

Microscopic Analysis of Interfacial Transition Zone of Cementitious Composites Prepared by Various Mixing Procedures

Josef Fládr, Jiří Němeček, Veronika Koudelková, Petr Bílý

I. INTRODUCTION

Abstract—Mechanical parameters of cementitious composites differ quite significantly based on the composition of cement matrix. They are also influenced by mixing times and procedure. The research presented in this paper was aimed at identification of differences in microstructure of normal strength (NSC) and differently mixed high strength (HSC) cementitious composites. Scanning electron microscopy (SEM) investigation together with energy dispersive X-ray spectroscopy (EDX) phase analysis of NSC and HSC samples was conducted. Evaluation of interfacial transition zone (ITZ) between the aggregate and cement matrix was performed. Volume share, thickness, porosity and composition of ITZ were studied. In case of HSC, samples obtained by several different mixing procedures were compared in order to find the most suitable procedure. In case of NSC, ITZ was identified around 40-50% of aggregate grains and its thickness typically ranged between 10 and 40 μm . Higher porosity and lower share of clinker was observed in this area as a result of increased water-to-cement ratio (w/c) and the lack of fine particles improving the grading curve of the aggregate. Typical ITZ with lower content of Ca was observed only in one HSC sample, where it was developed around less than 15% of aggregate grains. The typical thickness of ITZ in this sample was similar to ITZ in NSC (between 5 and 40 μm). In the remaining four HSC samples, no ITZ was observed. In general, the share of ITZ in HSC samples was found to be significantly smaller than in NSC samples. As ITZ is the weakest part of the material, this result explains to large extent the improved mechanical properties of HSC compared to NSC. Based on the comparison of characteristics of ITZ in HSC samples prepared by different mixing procedures, the most suitable mixing procedure from the point of view of properties of ITZ was identified.

Keywords—Energy dispersive X-ray spectroscopy, high strength concrete, interfacial transition zone, mixing procedure, normal strength concrete, scanning electron microscopy.

ITZ is a region in concrete with higher water-to-cement ratio (w/c), and thus higher porosity, lower compressive strength and elastic modulus than the bulk cement matrix (BCM). Cement particles in fresh concrete are suspended in the mix water. In the close vicinity of much larger aggregate grains, the grains of cement cannot be compacted as efficiently as in the bulk cement paste. During mixing, this effect is amplified by the shearing stresses between the cement paste and aggregate particles. These stresses tend to detach the water from the cement grains. As a result, a narrow region surrounding the aggregate grains, containing fewer cement particles and thus more water, is created. This region is called the interfacial transition zone, abbreviated as ITZ [10].

ITZ is very important for the mechanical properties of cementitious composites. This fact has been proven by various researchers. For example, Zhang et al. [1] quantified the effect of thickness and elasticity modulus of ITZ on the elasticity modulus of the homogenized fine concrete with the use of a numerical model verified against experimental results. The increase in thickness of ITZ from 0 to 100 μm resulted in 14% decrease of the elastic modulus of concrete. When the thickness of ITZ was kept constant (30 μm) and its elastic modulus was changed from 15 to 150% of that of BCM, the elastic modulus of concrete was increased by 23%. According to Erdem et al. [2], ITZ also strongly influences the dynamic characteristics of concrete. The resistance depends on the density and roughness of ITZ which is governed by the type of the aggregate used.

The properties of ITZ are determined by the composition of concrete and by the mixing procedure. There are many studies supporting this statement. Several examples are given hereafter.

Akcaoglu et al. [3] studied the influence of aggregate size and w/c on the structure of ITZ and the failure process in ITZ of different cementitious composites. With larger aggregate grains, lower w/c resulted in ITZ with large difference in strength compared to BCM. The critical stress for rapid crack propagation in NSC was close to the ultimate stress. For HSC, the critical stress was noticeably lower than the ultimate stress.

Ke et al. [5] found that porosity and thickness of ITZ are closely related to absorption capacity of aggregates. When aggregates have low absorption capacity, then there exists a transition zone more porous than the matrix. This zone disappears for concretes with low w/c and increased content of

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silica fume.

Leeman et al. [4] studied the influence of compaction on ITZ. They found that ITZ in conventionally compacted concrete is usually more porous and wider than in self-compacting concretes. A work by Hemalatha et al. [6] focused on investigation of ITZ in self-compacting concretes (SCC) lead to a conclusion that ITZ in these materials is smaller due to the presence of more fines in SCC.

