Optimisation of SEM-EDS to determine the C–A–S–H composition in matured cement paste samples

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44 **Abstract**

45 Microanalysis of characteristic X-rays in the SEM is a powerful method to assess the chemical
46 composition of phases in cement pastes, in particular the calcium silicate hydrate containing
47 aluminium (C–A–S–H). Nevertheless, many variables may influence the results obtained, due mainly
48 to the intimate mixing of C–A–S–H with other hydrate phases and the susceptibility of this phase to
49 damage by the electron beam. In this study the effect of various acquisition parameters was examined,
50 along with methods to determine an “average” C–A–S–H composition. The results acquired in the
51 SEM were compared with the analysis of the same samples in the TEM, where phases can be
52 analysed without intermixing. A simple method was used to obtain compositions from SEM based
53 analysis that are very close to those which can be obtained in the TEM.

54 **Keywords**

55 Cement, calcium silicate hydrate (C–S–H), scanning electron microscopy (SEM), transmission
56 electron microscopy (TEM), energy-dispersive spectrometry (EDS)

1. Introduction

Cement is composed of four main phases: alite (impure C_3S^*), belite (C_2S), aluminate (C_3A) and ferrite (C_4AF). They react with water at different rates to solidify the cement paste into a useful and cheap binding material widely used in construction. Calcium silicate hydrate (C–S–H) is the main product of the hydration of plain Portland cement (PC), constituting around 50% of the final volume of the paste and is the main phase responsible for its strength development and durability.

Other typical products which form in PC are crystalline and have well defined stoichiometries. These include Portlandite ($Ca(OH)_2$, CH), Ettringite ($C_6AS_3H_{32}$ also referred to as AFt) and three “so-called” AFm phases: calcium monosulfoaluminate (Ms or $C_4AS_2H_{12}$), calcium hemicarboaluminate (Hc or $C_3AC_{0.5}CH_{0.5}H_{11.5}$) and calcium monocarboaluminate (Mc or C_3ACCH_{11}).

In contrast C–S–H has a very variable stoichiometry and lacks long range order, being more nanocrystalline, with regions of well-defined structure on the scale of 5-20 nm. The hyphens in C–S–H are written because of the variable stoichiometry [1]. The most important variable for C–S–H is the calcium silicate ratio (Ca/Si), which has been reported to vary in the range of about 1.5 to 2.0 in cement pastes but has been observed to reach values as low as 0.8 in blends containing silica fume [2–4]. At the atomic level the structure of C–S–H consists of calcium oxygen layers flanked on both sides by chains of silicate tetrahedra. It is currently believed to mostly resemble a defective tobermorite [5] which can account for the variable Ca/Si ratio. C–S–H can incorporate other ions on or within its structure. Aluminium is present in real cements and may substitute for silicon [6–8]. The “calcium silicate” ratio can then be corrected as $Ca/(Si+Al)$ and we then use the more general C–A–S–H abbreviation for this phase. **Electrostatics [9,10] may cause anions such as sulfates to absorb on the charged surfaces.** This is considered to be a coupled absorption with calcium [11,12]. In general, ions such as N, K, S, Fe and Mg are known to be present in very small amounts, but these are not considered here.

* In cement notation for oxides, C = CaO, S = SiO₂, A = Al₂O₃, H = H₂O, \$ = SO₃, C = CO₂.

It is often of interest to determine the average C–A–S–H composition in a given cement paste as part of the study of the phase assemblage. In the past indirect methods were used, however the errors involved were usually high due to cumulative measurement errors. The composition of C–A–S–H is best estimated from microanalyses of characteristic X-rays in a scanning electron microscope (SEM) or microprobe of polished sections of cement paste [13]). Energy-dispersive spectrometry (EDS) is routinely used because it conveniently records the full chosen range of characteristic X-rays which may be processed and quantified. Wavelength dispersive analysis (WDS) is often considered to be more accurate, but in our experience it is less well suited for the analysis of the C–A–S–H composition because the higher electron dose needed leads to more sample damage as discussed further and because higher precision of an individual measurement is outweighed by the fact that many more measurements can be made by EDS in a given time. Given the variability in composition from point to point it is more important to do a lot of measurements, than fewer more accurately.

Scanning electron microscopy coupled with energy-dispersive spectrometry (SEM-EDS) is used to conduct quantitative X-Ray analyses on properly prepared samples. The basic assumptions for conventional quantitative analysis of flat-polished specimens using the standard k-ratio technique with $\phi(\rho z)$ matrix correction protocol as discussed by Sawyer et al [14] are: (i) a flat-polished surface, (ii) a homogeneous composition within the analytical volume, (iii) stability of the sample under the electron beam, (iv) the analysis is made in the same conditions as standards (standard-based analysis), (v) all elements are accounted for during the quantification of the analysis. High quality quantitative analysis of hydrated cement by SEM-EDS is a challenge because it violates most of these assumptions. (i) It is a highly heterogeneous material with hard unreacted grains and softer hydrated paste regions, making it very difficult to polish and which make it prone to rough surface effects [15]. (ii) Another limitation present in bulk samples is the phenomenon of “intermixing” which occurs between C–A–S–H and other phases. Several phases co-exist within the analytical volume, which can cause analyses to be biased towards higher or lower atomic ratios and must be considered while treating the data. This is also discussed further. Also phases like C–A–S–H can vary in composition, further complicating analyses. (iii) Hydrated phases contain water and degrade under the electron beam. This limitation is

discussed in this paper. (iv) The presence of bound water (hydrogen) affects the analysis totals and should be taken into account. However, effects due to the imperfect quantification of oxygen can be minimised by considering atomic ratios, rather than absolute amounts as in this work.

