Roughness of Steel Fibre and Composition of Cement Paste Close to Fibre Surface

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Abstract

The SEM and EDX methods were used to study both the profile along the perimeter of steel fibres and the composition of the cement paste close to the fibre surface. The paste was made of cement clinker blended with slag and limestone. The results indicate that a wavelength of 31.5 μm and an amplitude of 0.925 μm represent the changes of fibre radius on average, which can be used to estimate the size of empty spaces that particles touching the fibre surface may create and the particles that are able to fill these empty spaces. EDX line analyses in four orthogonal directions from the fibre surface were performed with a step of 0.5 μm along the lines of 60 μm. The distributions of elements indicated that the steel fibre mostly affected the relative amounts of Ca and Si. The comparison between the Si/Ca and Al/Ca ratios pointed out the presence of the AFm type phase close to the fibre surface and that the CSH gel was mostly intermixed with CH, as only a small amount of the AFt type phase was observed. Generally, the counts describing the existence of the CSH gel were larger than those of the CH within a distance of 60 μm from the fibre surface. The counts were closest to each other at about 20 μm from the fibre surface, where the CSH gel had its minimum and CH its maximum value.

1. Introduction

The behaviour of fibre reinforced cementitious (FRC) composites depends on both the individual properties of constituents and their interactions. The bond strength between the cement paste and inclusions, such as aggregates and fibres, provides bearing capacity and is affected by a thin layer called the interfacial transition zone (ITZ) surrounding the inclusion. The microstructure and the mineralogical composition of the ITZ depend on many factors, such as the composition of binder, material type and surface properties of inclusion, which may also lead to micro-bleeding increasing locally the water to cement (w/c) ratio.

The microstructure of the ITZ around the aggregate has been researched, for example, by Scrivener et al. (2004), Gao et al. (2013), Diamond and Huang (2001) and Horne et al. (2007). The characteristics of the ITZ around the fibre depend on its surface and material properties (Ranjarbar et al. 2016; Xu et al. 2017). The properties of the interface between the steel fibre and the cementitious matrix have been examined by several studies employing different micro-characterisation methods, including scanning electron microscopy (SEM) (Wang et al. 2009; Igarashi et al. 1996; Lee and Jacobsen 2011), nano-indentation (Wang et al. 2009; Xu et al. 2017), polarising microscopy (Uygunoglu 2008). The results received by Lee and Jacobsen (2011) from the bending tests on the samples made of ordinary Portland cement (OPC) with 10% of silica fume (SF) substituting the clinker, indicated elastic deformations before the debonding of the fibre. These deformations were explained by the presence of cement hydrates that formed a ductile bond with steel fibre. The energy dispersive X-ray (EDX) analysis of the ITZ up to the distance of 40 μm from the steel fibre surface revealed a larger amount of calcium silicate hydrate (CSH) gel in the samples with 10% of SF. In the samples without SF, the ITZ consisted substantially of calcium hydroxide (CH) and a minor amount of the CSH gel. Lee and Jacobsen (2011) assumed that the contact was ductile between the steel fibre and the CSH gel and brittle between the steel fibre and CH.