Li et al. [7] investigated the effect of different mixing approaches on the properties of ITZ. The results indicated that the two-stage mixing approach (in the first stage, coarse aggregate is mixed with cement and water, sand is added later) can improve the nanomechanical properties of ITZ by reducing the volume fraction of voids and calcium hydroxide. The SEM observation also indicated that an obviously denser and more homogeneous ITZ was obtained by TSMA, leading to beneficial influence on the mechanical properties of ITZ.

II. MOTIVATION AND GOAL

The compressive strength of aggregate used in concrete is in most cases higher than the compressive strength of hardened concrete. This is mainly caused by porosity of concrete due to non-ideal grading curve, poor compaction or shrinkage cracks. Therefore the first damage in a loaded element arises in the cement matrix, not in the aggregate grains.

In case of NSC, the first cracks occur in BCM which is porous due to high w/c of fresh concrete. HSC usually has lower w/c, BCM has lower porosity and higher strength and therefore the first cracks occur in more porous and weaker ITZ.

The modification of ITZ in NSC will not bring any significant benefits as BCM as such is porous and low-strength. On the other hand, in HSC the ITZ is by far the weakest part of the composite. Therefore the improvement of ITZ may significantly enhance the overall characteristics of the composite.

In the presented research, the authors focused on comparison of volume share, thickness, porosity and composition of ITZ in different composites prepared by different mixing procedures. Previous studies have shown that the mixing procedure influences the properties of ITZ (see e.g. [7]). The main goal was to find the mixing procedure leading to the best characteristics of ITZ in HSC.

III. METHODS

Prismatic concrete specimens of 40x40x160 mm size were produced in the laboratory. Mix compositions and mixing procedures are described in section IV.

From each specimen, 15x15 mm sample was cut, polished and coated with a thin layer of carbon to ensure adequate conductivity preventing the specimen charging. Investigation of composition and microstructure of specimens was performed in SEM Mira II LMU (Tescan corp., Brno, Czech Republic) equipped with energy dispersive X-ray (EDX) detector (Bruker corp., Berlin, Germany). Accelerating

voltage, probe current index and working distance were set on 15 kV, 1 and 15 mm respectively to ensure sufficient penetration depth of electrons and correct chemical composition of phases. The micrographs were acquired with back-scattered electron (BSE) detector since BSE reflects chemical composition and provides direct visualization of different phases in concrete specimens.

A presence of ITZ around aggregate particles was distinguished on the basis of the lower content of Ca in the binder. The composition was determined using linescan mode in EDX software showing the change of content of selected elements with the distance from an aggregate particle.

IV. MATERIALS

Six different concrete mixes were prepared for the analysis. Mix M1 was made of NSC (mean compressive strength of 50 MPa). Mixes M2 – M6 were made of HSC (mean compressive strength around 120 MPa). The compositions are given in Table I.

TABLE I
COMPOSITION OF CONCRETE MIXES

| Component | M1 mix (kg.m ⁻³) | M2 – M6 mixes (kg.m ⁻³) |
|------------------------------------|---------------------------------|--|
| Cement CEM I 42.5 | 490 | 650 |
| Water | 147 | 152 |
| Aggregate 0 – 4 mm | 1620 | 1710 |
| Aggregate type | Quartz | Basalt |
| Superplasticizer (polycarboxylate) | 5 | 27 |
| Silica fume | 0 | 80 |

The mixes differed in mixing procedure, see Tables II–VII.

Mix M1 was prepared using the standard mixing procedure for NSC. In the first step, aggregate was homogenized with cement and water with superplasticizer was added in the second step.

For mix M2, standard mixing procedure for HSC was used. At first, aggregate was homogenized, then cement was added, followed by silica fume and water with superplasticizer.

In mix M3, silica fume was added before cement and mixing time of silica fume was extended from 180 s to 300 s.

In case of mix M4, silica fume was added as the last component (after the water with superplasticizer).

The mixing procedure of M5 mix was the same as standard (M2), but the mixing time of silica fume was increased from 180 s to 600 s.

In the last mixture (M6), the effect of aggregate pre-wash (removal of dust by washing the aggregate by water) was tested. The mixing procedure was the same as standard with extended mixing time of silica fume (300 s).