Despite the challenges mentioned above, there is utility in using the technique as long as these limitations are understood. This study focuses mainly on the intermixing and the beam damage.

In this paper we examine systematically the effect of various acquisition parameters, acquisition methods and data treatments for estimating the C–A–S–H composition of cement paste by SEM-EDS. For several hydrated cement pastes, we compare composition measurements obtained in the SEM with those from transmission electron microscopy (TEM), where analyses can be made free from intermixing. A summary of guidelines regarding data acquisition and data treatment is given in the conclusions. The use of electron microscopy for the study of cement and concrete is discussed more extensively in [16] and the reader is referred to this reference for a more detailed practical approach to sample preparation and chemical analyses of cement pastes by both SEM-EDS and TEM-EDS.

2. Materials and specimen preparation

The detailed study of acquisition parameters was made on a white cement (WC) paste prepared previously [17] and was kept under water for five years. It is a CEM I 52.5, which contains mostly alite and belite but little iron. The second sample was a CEM I 32.5 grey cement (PC) from another study [4] and which contains more aluminate, ferrite and gypsum. It was reacted for 90 days. The third is another blend from [17] containing 60 wt% of WC with 40 wt% of ground granulated blast furnace slag (BFS), i.e. WC-BFS. The composition of the raw materials determined by X-ray fluorescence (XRF) is given in Table 1. XRF is typically used to conduct a bulk analysis of the anhydrous materials. Its accuracy is discussed in [18], with standard deviation values from inter-laboratory analyses given in Table 1 therein. Standard deviation is less than 0.4 wt% for all elements.

Table 1: Composition of the three raw materials used in this study, as given by XRF measurements.
*Na₂O equivalent

Name	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Mn ₂ O ₃	LOI
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WC	24.68	2.11	0.43	68.67	0.58	1.82	0.17	0.06	0.05	0.45	0.01	0.97
PC	21.07	5.56	2.56	64.89	1.58	2.77	0.20	0.85	0.33	0.11	0.08	1.93
BFS	34.6	20.0	0.5	32.5	9.2	2.0	0.7*	-	-	-	-	-

All samples were prepared with a water/solid ratio of 0.4 (by weight) with distilled water. After the first 24 hours they were stored at room temperature ($\approx 20\text{-}22^\circ\text{C}$) in sealed containers under distilled water. Hydration of the samples was stopped using solvent exchange to remove free water. This was done by cutting a slice about 2 mm thick, storing it in a large volume of isopropanol for seven days and then drying it under vacuum for five days in a desiccator. The solution was replaced at least once within the first day of solvent exchange to enhance the removal of water.

For SEM, one piece was impregnated using epoxy-based EPO-TEK® 301 resin and polished using diamond sprays of decreasing sizes (9, 3 and 1 μm) with petrol as a lubricant. The sample was coated with a 20-30 nm carbon film using a BAL-TEC CED 030 Carbon Evaporator.

For TEM, a smaller piece was impregnated using EMS Embed 812 resin, cut to a thin slice using a WELL diamond saw, thinned down mechanically to a bevel by mean of the Tripod method (supplied by ALLIED Tech) to yield a thickness of about 20-30 μm on the thick side. It was then ion-thinned with an Argon PIPS (GATAN Precision Ion Polishing System Model 691) operated at maximum 1.5 keV to achieve electron transparency and carbon coated with a 5 nm layer using a CRESSINGTON 208 high vacuum carbon coater.

Prior to each set of measurements in the electron microscope, preliminary measurements were done on alite or belite – both of known atomic ratios – to verify the stability of the EDS system before analysing hydrates. This was usually not possible in the TEM because either no anhydrous material was found or because anhydrous material is significantly thicker than C–A–S–H regions.

SEM results were obtained on a FEI Quanta 200 equipped with a tungsten thermionic filament. Images (1024×768 pixels²) were acquired in backscattered electron (BSE) imaging mode. The EDS detector was a Bruker AXS XFlash® Detector 4030 (with an active surface of 30 mm²). The dead time in EDS under these conditions was less than 1%, which is in the range of 10% or less

recommended by Ritchie and coworkers for quantitative analysis using a detector model similar to ours [19]. The Bruker Esprit software (version 1.9.3) allows definition of a number of counts rather than only a counting time. This allowed comparison of statistically equivalent points despite possible variations in current. There is a normalisation step which “calibrates” the intensities by the “system factor” measured on the EDS peak of a copper film placed on the metallic sample holder and used as a reference. Tests showed that the system factor is linearly related to the beam current by a factor of ≈ 8 . If the factor was 5.93, the beam current is reasonably estimated by $5.93/8 \approx 0.74$ nA. The “calibration” was done prior to analyses each time the filament was switched on and every two hours to limit the effect of possible beam current variations. The variations in probe current were measured during a two hour session and were $\approx 0.5\%$ /hour. The calibration ensures the analyses are conducted at the same current as that used for recording the standards database. A predefined list of elements (O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe) was used for identification and quantification as it facilitates calculations when treating several hundred points from the same sample. In this study the list covered all the elements present in all spectra but can be adjusted. For each spectrum the background was automatically modelled and subtracted, each peak was deconvoluted using a Gaussian fitting and then quantified using the $\phi(\rho z)$ matrix correction scheme with standards. Standards include relevant compounds such as wollastonite, jadeite, silica and alumina. The amount of oxygen is not reliably quantified as it is a low-energy peak and which can be sensitive to the thin EDS detector window. Therefore oxygen was quantified by stoichiometry. Atomic ratios are used for treating the data [20] to minimise the influence of errors in quantifying oxygen and slight variations in the probe current. Also, quantification of oxygen by stoichiometry can be used to differentiate between hydrates and anhydrous material. The presence of water causes the analysis totals in hydrates to never reach 100% because hydrogen is not taken into account. In the high vacuum of a microscope, it is estimated from thermal dehydration and intensive drying at room temperature that the water content in hydrates is around 15–25 wt.% [21]. In addition, porosity and irradiation damage may also lead to low analysis totals [20,22]. So while anhydrous phases such as alite and belite will give analysis totals of $\approx 95\%$ – 105% , the total from hydrates may range from 65% to 85%.