The research work reported in Xu et al. (2017) utilized nano-indentation and SEM, EDX, and X-ray diffraction (XRD) to characterize the composition and the mechanical properties of the ITZ as a function of the distance from the steel and polypropylene fibres. They pointed out that the fibre material influenced the microstructure of the ITZ and its composition. In the vicinity of steel fibre, the cementitious matrix had a lower porosity and larger amount of the CSH gel than it was observed around the polypropylene fibres. As an explanation for these results was given the effect of hydrophilic behaviour of steel fibre combined with the formation of iron oxide on the fibre surface. In contrary to steel fibre, the polypropylene fibre had hydrophobic properties. The effect of fibre material on the wettability coupled with
surface roughness was studied by Ranjbar et al. (2016). They also observed that a steel fibre was more hydrophilic and had the larger roughness compared to the surface of polypropylene fibre. The higher wettability of the steel fibre surface was explained to lead to a more efficient contact with water-based geopolymers. Xu et al. (2017) and Ranjbar et al. (2016) noted that a uniform and proper wetting of the fibre surface can refine the compaction of the hydration phases in the vicinity of fibre leading to the finer pores and improved bonding. Nowadays, most of the cements used for concrete production are blended with supplementary cementitious materials (SCMs), especially in concreting the massive structural members. The SCMs can reduce the hydration temperature and affect the porosity (Barnes and Bensted 2002). Usually, the particles of SCMs are smaller than the ones of cement clinker. For example, the average size of slag particles can vary between 7 and 8 μm, which is smaller than the size of clinker grains with an average diameter between 15 and 20 μm. A smaller grain size makes a more dense packing of the particles close to the fibre surface possible. The principal hydration products of slag cement are similar to those formed in OPC: CSH gel, calcium aluminate hydrates (CAH), ettringite and monosulphate type phases (AFt and AFm type phases) including compositional variations. Compared to OPC, the hydration of slag cements produces the CSH gel that contains more aluminate, which supports a small addition of limestone. CAH as well as sulphate-AFm can react with limestone binding more water and increasing the total volume of the solid phase (Justnes 2015). Slag grains modify hydration by producing a more disoriented crystallisation of CH (Barnes and Bensted 2002). The platy or prismatic CH crystals can be two or three orders of magnitude larger than the CSH gel and may enrich within the empty spaces close to the inclusion surface.

To investigate the formation of the bond between the fibre and the cement paste, it is first necessary to study and identify the nature of its origin. The motivation for the present research was to quantify the roughness profile along the perimeter of steel fibres to estimate the size of particles capable to fill the empty spaces that larger grains may create along the fibre surface. This can be used for developing concrete recipes to guarantee a good bonding between the fibres and the cementitious matrix. The profile may further be employed to evaluate the characteristics that determine the extent and homogeneity of wetting of the fibre surface. The study also evaluates the composition of the cement paste, as a function of the distance from the fibre. This is well motivated as a quite limited number of the studies exists where the composition of the transition zone close to the steel fibre surface has been investigated by measuring the chemical elements and analysing their ratios. In this study, cement made of cement clinker blended with slag and limestone was used. It is also important that results are available from different cementitious blends. The distributions of the CSH gel and CH close to the steel fibre surface utilising the Si/ Ca ratios measured by the EDX individual micro-analysis of the compounds was also a reason for this study. The simultaneous presentation of the ratios of Si/ Ca versus Al/Ca can be used to estimate also the content of AFt type and AFm type phases close to the fibre surface.

The type of steel fibres selected is widely used in civil engineering structures, as, for example, in airport runways, industrial floors and tunnels (Bentur and Mindess 2006; Blaszczyński and Przybylska-Falek 2015). As the large crystals of CH have low binding power (Barnes and Bensted 2002; Ghosh 2003), the focus of the present study was on the ratio between the CSH gel and CH. The bond strength between the steel fibre and the cement paste would benefit more from the presence of the CSH gel than that of the CH crystals.

## 2. Materials and methods

### 2.1 Materials

The samples were made of cement type CEM II/B-M (S-LL) 42.5 of the Finnish Standard for common cements (SFS-EN 197-1 2012). The cement contains 16% of blast furnace slag and 8% of limestone (CaCO₃). The chemical composition of cement used is represented in Table 1. The w/c ratio of 0.56 was used based on practical recommendations (Taylor 1997; Finland Concrete Association 2018).

### 2.2 Sample preparation

The fresh cement paste was mixed by a special device and after one minute of mixing, the process was stopped, and the cement paste was wiped from the walls of the mixing cup. Then, mixing continued for another three minutes.

Rectangular metal moulds were used to cast small blocks with a size of 22 × 40 × 160 mm³ [Fig. 1(a)]. The hooked ends of the fibres were cut from both sides, and the fibres were fixed vertically into the holes drilled in plywood plate placed on the bottom of the mould [Fig. 1(a)].