TABLE II
MIXING PROCEDURE – MIX M1

| Step | Mixing time (s) |
|--------------------------|-----------------|
| Cement + aggregate | 30 |
| Water + superplasticizer | 30 |

TABLE III
MIXING PROCEDURE – MIX M2

| Step | Mixing time (s) |
|--------------------------|-----------------|
| Aggregate | 10 |
| Cement | 60 |
| Silica fume | 180 |
| Water + superplasticizer | 30 |

TABLE IV
MIXING PROCEDURE – MIX M3

| Step | Mixing time (s) |
|--------------------------|-----------------|
| Aggregate | 10 |
| Silica fume | 300 |
| Cement | 60 |
| Water + superplasticizer | 30 |

TABLE V
MIXING PROCEDURE – MIX M4

| Step | Mixing time (s) |
|--------------------------|-----------------|
| Aggregate | 10 |
| Cement | 60 |
| Water + superplasticizer | 30 |
| Silica fume | 300 |

TABLE VI
MIXING PROCEDURE – MIX M5

| Step | Mixing time (s) |
|--------------------------|-----------------|
| Aggregate | 10 |
| Cement | 60 |
| Silica fume | 600 |
| Water + superplasticizer | 30 |

TABLE VII
MIXING PROCEDURE – MIX M6

| Step | Mixing time (s) |
|--------------------------|-----------------|
| Aggregate (pre-washed) | 10 |
| Cement | 60 |
| Silica fume | 300 |
| Water + superplasticizer | 30 |

V. RESULTS

The following paragraphs describe the results of SEM analysis of the samples. The resolution of the SEM micrographs was 768x768 pixels; therefore, there are 768 points in each linescan. The yellow arrow in each micrograph determines the positions and direction of linescans along which the EDX detector analyzed the chemical composition of the phase in each point.

ITZ was found around almost all the aggregate grains in sample M1 (NSC, standard mixing procedure; Figs. 1 and 2). However, the grains were just partially surrounded by ITZ which was developed around 40-50% of surface of the grains. The thickness of ITZ ranged on average between 10 and 40 μm (in very limited areas up to 80 μm). Based on element analysis of C-S-H binder in ITZ and in BCM, the content of Ca was lower in ITZ (by almost 18 percent by weight – wt.%) while the content of Si was higher (by 6 wt.%) than in the BCM which means that ITZ had lower clinker content. Portlandite particles ($\text{Ca}(\text{OH})_2$) were much more visible in

ITZ as a result of higher difference between chemical composition of the binder and portlandite in this area than in BCM.

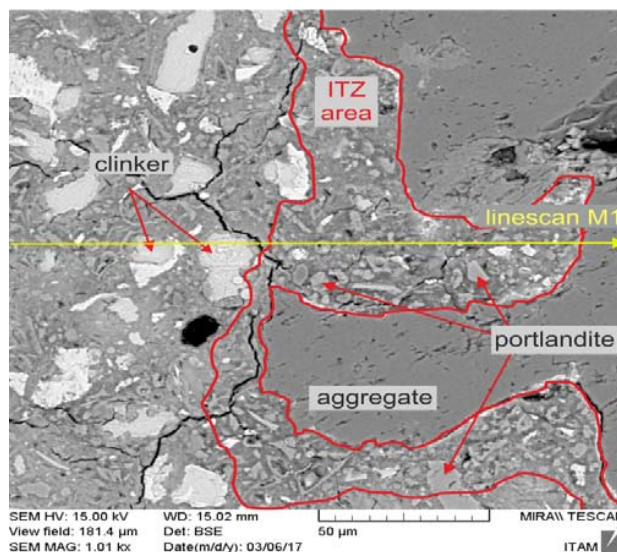


Fig. 1 SEM micrograph of M1 with marked phases, ITZ area and position and direction of linescan