The TEM was a FEI Tecnai OsirisTM (CIME, EPFL) with a high brightness XFEG source and coupled with a set of Super-X Windowless SDD EDS detectors integrated into the pole piece. The system was optimised for cementitious materials [23] and operated in scanning (STEM) mode to acquire bright field (BF) and high angle annular dark field (HAADF) images and spectral maps (*HyperMaps*). Details of the setup are given in Section 7. After acquisition, polygonal regions could be defined in the *HyperMaps* after acquisition to form a cumulative EDS spectrum ready for quantification. Each spectrum was corrected for possible thermal drift in the SDD detectors by calibrating the energies to the zero-peak and the Ca peak (K_{α} series at 3.692 keV). Background correction for each spectrum was done semi-manually. The corrected spectra were quantified using a standardless Cliff-Lorimer ratio technique [24] with the same predefined list of elements as in SEM-EDS and with, in addition, C, Cl, Co and Cu peaks for deconvolution of overlapping spectra only. The Cliff-Lorimer ratio technique assumes the effects of absorption and fluorescence are negligible where the sample is thin enough. The background is subtracted from the intensity peaks before concentrations C_A and C_B of elements A and B are calculated using the following equation

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \quad (1)$$

This equation gives the relationship between the above-background characteristic intensities I_A and I_B and the concentrations using the factor k_{AB} which depends on the system and the accelerating voltage. In this study this technique is seen to be accurate for the main elements (Ca, Si) despite the absence of standards as long as the quantified area is thin enough. Due to low statistics on the peaks of low-concentration elements such as Al and S for example, the accuracy of the Cliff-Lorimer algorithm is lower in those cases. The software (Bruker Esprit 1.9.4) also required a fixed sample thickness to be inputted. Based on the difficulty in preparing cementitious materials for TEM-EDS analysis using the Tripod and PIPS a fixed inputted thickness value of 150 nm was chosen. This allowed us to keep a fixed methodology for quantifying the EDS spectra. We initially noticed that increasing the inputted thickness increased the quantified Ca/Si ratio in thicker areas (due to unwanted absorption effects which invalidate the Cliff-Lorimer technique), but did not influence results in thin areas. This helped us differentiate thin from thick areas.

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212 3. Microstructure development of hydrated cement pastes in SEM

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214 **Figure 1: BSE-SEM images of polished sections of the plain cement (PC) paste at two different times of**
 215 **hydration. Each image is taken from a separate sample. The grey level histograms are shown for both**
 216 **images, between 0 and 255 (2^8 or 8 bit). (a) PC after 1 day of hydration. (b) PC after 90 days of hydration.**

217 **Figure 1** shows typical microstructures and C-A-S-H as observed in BSE-SEM images of polished
 218 sections of a plain cement paste at early (1 day) and late (90 days) ages. The corresponding grey level
 219 histograms are given below the micrographs. In these images, the large bright grains are unreacted
 220 alite, the light grey product is CH, the darker grey product corresponds mainly to C-A-S-H and the
 221 dark regions indicate porous regions or low-density products. The brightest spots are typically iron
 222 from the ferrite phase.

Within the first day (Figure 1a), the first C–A–S–H products grow from the original surface of the cement grains, and CH forms mostly in originally water-filled space. C–A–S–H here forms a shell of “outer product” (OP) fibrillar hydrates (directional rods typically 10 nm wide and 200 nm long) and a small gap (“Hadley grain”) typical in plain cement pastes exists between the C–A–S–H and grain of alite. The porosity is high at early age. As hydration proceeds the reaction slows down significantly. C–A–S–H continues to precipitate around the clinker grains as “outer product” (OP) and more CH forms. The space is progressively filled with hydrates and the porosity decreases. From this point in time the C–A–S–H also forms in the place of the original cement grain. This forms “inner product” (IP) rims of C–A–S–H regions that grow over time (Figure 1b). The IP and OP, shown in Figure 1b after 90 days of hydration, differ in morphology. The morphology of the IP cannot be resolved in the SEM.

Knowing the location of C–A–S–H in the microstructure, it is common practice to conduct manually placed point analyses to estimate its composition. The following sections discuss how the acquisition parameters and the data treatment can affect the obtained results.

