of ettringite occurs.
- At early ages (before 24 hours) there is very little sign of ettringite (product of reaction of aluminate phase and added calcium sulphate). This puts into question the commonly held view that early ettringite formation retards the otherwise rapid reaction of the aluminate phase and lends support to more recently proposed hypothesis that the reaction of the aluminate phase is inhibited by the absorption of sulphate on reactive sites.
- The ettringite and AFm phases mostly contain only alumina and no iron. At 48 hours a proportion of the analyses show that about one third of the alumina is substituted by iron.

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