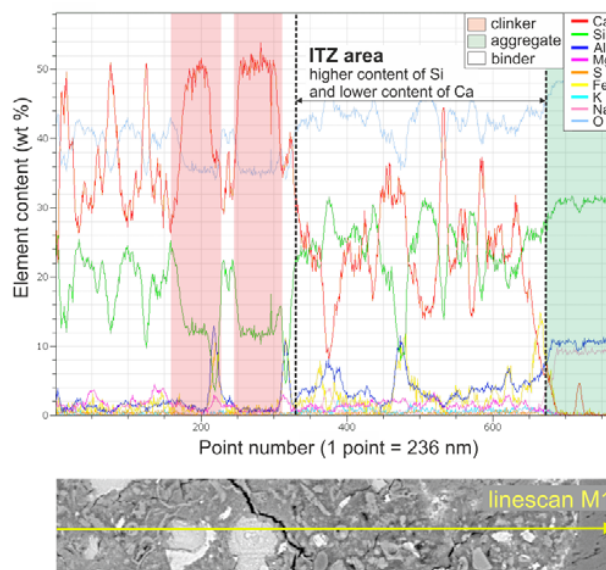


Fig. 2 Composition of phases along linescan M1

In samples M2 (HSC, standard mixing procedure), M3 (HSC, silica fume added before cement), M4 (HSC, silica fume added to wet mix) and M5 (HSC, silica fume mixed for 600 s), no typical ITZ with decreased amount of Ca around the aggregate grains was observed.

The appearance of contact zone between binder and aggregates in M2 – M5 samples is presented in Fig. 3. Along the right half of the linescan, a zone without larger clinker particles is visible. The composition along the linescan in

sample M3 is depicted in Fig. 4. It is obvious that there is practically no modification in chemical composition of binder between the zone with larger clinkers (left white zone in figure 4, 31.1 wt.% of Ca and 16.9 wt.% of Si) and the zone without these particles (right white zone in figure 4, 32.8 wt.% of Ca and 15.8 wt.% of Si). Similar composition was detected also in the samples M2, M4 and M5.

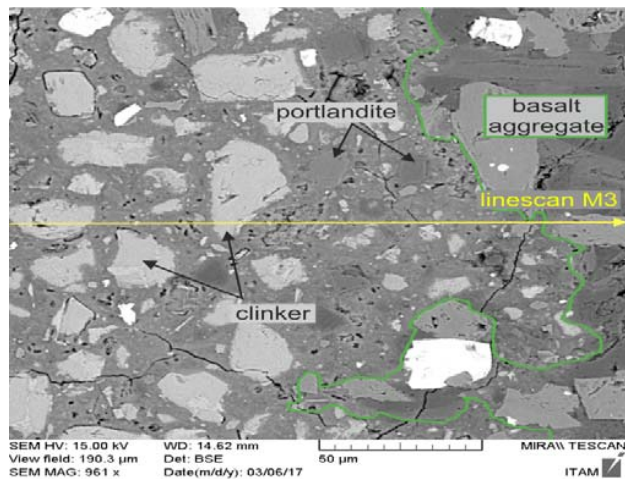


Fig. 3 SEM micrograph of M3 with marked phases and position and direction of linescan

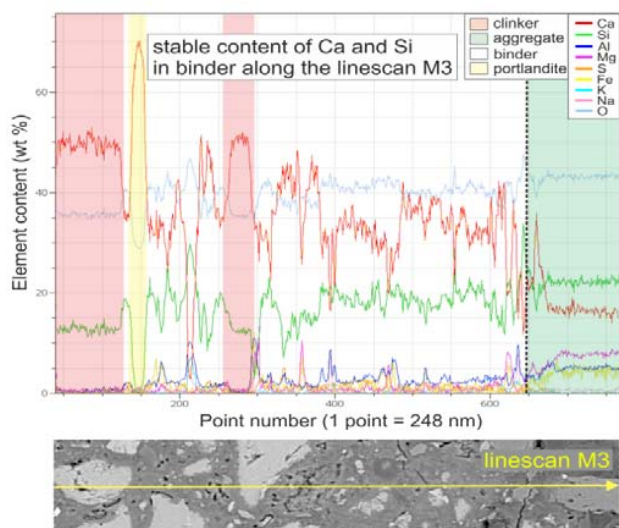


Fig. 4 Composition of phases along linescan M3

The appearance of interface between the binder and aggregates in sample M6 was different from the previous HSC samples. Distinct ITZ areas partially developed around approximately 10-15% of aggregate grains were observed. The ITZ area is marked in Fig. 5. The corresponding composition along linescan M6 is depicted in Fig. 6 where the decreasing trend of Ca content with the shortening of the distance from aggregate is marked. The Ca content has been halved in comparison to bulk composition (from 37.1 wt.% to 15.9 wt.%). In contrast to M1 sample, the content of Si

remained constant (~ 18.6 wt.%). The thickness of ITZ area in M6 ranged on average between 5 and 40 µm (up to 80 µm in some areas).