4. Parameters of the SEM-EDS

The parameters of the SEM should be set to get good counting statistics, but limit beam damage. The hydrated phases of cement pastes contain significant amounts of bound water even after the sample preparation, making them highly susceptible to beam damage in both the SEM and TEM. In classical TEM, a static electron beam causes almost immediate damage [25], usually within 30 seconds. If the damage is excessive it changes the chemical structure and composition entirely as the transformation to wollastonite may occur [25]. Use of a cooling stage has been proposed to limit such damage [26]. Other solutions include rastering the beam to limit damage to the sample [27] or defocusing the beam. In SEM, damage can occur as well even in the bulk samples. In SEM, point analyses were preferred because rastering the beam over areas larger than that of point analyses greatly increases the chance of intermixing, which is discussed further. Defocusing the beam was not necessary because of the low current density of tungsten sources but can be with FEG sources, as mentioned further.

For the purpose of this paper, data points of the atomic ratios (e.g. Si/Ca) can be shown as histograms and box plots (Figure 2). In the histograms a binning of 0.01 was used to best observe the peak in the frequencies of the atomic ratios and to later fit the data. The box plot is a simple way to compare different sets of data while extracting useful values and without the need to assume any type of distribution. In the box plots are shown the median value (-), the first and third quartiles (the box edges at 25% and 75%), the edges at 5% and 95% of the data (whiskers) and the mean value (■).

Figure 2: Histogram of the SEM-EDS data points (Si/Ca) of the OP C–A–S–H from Figure 8 and the box plot representation of the same data. In the box plot are shown the median value (-), the mean (■), the values at 25 and 75% (box edges) and the values at 5% and 95% (whiskers).

4.1. Choice of the electron beam voltage

The interaction volume increases with the accelerating voltage and should be minimised to increase spatial resolution [28] and also to minimize the energy of the beam which can cause damage to the sample. However at lower voltages the influence of the quality of the surface and the carbon coating increases. Cement samples contain elements with relatively low atomic number (typically O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe) with Fe usually having the highest atomic number. This limits the choice as an overvoltage $U = E_0/E_c$ of 1.5-2.0 is required to properly measure the element with the highest edge energy (E_0 being the SEM beam energy in [keV] and E_c the considered X-ray energy in [keV]). With the edge energy E_c for the iron K-shell of 7.112 keV, 15 kV is the recommended voltage

[20] because $U = 15/7.112 = 2.1$. This voltage is commonly used for the study of polished sections.

The interaction volume at 15 kV has a radius of about 1-2 μm – as estimated using CASINO Software for a Ca-Si substrate – but is possibly more due to the porosity of C-A-S-H.

4.2. Choice of the beam current

Hydrates are highly susceptible to electron beam damage. For SEM-EDS, tungsten sources may be regarded as more appropriate as they provide high beam currents for recording many characteristic X-rays per given time with the advantage of a low current density to limit the amount of damage. With field-emission guns (FEG) it could be necessary to defocus the beam to prevent damage at higher current density.

Figure 3 is a backscattered electron BSE-SEM image from the white cement paste (WC) observed with a beam current of about 0.8 nA. It was recorded in the FEI Quanta 200 with a tungsten source after short EDS point analyses with a static beam at locations indicated by the circles. Markings are observed in the hydrates after exposure to the electron beam (only 3 seconds per analysis).

Figure 3: BSE-SEM image of WC. The markings indicated by a circle are damage in the hydrates after 3 seconds of exposure to a static electron beam at a current of 0.8 nA.

The effect of the beam current on the SEM-EDS results was investigated in the same microscope by changing the spot size and adjusting the counting time to have the same number of X-rays per acquisition (50,000 counts per spectrum). Typical acquisition times were 1 second (at high current) to 4-5 seconds (at lowest current). In a series of acquisitions made during a same session – i.e. without switching the beam off –, the spot size was varied to increase the beam current from ≈ 0.74 to 2.75 nA. Analyses were made of the IP C–A–S–H of WC (≈ 100 points for each current). Despite the obvious visual damage, the results shown in Figure 4 suggest that the beam current (at constant total electron dose) does not have a significant effect on the measured composition. As discussed below, the composition of the least intermixed C–A–S–H is best estimated by the top whisker (at 95%). The measured values of this top whisker do not vary much.

Figure 4: Effect of the beam current on measurements of the IP C–A–S–H from WC at constant exposure of 50,000 counts per spectrum. The currents are ≈ 0.74 , 1.5 and 2.75 nA for system factors of 5.93, 11.74 and 21.92 respectively.

4.3. Choice of counting time

Figure 5 shows the influence of **total counts per analysis** on the Si/Ca of IP C–A–S–H from WC. The **total counts per analysis** were increased from 25,000 to 400,000 in a single one day experiment without switching the filament off. There is an overall decrease in Si/Ca from ≈ 0.56 to 0.54 between

50,000 and 100,000 counts per analysis, but the top whisker (95%) remains at Si/Ca ≈ 0.54 for higher counts per analysis. The median and mean values follow a similar trend. The distribution shifts slightly up at 400,000 counts per analysis, except for its top whisker. This is probably due to the random intermixing of phases.

Figure 5: Results from EDS analyses of the IP C–A–S–H from WC for different counts per analysis, i.e. 25,000 to 400,000.

The sum for Ca+Si (unnormalised mass totals) in these analyses showed a clear decrease with the total counts per analysis (Figure 6). The drop is most significant from ≈ 40 wt% at 25,000 counts per analysis (approx. 1-2 seconds counting time) to ≈ 38 wt% at 50,000 counts per analysis (approx. 3-4 seconds) and further decreases to ≈ 37 -38 wt% for higher total counts per analysis. This confirms what is seen in Figure 3, i.e. even at low beam currents, the damage occurs almost instantly in hydrate phases due to the stationary beam, which translates in a decrease in mass totals, in part due to increased porosity [22]. These results further suggest that despite the low probe brightness given by the Tungsten source, there is always some beam damage [29,30] which can affect the measured composition.

