Raman spectroscopy of interfacial transition zone in concrete doped with limestone powder and metakaolin

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Abstract. The interfacial transition zone in concrete with ordinary Portland cement (OPC) and concrete containing OPC and doped with 20% of limestone powder and 30% of metakaolin was studied by Raman spectroscopy - optical profilometry and cluster analysis. Mechanical properties, including strength characteristics and absorbability were tested after 28 days of curing. Concrete with ordinary Portland cement has lower density and absorbability and higher compressive and tensile strength than concrete with limestone powder and metakaolin. It has been found that a large amount of portlandite is formed in the interfacial transition zone in concrete with ordinary Portland cement. In concrete with the addition of metakaolin and limestone powder, the thickness of the interfacial transition zone is reduced, less portlandite is produced, but a thin layer of calcite is formed around quartz grains. This results in lower concrete strength in the area of the interfacial transition zone.

1. Introduction

Nowadays, there is the effort to reduce CO₂ in production of concrete. So, Portland cement can be partly replaced by supplementary cementitious materials (SCM’s), such as metakaolin, diatomite, silica fumes, limestone powder, pulverized fly ash or ground granulated blast furnace slag [1, 2].

SCM’s have a lot of advantages for cement industry. First is economic aspect of the matter – replacing Portland cement by industrial by-products. Second advantage is environmental aspect – to reduce greenhouse gases associated with Portland cement production. And third, performance advantage – SCM’s can greatly improve the workability and durability of concrete [3].

Clays and limestone are a strategic raw material available worldwide. Recent research [4] focused on the study of limestone calcined clay cement (LC³), which contains 40–50% of clinker, 30–40% of calcined clay, 15–20% of limestone powder and 4–7% of gypsum, has shown that LC³ has comparable development of compressive strength as ordinary Portland cement (OPC), higher resistance to penetration of chlorides, moisture, gas and sulphate attack, higher corrosion resistance and lower porosity. Nevertheless, the highest disadvantage is lower resistance to carbonation [5].

1.1. Interfacial transition zone

The interfacial transition zone (ITZ) is a weak area between cement paste and aggregate particles (figure 1). The thickness of this zone is mostly from 15 to 50 µm in concrete with ordinary Portland cement [6]. The ITZ is more porous than the cement paste and has high w/c. In the ITZ, crystallization of larger
portlandite crystals, ettringite and very porous hydration products occur [7, 8]. C-axes of ettringite crystals are often oriented perpendicular to the aggregate surface [9].

Recent research [10] has shown that ITZ is formed when the packing of anhydrous cement grain is disrupted in the area between filler and binder. The ITZ change can therefore occur when we change the particle size distribution of cement materials. The addition of SCM’s to binder can improve the resulting concrete properties and reduce the thickness and porosity of ITZ. Only a few authors studied the ITZ using Raman spectroscopy [e.g. 11, 12, 13], but none of them studied ITZ in concrete with the addition of metakaolin and limestone powder.

![Schematic diagram of ITZ in concrete with ordinary Portland cement according to Al Bayati et al. [14], modified.](image)

**Figure 1.** Schematic diagram of ITZ in concrete with ordinary Portland cement according to Al Bayati et al. [14], modified.

### 2. Materials and methods

Concrete sample OPC-1 was prepared from ordinary Portland cement 52.5 N. River sand from locality Bzenec was used as fine-grained aggregate and crushed granitoids from the Olbramovice quarry were used as coarse-grained aggregate. Fractions 0/2 and 2/4 were used in the mixture (table 1). The binder for VPC-1 sample was prepared from 50% of ordinary Portland cement, 30% of metakaolin and 20% of limestone powder. The filler was the same as in the case of OPC-1. According to XRD analysis, the used metakaolin Mefisto K05 has the following phase composition: amorphous phase 70.5%, mullite 7.7%, microcline 6.8%, illite/muscovite 4.9%, quartz 4.7%, kaolinite 4.2% and anatase 1.2%. Mixtures were casted in 40 × 40 × 160 mm moulds and cured for 28 days in a bath of distilled water. Then mechanical properties were measured on samples. After that, a small block was cut from both samples and the samples were ground. Subsequently, Raman spectroscopy measurements were done.