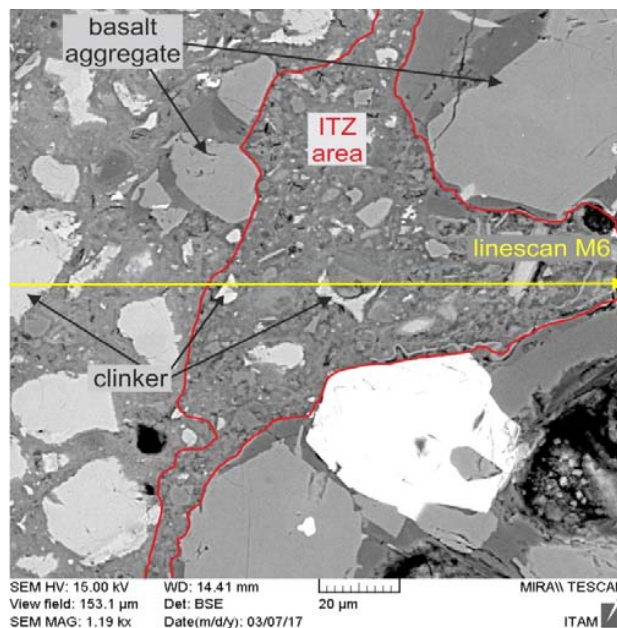


Fig. 5 SEM micrograph of M6 with marked phases, ITZ area and position and direction of linescan M6

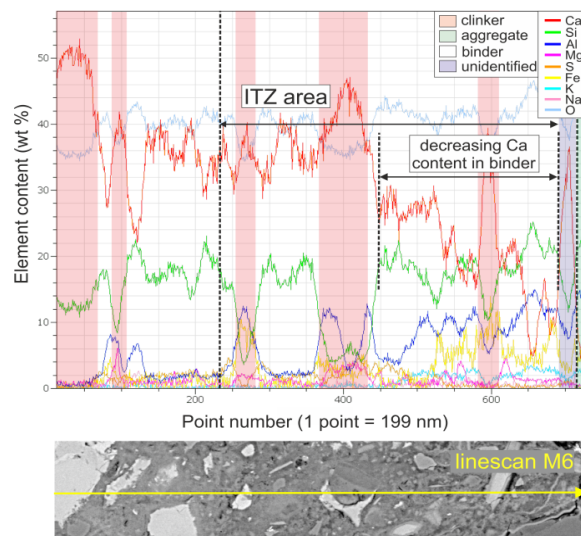


Fig. 6 Composition of phases along linescan M6

Quantification of mechanical properties of the studied samples is underway and has been partially presented elsewhere [8], [9].

VI. DISCUSSION

The measured thickness of ITZ was in most cases between 5 and 40 µm which approximately agreed to the typical range of 20-40 µm quoted in the literature [10].

In the M2 – M5 samples, no typical ITZ was determined. Aggregate particles were surrounded by areas with lower share of clinker, but Ca content in ITZ was the same as in BCM. In accordance with Ke et al. [5] and Hemalatha et al. [6], the authors attribute this fact to low w/c and presence of silica fume in the composition of all HSC mixes. Reduced w/c decreased the overall porosity of the matrix and silica fume particles further improved packing of the grains, leading to reduction of porous zone on the surface of aggregate grains. All these factors together can be identified as a source of improved compressive strength of HSC (approximately 120 MPa) compared to NSC (approximately 50 MPa).

Standard mixing procedure (mix M2, Table II) was confirmed to be the most suitable for HSC. No ITZ was found in the sample when this approach was used. Extending the mixing time of silica fume from 180 s to 600 s (mix M5) did not bring any improvement of the chemical composition of BCM; therefore, this amendment has no point as it only increases the consumption of energy and time required for preparation of fresh concrete.

When silica fume was added before cement (mix M3), the properties of the cement matrix were not improved either. The content of clinker around the aggregate grains was lower than in BCM. A possible explanation is that the silica particles covered the surface of aggregate grains, prevented the contact between aggregate grains and cement and therefore inhibited the formation of C-S-H gels on the surface of aggregate grains. This hypothesis is supported by the fact that the porosity of the zone around the aggregates was the same as the porosity of the BCM, most likely thanks to the silica fume grains filling the voids in cement matrix on the surface of the aggregate grains.