Figure 6: Ca+Si mass totals (%) as a function of counts per analysis. Data is from the IP C–A–S–H of WC.

The shortest counting time (25 kcps) shows that the peaks for Ca, Si and Al contain (with background) $\approx 6,000$, $\approx 3,500$ and ≈ 511 counts respectively. Because X-ray generation obeys Poisson statistics – which can be approximated by a normal distribution given the high number of counts – the standard deviation σ for a distribution having a mean value $\bar{N}$ is given [14] can be estimated as:

$$\sigma = \sqrt{\bar{N}} \quad (1)$$

The relative standard deviation σ/N is 0.013 (Ca) 0.017 (Si) and 0.045 (Al). For aluminium it is 4.5%. In order to enhance the precision of the EDS 400,000 could be chosen. However because of beam damage a value of 50,000 counts per analysis was preferred for our setup. It suffices because standards are used and has the advantage of increasing the number of points acquired per session compared to the use of longer counting times.

4.4. Effect of number of points

Figure 7 show the influence of the number of points taken for the data treatment. Points in the OP C–A–S–H of the WC sample were chosen to show the possible influence of intermixing. 380 points were acquired, and each subset of points (100, 200 and 300 points) was chosen at random from the complete dataset and represented as a box-plot. The results show the distribution between 5% and

95% of the values is the same in all subsets of data, suggesting that manually choosing approximately 100 points should be sufficient to estimate the atomic composition of C–A–S–H.

Figure 7: Box plots of different subsets of a dataset of 380 OP C–A–S–H analyses from WC (acquired with an exposure time of 100 kcps).

4.5. Settings used in this study

The FEI Quanta 200 SEM was therefore operated at 15 kV with a spot size and current small enough (0.8 nA) to have a sufficient BSE image resolution and low damage. The beam produced on average 12,000 counts per second in hydrate phases. The counting time was fixed at 50,000 counts per spectrum (typically 3-4 seconds).

5. 2D scatter plots of point analyses of C–A–S–H

It is common practice to present the data from chosen SEM-EDS point analyses as atomic ratio plots [20]. Figure 8a and Figure 8b show data points from the WC cement paste with IP and OP C–A–S–H separated into two datasets. Because of the interaction volume in the SEM, chemical analyses of C–A–S–H by SEM-EDS can contain signals from two or more different phases (often C–A–S–H and CH or C–A–S–H and ettringite), i.e. “intermixing” of phases is illustrated in Figure 8c. Such a representation of the data allows some discrimination of the different phases based on the Si/Ca,

Al/Ca, S/Ca or any other ratio of interest. General features of such plots are a cloud of points (indicated by ovals) and some data points which scatter outside those groups of points. In Figure 8a, (Si/Ca vs Al/Ca) points outside the cloud of points tend to be aligned between the composition of phases such as CH, AFt and AFm, and those of C–A–S–H and correspond to mixtures between these phases. This plot of Si/Ca vs Al/Ca indicates the presence of C–A–S–H, CH, AFt and AFm although it is not possible to identify which AFm is present (Ms, Hc or Mc). Figure 8b, using the S/Ca and Al/Ca ratios instead, indicates that Ms is the AFm present in this cement paste. Tie lines can be placed manually in such a way to find an edge to the cloud of points which could be considered to be the “pure” (least intermixed) C–A–S–H. However, before now, it has not been experimentally verified if this is really the best way to estimate the C–A–S–H composition by SEM-EDS. This is the main point addressed in the following sections.

(a)

(b)

Figure 8: SEM-EDS data points (beam voltage = 15 kV, beam current = 0.8 nA, courting time = 50 keps) from WC hydrated for five years. a) 2D Scatter plot of EDS analyses of IP and OP C-A-S-H. x axis is Si/Ca and y axis is Al/Ca. b) Same with the x axis being Al/Ca and y axis being S/Ca. c) A simple illustration of the intermixing of phases. The interaction volume is shown to contain information from C-A-S-H (dark grey) and Portlandite (left) or C-A-S-H and Ettringite (right).

6. Instrumental error in SEM-EDS and intermixing

There are always **instrumental variability and statistical fluctuations** which limit precision and accuracy [14,31] of any measurement. The use of standards recorded in the same conditions as for the sample significantly improves the performance of the SEM-EDS. In our system, the precision of the SEM-EDS analyses was estimated using a set of data from pure unreacted belite, slag and OP C-A-S-H (of the WC paste) all measured in the microstructure of a cement paste. Each set of data was acquired and quantified during a same two-hour session. The mean Si/Ca, $\bar{x}$, and sample standard

deviation, s , were determined. The relative variation (in %) was calculated using $s/\bar{x}$. Results are given in Table 2 and show that the dispersion of the data is 2.53% for pure belite, 4.61% for anhydrous slag and 9.08% for the OP C–A–S–H.

Table 2: Calculations from EDS analyses of belite in the plain WC sample hydrated for 5 years at 20°C.