The freshly cast samples were covered with plastic

### Table 1 Chemical composition of the cement used.

| Oxides (%)    | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ | TiO₂ | Na₂O | K₂O |
|---------------|-----|------|-------|-------|-----|-----|------|------|-----|
| Clinker       | 64  | 21   | 5.2   | 3.3   | -   | -   | 3.2  | -    | -   |
| Slag          | 39  | 38   | 9     | -     | -   | 1   | 1    | 0.5  | 0.5 |
| Limestone     | 90  | 5    | 1.5   | -     | -   | 2.5 | -    | 1    | -   |

1Manufacturer’s data (Finnsementti Ltd. 2016a, 2016b).
2Determined with the EDX point analysis.
film and loaded with metallic plate with the weight of 3.93 kN/m² to encourage the packing of the cement grains around the fibre due to the hydrostatic pressure created [Fig. 1(b)]. After 24 hours, the blocks were demoulded and placed into water at +20°C. After one week, the blocks were placed into the environmental room with relative humidity (RH) of 65% at +20°C to imitate the decrease in RH that could be caused by the varying outdoor conditions on the building site. After 28 days of curing, the cylinders with the diameter of about 7 mm were drilled out of the blocks (Fig. 2).

The cylinders were cut into two parts by a low speed diamond saw so that the height of one part was about 7 to 8 mm (Fig. 3). A cross section of one cut cylinder was used for further analysis. Five samples of the cylinders were impregnated with epoxy resin at 0 to 20 mbar vacuum pressure [Fig. 4(a)]. The machine used for grinding and polishing the samples, as well as the procedures used are given in Fig. 4(b) and Table 2, respectively. Between the steps of grinding and polishing, the samples were cleaned with ethanol in an ultrasonic bath for three minutes and the surface of each section was
checked by an optical microscope. Possible segregation of the cement particles and the bleeding of water close to the fibre surface were examined using the backscattered electrons (BSE) images taken from the sample that was cut along the length of the fibre [Fig. 5(a)]. The sample was impregnated with epoxy resin, grinding and polished following the procedure given in Table 2. The examination of the BSE image revealed no settlement of unhydrated cement particles, which was also supported by the image analysis of the unhydrated particles segmented based on the grey-level threshold measured [Fig. 5(b)]. The area fractions of segmented unhydrated phases in the top, middle and bottom parts of the sample are given in Table 3.

### 2.3 SEM and EDX investigations

An environmental SEM (FEI Quanta FEG 450) equipped with BSE and EDX detectors was utilised with an accelerating voltage of 15 kV. The BSE detector was used to receive images with the scale of 500 μm and magnification of 260 to evaluate the profile along the perimeter of steel fibres used. Secondary electrons (SE) images represented in Fig. 6 demonstrate the surface roughness of the steel fibres used.

An EDX detector (Bruker XFlash 6|60) was utilised for chemical line analysis to identify the distributions of the typical chemical elements present in the cement paste,

### Table 2 Grinding and polishing program used.

| Step | Name of plate | Lubricant | Abrasive | Time (min) | Force, (N) | Rotation speed, (rpm) |
|------|---------------|-----------|----------|------------|------------|-----------------------|
| 1    | Diamond pad   | Industol  | 125 μm grain size | Remove extra epoxy | 150        |                       |
| 2    | Diamond pad   | Industol  | 20 μm grain size  | Remove extra epoxy | 150        |                       |
| 3    | Composite disc| Lamp oil  | 9 μm diamond grit | 30          | 25         | 150                   |
| 4    | Composite disc| Lamp oil  | 6 μm diamond grit | 45          | 25         | 150                   |
| 5    | Polishing Cloth| Lamp oil | 3 μm diamond grit | 60          | 25         | 150                   |

![Fig. 4 (a): Samples impregnated with epoxy resin, (b): Grinding and polishing machine.](image)

![Fig. 5 (a): BSE image taken from the sample that was cut along the length of the fibre, (b): Segmented image of the sample demonstrating the unhydrated cement particles.](image)
such as Ca, Si, Al, S. The iron was excluded from the chemical analysis, as grinding and polishing may have affected the amount of iron near the fibre surface. The EDX line analyses of the cement paste were performed with a step of 0.5 μm along the line of 60 μm from the steel fibre surface. The line analyses were made along four lines in four orthogonal directions per each sample, as it is represented in Fig. 7. Altogether, five samples were measured for the evaluation of the profiles along the perimeter of steel fibres and twenty lines, i.e., four lines from each of five samples, were analysed to specify the distributions of the typical chemical elements of the cement paste.