Adding the silica fume to the wet mix (mix M4) was also found to be inapt. Due to its fine nature, silica fume could not be properly dispersed in the wet mix, clusters of silica fume grains were created. On the other hand, the granulometry of the zone around the aggregate grains was improved in M4 mix, finer clinker grains were observed, possibly due to increased mixing time of the wet mix which lead to better homogenization of dry constituents and the water.

In case that aggregate pre-wash was applied (mix M6), ITZ similar to the NSC sample M1 was observed. However, ITZ comprised significantly smaller part of the volume of cement matrix in HSC (sample M6) than in NSC (sample M1). The porosity of the contact zone between the aggregate grains and cement matrix was increased compared to all other samples, probably due to the lack of dust particles acting as filler on the surface of aggregate grains. Specimen M6 was the only HSC sample in which ITZ was found. It means that aggregate pre-wash had adverse effect on the characteristics of the mix.

VII. CONCLUSIONS

The main conclusions of the work can be summarized as:

- No typical ITZ with decreased Ca content was found in most of the HSC samples, possibly thanks to lower w/c and presence of silica fume particles. The absence of ITZ can be identified as one of the reasons of better
- mechanical properties of HSC compared to NSC.
- The optimal mixing procedure for HSC was to homogenize the aggregate grains with cement first, then to add the silica fume and only after that to add the water with superplasticizer.
- Extension of silica fume mixing time from 180 s to 300 s or 600 s did not bring any additional benefits.
- Addition of silica fume before the cement decreased the amount of clinker in the area around aggregate grains.
- Silica fume could not be properly dispersed when added to wet mix (after addition of water).
- Aggregate pre-wash had adverse effect on the characteristics of contact zone between aggregate and cement matrix, the sample with pre-washed aggregate was the only HSC sample where typical ITZ with decreased Ca content was found.

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REFERENCES

- [1] J. L. Zhang, X. Liu, Y. Yuan, H. A. Mang, “Multiscale modeling of the effect of the interfacial transition zone on the modulus of elasticity of fiber-reinforced fine concrete,” *Computational Mechanics*, vol. 55, issue 1, pp. 37–55, 2015.
- [2] S. Erdem, A. R. Dawson, N. H. Thom, “Influence of the micro- and nanoscale local mechanical properties of the interfacial transition zone on impact behavior of concrete made with different aggregates,” *Cement and Concrete Research*, vol. 42, pp. 447–458, 2012.
- [3] T. Akcaoglu, M. Tokyay, T. Celik, “Assessing the ITZ microcracking via scanning electron microscope and its effect on the failure behavior of concrete,” *Cement and Concrete Research*, vol. 35, pp. 358–363, 2005.
- [4] A. Leemann, B. Münch, P. Gasser, L. Holzer, “Influence of compaction on the interfacial transition zone and the permeability of concrete,” *Cement and Concrete Research*, vol. 36, pp. 1425–1433, 2006.
- [5] Y. Ke, S. Ortola, A. L. Beaucour, H. Dumontet, “Identification of microstructural characteristics in lightweight aggregate concretes by micromechanical modelling including the interfacial transition zone (ITZ),” *Cement and Concrete Research*, vol. 40, pp. 1590–1600, 2010.
- [6] T. Hemalatha, A. Ramaswamy, J.M. Chandra Hishen, “Micromechanical analysis of self compacting concrete,” *Materials and Structures*, vol. 48, issue 11, pp. 3719–3734, 2015.
- [7] W. Li, J. Xiao, Z. Sun, S. Kawashima, S. P. Shah, “Interfacial transition zones in recycled aggregate concrete with different mixing approaches,” *Construction and Building Materials*, vol. 35, pp. 1046–1055, 2012.
- [8] V. Petráňová, T. Sajdlová, J. Němeček, “Micromechanical Homogenization of Ultra-High Performance Concrete”, *Applied Mechanics and Materials*, vol. 821, pp. 518–525, 2016.
- [9] J. Němeček, Z. Keršner, P. Schmidt, I. Havlíková, H. Šimonová, L. Topolář, V. Veselý, P. Rovnaník, “Fracture Process in a Fine - Grained Cement - Based Composite Monitored with Nanoindentation and Acoustic Emission,” *Key Engineering Materials*, vol. 662, pp. 47–50, 2015.
- [10] J. Thomas, H. Jennings, *The Science of Concrete*, online textbook of the Northwestern University, cited on 15th February 2017, http://iti.northwestern.edu/cement/monograph/Monograph5_5_2.html