		Belite (C ₂ S)	Slag	OP C–A–S–H
Number of points	N	24	25	108
Mean Si/Ca	$\bar{x}$	0.491	0.937	0.487
Sample standard deviation	s	0.012	0.043	0.044
Variation [%]	$s/\bar{x}$	2.53	4.61	9.08

The lowest dispersion of 2.53% measured for belite is very satisfactory given that the precision of a stable SEM-EDS setup is about 1-2% [14] and is likely because the analyses of belite can be made in the middle of large homogeneous grains where intermixing is unlikely.

The dispersion is larger (4.61%) for slag grains because slags are glassy materials which can vary in composition.

The largest dispersion is for the OP C–A–S–H (9.08%) despite a high number of points (108). This result clearly shows how both the intermixing of C–A–S–H with other phases and the variable composition of C–A–S–H are the main factors which cause dispersion in the analysis results of the hydrates.

7. Transmission electron microscopy

In order to avoid the problem of intermixing TEM-EDS can be used [32]. As TEM specimens must be thinned to around 100-150 nm, this limits the size of the interaction volume to similar dimensions and allows areas of C–A–S–H to be analysed free of intermixing. However, this advantage is typically outweighed by the difficulty, time consuming nature and expense of sample preparation and the much lower availability of TEM instruments compared to SEM.

Technical improvements in SEM-EDS and TEM-EDS which allow the use of lower electron doses have the potential to improve the agreement between both methods. In particular, silicon drift

detectors (SDD) are more frequently used, which have greatly improved EDS analyses in the SEM. The **increased solid angle** SDDs provide and their thermal stability enable the use of low beam currents and low exposure times while recording sufficient X-ray counts in each spectrum. The same applies to modern TEM instruments which now integrate such detectors.

The FEI Tecnai OsirisTM TEM (CIME, EPFL) was operated in scanning mode (STEM). Images (1024×1024 pixels²) were acquired on thin regions and simultaneously in bright field (BF) and high angle annular dark field (HAADF) mode. EDS spectral maps (*HyperMaps*) with a full area resolution of 512×512 pixels² were recorded for 15-20 minutes each. Drift correction was used to ensure the microscope always analysed the same area. The samples were systematically tilted by $\alpha = 20^\circ$ towards the detector to limit “shadowing”, i.e. absorption effects from the sample at low collection angles. The following settings were found to be best for imaging and EDS mappings with minimal degradation of the sample: accelerating voltage of 80 kV with a large spot size and the “nanoprobe” setting to yield a low beam current (0.160 nA or less with a high “gun lens” value) and limit damage. The count rate was quite sensitive to the thickness of the sample and ranged between 3,000 and 12,000 counts per second. The areas (512×512 pixels²) were scanned for 10 to 15 minutes with a short dwell time per pixel of 100 μ s. **Several frames were therefore scanned and with drift correction activated.** Prior to each EDS analysis, the beam was defocused by 200-250 nm to further limit damage.

Figure 9a and Figure 9b show two STEM-HAADF images of a same region of sample WC. Figure 9a is an image taken shortly after exposing the sample. Here the typical morphologies we can expect from C–A–S–H in plain cement paste are observed. The OP region is fibrillar while the IP has a non-directional morphology. After 15 minutes of exposure to the beam during EDS mapping, as shown in Figure 9b, the morphologies are no longer distinguishable due to damage, i.e. “bubbling” of the C–A–S–H. Figure 9c and Figure 9d are two STEM-BF images of the WC-BFS sample illustrating more severe damage in the microstructure due to bubbling. Figure 9c also shows the effect of observing **the sample for a short time at** very high magnification. Damage was almost instantaneous.

Figure 9: STEM-HAADF images of a thin region of WC (top) and STEM-BF images WC-BFS (bottom).
 a) The image shows characteristic morphologies of C–A–S–H found in Portland cement. There are fibrillar regions corresponding to outer product and dense regions likely from inner product. There is an apparent diffuse interface between both regions indicated by dashed lines. b) The image is the same region after 15 minutes of EDS mapping with only some damage but a loss of information due to bubbling of the C–A–S–H. c) An image of mostly undamaged C–A–S–H in WC-BFS, except for the small square which is due to a short exposure at high magnification. d) The damaged microstructure of WC-BFS after 15 minutes.

Figure 10 shows the elemental maps for Ca and Al cumulated during 15 minutes. The map of Ca gives detailed elemental distribution on the different regions, while the map for Al contains more noise as it is present in small amounts. After EDS acquisition the data from the *HyperMaps* was treated. This was done by placing virtual objects (Figure 11a) on thin regions of C–A–S–H. Care was taken to select only the thinnest regions as calcium is easily overestimated in thicker regions because

of absorption. Within each virtual object the EDS data from each pixel is cumulated to form a spectrum with sufficient statistics. Also, regions were chosen with other elements such as Mg excluded (Figure 11b).

Figure 10: Elemental maps (raw counts) for Ca and Al on a thin region of WC. No pixel data filtering was used.

Figure 11: a) HAADF image of another area of WC. Virtual objects are placed on the spectral map for quantification of the different phases such as IP or OP regions. b) Ca-Mg map of the same area which allows choice of regions of pure C-A-S-H without the otherwise hidden small phases containing Mg. Refer to the online version to see the different colours.

8. Comparison of SEM-EDS with STEM-EDS

Analyses of C–A–S–H in both SEM-EDS and STEM-EDS are compared for three samples: WC (Figure 12a and Figure 12b), PC (Figure 12c and Figure 12d) and WC-BFS (Figure 12e and Figure 12f).