The problem of the overlapping of the gray scale levels of CH with unreacted slag and/or limestone and of CSH gel with pores was avoided by using the EDX line analysis instead of the BSE images.

3. Results and discussion

BSE images were processed and analysed by ImageJ, which is an image processing program for scientific multi-dimensional images, and the associated image processing package named Fiji (Schindelin et al. 2012, 2015). The measured results were processed with R-programming language (R Foundation 2011).

3.1 The profile along the perimeter of steel fibre

It is generally presumed that the interfacial bond increases with increasing the surface area available for bonding, e.g., by increasing the roughness of fibre surface (Barnes and Bensted 2002).

The BSE image of a cut fibre represented in Fig. 8 was binarised to identify the profile along the fibre perimeter, which was then unfolded providing thus the X and Y coordinates of each pixel representing the profile (Fig. 9). To estimate the average maximum variation of the profile...
along the perimeter of steel fibre, the location of the mean line was calculated as an average of all Y coordinates measured.

The height of each peak and valley was found relative to the mean line, and their sum \( h_{av} \) gave the local difference between the peaks. \( h_{av} \) was calculated as the average of all \( l_h \) measured [Fig. 9(b)]. The average wavelength \( l_{av} \) of the profile was the average distance between the local peaks along the fibre perimeter. As a result, the values of 1.85 \( \mu \text{m} \) and 31.5 \( \mu \text{m} \) were received for \( h_{av} \) and \( l_{av} \), respectively. The profile of the fibre can be mapped to polar coordinates by using the polar angle \( \phi \) and the radius \( r_{eq} \) for the fibre. A change of the radius along the fibre perimeter can be given as follows [Fig. 9(a)]:

\[
r_i(\phi) = r_{eq} + \Delta r(\phi)
\]

\[
r_{eq} = \frac{\sum_{i=1}^{N} l_i}{2\pi}
\]

\[
\Delta r(\phi) = \left( \frac{h_{av}}{2} \right) \sin \left( \frac{\phi \cdot r_{eq}}{l_{av}} \right)
\]

If \( l_{av} = \frac{2\pi r_{eq}}{N_{av}} \), then \( \Delta r(\phi) = \left( \frac{h_{av}}{2} \right) \sin \left( \frac{\phi \cdot N_{av}}{2\pi} \right) \)

where \( N_{av} \) shows the number of the waves \( N_i \) within the circle segment \( s_i \) defined by the angle \( \phi \). The radius \( r_{eq} \) shall be selected so that the length of the fibre perimeter and an integer number of the wavelengths will match.

The approach proposed quantifies the roughness of the steel fibre along its perimeter. Surface topology affects the wettability, as it was reported in the studies by Wenzel (1936), Shanahan (1995) and Kubiak et al. (2011). Slip-stick behaviour of the water droplet on the rough surfaces was reported by Shanahan (1995) and was explained as the result of the anchoring effect occurring between the edge of a droplet and the peaks of the profile working as barriers. Similarly, the roughness of the fibre surface can define the extent and homogeneity of wetting along its surface, thus affecting the formation of hydrates within the transition zone.

The size of cement clinker grains is between 15 and 20 \( \mu \text{m} \) on average, while the size of metakaolin, calcined marl or silica fume is < 2 \( \mu \text{m} \), 5 \( \mu \text{m} \) and 0.15 \( \mu \text{m} \), respectively (SRNL 2006; Barnes and Bensted 2002; Justnes 2015). The empty spaces represented in Fig. 10 can be well filled with the particles having the diameter less than the one of the clinker grains. Most probably that these particles should belong to the fine or ultra fine SCMs.

The measurement results are subjected to the resolution of SEM images, but they provide the information along the curved circumferential surface, which is not possible by a typical atomic force microscope.

### 3.2 EDX line analysis

The distributions of the typical chemical elements of the cement paste, such as Ca, Si, Al and S, along the line of 60 \( \mu \text{m} \) with a step of 0.5 \( \mu \text{m} \) from the steel fibre surface are represented in Fig. 11(a). Based on the diagrams a slight decrease in content of Ca and increase in Si within the distance of about 20 to 25 \( \mu \text{m} \) from the fibre surface were observed. The amount of Al was nearly constant with a slight increase within the distance of 15 \( \mu \text{m} \) from the fibre surface. The distribution of S was more or less stable along the whole line.

The scatter plots of the ratios of the normalised atomic
percentages of Si/Ca versus Al/Ca in Figs. 11(b) to 11(f) represent the mineralogical complexity of the cementitious matrix based on the EDX line analysis given in Fig. 11(a).

The scatter plots indicate that AFm type phase is almost absent in the vicinity of fibre, while a small amount of AFt type phase is still present. Most likely, this is the result of reaction between the CAH and/or sulphate-AFm with limestone, which produces calcium hemi- and monocarboaluminate hydrates and stabilises the AFt type phase (Justnes 2015). The resulting denser microstructure of the CSH gel and the reduced porosity restrict the
occurrence of large CH crystals. The hydration phase of the cement paste that has a high concentration of Ca and low concentrations of Si and Al was previously defined as a phase close to CH (Odler 1998; Bonen and Diamond 1994). In the present work the hydration phase most probably representing the CH was specified using the BSE images and EDX micro-analysis of deposits formed in the near field region of the fibre [Figs. 12(a) and 12(b)]. The normalised atomic percentages of Ca and Si/Ca atomic ratios measured in CH varied from 75 to 78% and 0.034 to 0.14 (Ca/Si: 7 to 29), respectively. The unhydrated limestone powder (CaCO₃) has the same content of Ca as CH (Ca(OH)₂) has. Using the SEM-EDX method these compounds cannot be distinguished, since the elements of CO₃ and (OH)₂ belong to light elements. In further analysis, the results with normalised atomic percentage of Ca larger than 75% and Si/Ca atomic ratio less than 0.14 were considered to represent CH, but they may also contain some amount of the unreacted limestone powder. The transition region between the CH and CSH gel, which can be observed in Fig. 12(b), indicates sharp decrease of Ca and increase of Si at a distance of 24 to 25.5 μm from the fibre surface. The atomic ratio of Si/Ca of the transition region varied from 0.14 to 0.25 (Ca/Si: 4 to 7). Based on this measurement, Si/Ca atomic ratio equal to 0.25 (Ca/Si: 4) was adopted as the bottom boundary for identifying the CSH gel from the results of EDX line analysis.

The chemical composition of the CSH gel can be highly variable, which is a consequence of both the impurity of raw materials used for the clinker and the complexity of the hydration process, including isomorphic substitutions. All these lead to the CSH gel, where sulphates, alumina, iron, alkalies, and other species can be found. Based on the previous studies on the hydration of OPC reported by Richardson (2000) and Bonen and Diamond (1994), the average Si/Ca atomic ratios measured in the CSH gel varied from 0.56 to 0.59 (Ca/Si: 1.7 to 1.8). According to the results reported in Richardson et al. (2002), in case of cement blended with slag the average value of Si/Ca atomic ratio in the CSH gel was increased up to 0.67 (Ca/Si: 1.5). An overall range of Si/Ca atomic ratios measured in the CSH gel formed from both OPC and cements blended with slag varied from 0.44 to 0.83 (Ca/Si: 1.2 to 2.3) (Taylor et al. 1985; Richardson and Groves 1993; Richardson 1999; Richardson et al. 2002).