Figure 12: Comparison between SEM-EDS and STEM-EDS analyses on a-b) WC, c-d) PC, e-f) WC-BFS. The error bars are calculated from the standard deviation of the series of points. a-c-e) Si/Ca-Al/Ca. b-d-f) Al/Ca-S/Ca.

These three examples all show that the best estimation for the Si/Ca and the Al/Ca are on the edge of the cloud of points, near the highest Si/Ca, where we expect the “least-intermixed” C–A–S–H EDS analyses to be located.

Some STEM-EDS point analyses appear to give higher Al/Ca and S/Ca than the SEM. As the STEM-EDS analyses are done without standards and because the Al and S peaks are very small (their concentration is generally less than 1-3 at% for Al and less than 1-1.5 at% for S), results for Al/Ca and S/Ca are likely to be less accurate and less precise than the values of Si/Ca, which are major elements (15-20%) in the spectra.

9. Method to automatically find the edge of the cloud of points

The comparisons between SEM-EDS and STEM-EDS analyses gave the confirmation that the best estimation for the C–A–S–H atomic composition lies at the edge of the cloud of points. To avoid user subjectivity it was felt better to use a simple method to fit the distributions of Si/Ca and Al/Ca rather than placing tie-lines manually (Figure 13 shows the example of the OP C–A–S–H of WC). The binning of the histograms was 0.01 and the fit was a simple Gaussian with minimisation of the least squares using the Solver function in Microsoft® Excel. If μ is the mean value of the fitted distribution and σ its standard deviation, then the chosen Si/Ca was taken on the higher side of the distribution, at $\mu + 2\sigma$. This choice was arbitrary but is typically used in statistics. It is considered reasonable as more than 95% percent of the values in a normal distribution lie within 2σ and thus the chosen value at $\mu + 2\sigma$ lies close to the edge. The mean value μ was chosen for the Al/Ca distribution. If needed, the Al/Si was simply deduced from the two fitted values for Si/Ca and Al/Ca.

Figure 13: Examples of the simple fitting procedure (OP C–A–S–H of WC). The raw data (histogram binning = 0.01) is fitted with a Gaussian curve. The mean (μ) and the standard deviation of the fitted distribution (σ) are used to find the a) Si/Ca (at $\mu + 2\sigma$) and b) the Al/Ca (at μ).

The fitted values are shown as the square data points in Figure 14. This simple fitting method is sufficient to find the edge of the cloud of points in the scatter plots. The choice of $\mu + 2\sigma$ for the fitted point is confirmed to be reasonable because it is within ≈ 0.2 (Si/Ca), similar to the variability of the analysis of belite (C_2S), i.e. 0.491 ± 0.012 given in Table 2. This methodology was then applied to samples from another study [33].

Figure 14: Scatter plots of the C–A–S–H in three cement pastes with the average STEM-EDS value and the fitted SEM-EDS value. The IP C–A–S–H and OP C–A–S–H are shown. a-b) WC. c-d) PC. e-f) WC-BFS.

The use of the extreme value of points is valid only when the intermixing does not occur with very small particles (typically less than 1 μm in radius) rather than hydrates. For example, when unreacted particles of silica fume or metakaolin are still present, it is more reasonable to use the mean Si/Ca. Examples can be seen at the end of Chapter 4 in [34] and on page 408 in [16].

10. How to choose the points

10.1. Manual choice of points

Intermixing of C–A–S–H with other phases is unavoidable in SEM, but can be minimized by avoiding the interfaces between several phases seen in the 2D section of the microstructure. A manual placement of points is appropriate to choose C–A–S–H regions as far from other phases as possible.

IP rims less than about 5 μm wide were considered too thin for reliable analysis. To ensure the best choice of points, the magnification should be relatively high. It should typically be at least $\approx 4000\times$ in the FEI Quanta 200 SEM (horizontal field-of-view of $\approx 60\ \mu\text{m}$) and $\approx 60,000\times$ in the FEI Tecnai Osiris TEM (horizontal field-of-view of $\approx 1.8\ \mu\text{m}$).

Based on our experience [16], a representative dataset of SEM-EDS analyses can be obtained by measuring no more than 20 points in each of about 10 different zones across the sample and at high magnification. The goal is to record about 100 points for the IP C–A–S–H and at least 100 points for the OP C–A–S–H. In STEM-EDS, the number of possible analyses depends on the total observable area.

10.2. Comparison with automated analyses

To better illustrate how the manual choice of point analyses is the most appropriate, data from the WC was also recorded using two automated methods, with a counting time of 50 kcps for all series of data in Figure 15. Two scenarios were chosen and compared with manually selected points (shown in Figure 15a). The first considers data acquired from a single grid of 500 points recorded at $500\times$ magnification (Figure 15b). The second considers a set of $5 \times 5 = 25$ images recorded at a magnification of $4000\times$ and each containing a grid of 20 points (Figure 15c). In both cases we cannot distinguish between inner and outer product and there is a large degree of spread caused by intermixing with CH, as shown in the box-plots of Figure 16 where the data are compared as well. In the case of the single grid the values of Si/Ca are overall lower. With the multiple grids the spread is the largest and the Si/Ca is erroneously higher.

Figure 15: Scatter plots of the C–A–S–H of WC. a) Manually placed analyses of the IP and OP C–A–S–H. b) The same data with a set of 500 points recorded on a single low-magnification (500×) grid. c) The same data with a series of grids (25 series of 20 points at 4000× magnification).

Figure 16: Comparison of the box-plot distributions of manually placed analyses with the two automated scenarios.

In both scenarios the quality of analyses was decreased by the fact that interfaces were not avoided and because CH or other phases were often measured. Figure 17, illustrates the choice of points. Most points have been manually placed at a sufficient distance from the interfaces. Analyses from points 167 and 180 (purposely placed wrong) have high calcium concentrations because they contain information from both CH and C–A–S–H. The time spent on those is better used on additional manually placed analyses.

Figure 17: BSE image of WC taken at 4000× magnification. Points in these examples were placed manually. Points number 167 and 180 were intentionally placed at an interface as an example of unsatisfactory point placement.

11. Ternary diagrams

Durdziński and co-workers [35] recently developed a method to assess the reactivity of highly heterogeneous siliceous fly ash materials in cement blends. Full resolution (1024×768 pixels²) SEM-EDS spectral maps were quantified, treated and presented as Ca-Si-Al ternary frequency plots such as the one in Figure 18b to follow the reaction of different subclasses of fly ash particles otherwise not distinguishable without this data treatment. The methodology was applied here to assess if it could improve the estimation of the C–A–S–H composition. For the SEM-EDS maps, the microscope was set up with a current of ≈ 6 nA and scanned 4 full resolution maps (1024×768 pixels²) in manually preselected areas of the sample. For each map the SEM scanned for 12 cycles with a dwell time of 256 μs/pixel. Maps were then quantified and the data was represented as ternary frequency plots. The colour scale indicates the normalised frequency for each pixel.

Figure 18: Ternary frequency plot of EDS analyses of the C–A–S–H of PC. a) Comparison of SEM-EDS point analyses with STEM-EDS analyses. b) Comparison of SEM-EDS quantified maps according to the protocol and code of [35] with STEM-EDS analyses. See online version for colour.

When comparing the point analyses from Figure 18a with the fully quantitative mapping method shown in Figure 18b, it is evident that the additional efforts provide us with useful information about the phase assemblage. Alite (at $\approx 75\%$ of Ca) is measured and the intermixing lines between either C–A–S–H and CH or C–A–S–H and AFm are seen. However analyses of belite (at $\approx 66\%$ of Ca) are convoluted with those of C–A–S–H (around 70% of Ca) and may increase the error in the estimation of the C–A–S–H composition. Intermixing is a limiting factor which is difficult to remove in bulk

samples in the SEM-EDS, and such time-consuming data treatment does not provide any advantage for estimating the C–A–S–H composition.

12. Concluding remarks and perspectives

The study of the C–A–S–H phase from cementitious materials in the SEM and TEM is not a straightforward process and must be done with **caution**. Guidelines for a satisfactory protocol were highlighted and are summarised here. Parameters of the instruments may not directly apply to other combinations of electron microscopes and detectors and should be optimised for each setup.

- The microscope operating conditions should be set up to limit damage by using a **proper accelerating voltage** (15 kV to properly detect iron), low currents and if possible a **low probe brightness**. In our combination of SEM and EDS detector the optimal beam current in SEM should remain in the range 0.7–1.0 nA. With a Tungsten source, the **probe brightness** is much lower than with field emission gun (FEG) electron sources which produce more focussed beams. Damage can be further limited by slightly defocussing the beam.
- **We recommend that the total number of X-ray counts per analysis should remain constant for each analysis.** If possible, the optimal exposure time – which is dependent on the SEM and EDS detector – should also compensate for slight variations in the beam current. This is done by fixing a total number of X-ray counts as the criteria for stopping an analysis (50,000 in our system), rather than a fixed counting time.
- **Standards are essential because the accuracy of standardless analysis is unpredictable. In the SEM this is because of matrix corrections and for spectra with low counting statistics (e.g. Al and S).**
- The estimation of C–A–S–H atomic composition is best conducted using data acquired by manual choice of the regions of interest (particularly the inner and outer product C–A–S–H). Points should be measured in many zones across the sample and at sufficiently high magnification (at least 4000× in our setup). Automated analyses cannot distinguish the IP and

OP regions and are not as reliable because the anhydrous grains, the CH and interfaces are often measured. Fully quantitative SEM-EDS maps currently do not provide any advantage.

- The main limitation in the treatment of SEM-EDS analyses is the intermixing of phases. Ratio plots are a convenient way to try and discriminate the phases present in the sample. The edge of the cloud of C–A–S–H points corresponds to the best estimation of the C–A–S–H atomic composition.

- The TEM was optimised for the observation of C–A–S–H free from intermixing and used in scanning mode (STEM) to limit damage. Comparison of SEM-EDS with STEM-EDS analyses of three samples confirmed that the “least-intermixed” SEM-EDS analyses of C–A–S–H are the best estimation of the C–A–S–H composition. This permitted the use of SEM-EDS to study numerous samples without the need for STEM-EDS. Despite how TEM allows analyses of C–A–S–H to be made free from intermixing, the non-use of standards makes it probably less accurate compared to SEM-EDS which relied on a standard database. This is true particularly for low concentration elements such as Al and S.

- To eliminate subjective user bias, a simple fitting procedure allows determination of an unbiased value similar to simply choosing the extreme value of the scatter plot. This however may only be valid in absence of very small particles such as unreacted silica fume (additional Si) and unreacted metakaolin clays (additional Si and Al) which small particle size (less than a micron). The presence of these small particles often does not permit such a straightforward estimation of the C–A–S–H composition.

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