In the present study, the BSE images and EDX individual micro-analysis were performed for more or less pure CSH formed around the alite and for the CSH gel formed in the vicinity of steel fibre surface (Figs. 13 and 14). As represented in Fig. 13(b), the ranges of Si/Ca and Al/Ca atomic ratios in the more or less pure CSH around the hydrating alite grain varied from 0.34 to 0.53 (Ca/Si: 1.89 to 2.97) and 0.03 to 0.05, respectively, while the ranges of the same atomic ratios of the unhydrated part of alite grain varied from 0.31 and 0.36 (Ca/Si: 2.78 to 3.28) and 0.005 to 0.03, respectively. The EDX micro-analysis of the CSH gel represented in Fig. 14 demonstrated a wide variation in chemical composition. The ranges of Si/Ca and Al/Ca atomic ratios varied from 0.19 to 1.1 (Ca/Si: 0.9 to 5.25) and 0.026 to 0.35, respectively. The significant change in the ranges can be partly explained by isomorphic substitutions, when other ions, such as Al³⁺, substitute Si⁴⁺ in silicon-oxygen tetrahedra. The additional supply of Al³⁺ ions is provided by the hydration of slag. The values of Si/Ca and Al/Ca atomic ratios equal to 0.19 (Ca/Si: 5.26) and 0.35, respectively, may indicate the existence of regions in the CSH gel that are highly deficient in silica and rich in aluminium. The value of Si/Ca atomic ratio, such as 1.1 (Ca/Si: 0.9), can be attributed to the tobermorite-like structure. Its values of Si/Ca atomic ratios are supposed to vary from 0.8 to 1.2 (Ca/Si: 0.83 to 1.25), as it was noted in Taylor (1986). The measurement values described were used to define the boundary values for the CSH gel. As the upper boundary a value of 0.53 was used for the Si/Ca ratio (Ca/Si: 1.89) and as the bottom boundary a value of 0.03 was used for the Al/Ca ratio.

The individual EDX micro-analyses of CSH formed around the hydrating alite grain and the CSH gel formed...
close to the fibre surface indicated no obvious value for the upper boundary of Al/Ca atomic ratio. Thus, this boundary was chosen as equal to 0.13 and was based on the clustering tendencies observed in the scatter plots in Figs. 11(b) to 11(f).

### 3.3 Distributions of CH and CSH gel as a function of the distance from the fibre

The amounts of CH and CSH gel along the line of 60 μm from the fibre surface are represented in Fig. 15. The compounds were estimated based on the ranges of Si/Ca and Al/Ca atomic ratios that were selected considering the clustering tendencies observed in the scatter plots in Figs. 11(b) to 11(f), and reported in the previous studies, for example, in the works of Scrivener et al. (2018) and Richardson (2000).

The scatter plots represented in Figs. 11(b) to 11(f) demonstrate that close to the fibre surface the CSH gel is mostly interwoven with CH rather than with AFt type phase.

Based on the occurrences of CH and CSH gel in Fig. 15, the CSH gel dominated over CH. In the close vicinity to the fibre, both the CSH gel and CH were increasing having the peaks at 2.5 μm and 7 μm, respectively, from the fibre surface. The CSH gel had the global minimum at 10 μm from the fibre and the global maximum at 60 μm indicating that the general tendency of the CSH gel was to increase with the distance from the fibre. The CH...
increased up to 7 μm from the fibre surface, where it reached its global maximum. The global minimum of the CH was at 36 μm, which demonstrated its general tendency to decrease with the distance from the fibre. At a distance of about 20 μm from the fibre surface, the content of CSH gel increased sharply. This increase was preceded by the sharp decrease of CH content. The changes in the distributions of Ca and Si were also observed at a distance of about 20 μm from the fibre surface [Fig. 11(a)].

4. Conclusions

In this research, the profile along the perimeter of steel fibre was measured and a mathematical formulation for the surface roughness of the steel fibre was derived. From the mineralogical point of view, the research focused on the identification of the CSH gel and CH close to the fibre surface, as the bond between the steel fibre and the cement paste would benefit from dense CSH gel rather than large CH crystals. The main findings and the conclusions of the study are:

(1) The profile along the perimeter of steel fibres studied had a wavelength of 31.5 μm and an amplitude of 0.925 μm on average. This means that cement clinker grains with diameters between 15 and 20 μm can create empty spaces close to the fibre surface and to fill these empty spaces the cementitious blend should include small particles, such as metakaolin, calcined marl or silica fume.

(2) The distributions of chemical elements along the lines of 60 μm with a step of 0.5 μm from the fibre surface indicated that the steel fibre mostly affected the distributions of Ca and Si.

(3) AFm type phase was absent in the vicinity of fibre, while a small amount of AFt type phase was observed.

(4) The scatter plots revealed that close to the fibre surface the CSH gel was mostly interwoven with CH rather than with AFt type phase.

(5) Generally, the counts describing the existence of CSH gel were larger than those of the CH within the distance of 60 μm from the fibre surface. The counts were closest to each other at about 20 μm from the fibre surface, where the counts of CSH had its minimum and CH its maximum value.

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