Mechanical properties, including strength characteristics and absorbability were tested at Research Institute of Building Materials in Brno, Czech Republic. Raman spectroscopy of selected samples was performed at Institute of Molecular and Translation Medicine at the Palacky University in Olomouc, Czech Republic on a WITec Confocal Raman Imaging Microscope System alpha300 R + with excitation of 532 nm (power incident on the sample - 35 mW, objectives Zeiss EC Epiplan 20x/0.4 and Zeiss EC Epiplan-Neofluar Die 50x/0.8, scan bitmap (step) = 1 pixel/µm, integration time at each point = 200 ms. Mapping area was 200 × 200 µm for sample OPC-1 and 400 × 400 µm for sample VPC-1. Before the Raman measurement, the selected area was scanned using optical profilometry WITec TrueSurface.
Table 1. Mixture proportions for OPC-1 and VPC-1.

|                        | OPC-1 | VPC-1 |
|------------------------|-------|-------|
| CEM I (52.5 N) [g]     | 450   | 225   |
| Limestone powder - Štramberk [g] | -     | 90    |
| Metakaolin Mefisto K05 [g] | -     | 135   |
| River sand - Bzenec [g] | 450   | 450   |
| Aggregate 0-2 mm - Olbramovice [g] | 450   | 450   |
| Aggregate 2-4 mm - Olbramovice [g] | 273   | 355   |
| Water [g]              |       |       |

3. Results

3.1. Mechanical properties

Mechanical properties, including strength characteristics and absorbability were tested after 28 days of curing. Concrete with ordinary Portland cement has lower density and absorbability and higher compressive and tensile strength than concrete with limestone powder and metakaolin (table 2).

Table 2. Mechanical properties of OPC-1 and VPC-1 samples in 28 days.

|           | Density (kg/m$^3$) | Tensile strength (MPa) | Compressive strength (MPa) | Absorbability (%) |
|-----------|--------------------|------------------------|---------------------------|-------------------|
| OPC-1     | 2056               | 7.3                    | 51.0                      | 10.3              |
| VPC-1     | 2168               | 5.6                    | 27.0                      | 15.6              |

3.2. Raman spectroscopy

Raman spectroscopy was performed on both samples. Suitable binder-filler interfaces were selected for study and then a cluster analysis was performed, in which the individual average spectra of the measured area are categorized into clusters with different spectra properties. Due to the imperfections of the sample surface, the optical profilometry method was chosen, when the laser beam copies the real sample surface, not as in conventional Raman analysis, where the beam analyses the plane, but doesn’t solve the roughness of the sample.

3.2.1. Sample OPC-1. The boundary between feldspar and cement paste (figure 2a) was selected for study by Raman spectroscopy. Analysis distinguished seven clusters (figure 2b) differing in their average spectra. Real profile of the sample was analysed by optical profilometry and is shown on figure 2c. Cluster analysis delimited the ITZ quite well, three clusters define ITZ and the thickness of this zone is between 5 and 45 µm. Raman spectra for concrete with OPC are shown on figure 3. C-S-H is a major hydration product of Portland cement in concrete and corresponds to the bending mode at 645-654 cm$^{-1}$. Portlandite was found in all the three clusters, in contrast, ettringite wasn’t detected in any of these clusters. A large amount of iron oxides is formed in the ITZ, iron can come from C4AF present in the OPC. It’s not easy to distinguish some phases since two or more phases may have some similar peaks. Raman band at 1000 cm$^{-1}$ in brown spectra (figure 3) probably corresponds to some sulphates or C-S-H.
Figure 2. Concrete sample OPC-1 A) Bright-field image under the confocal optical microscope; B) Raman image of the ITZ of the sample; C) Sample profile analysed by optical profilometry.

Figure 3. Raman spectra for individual clusters in sample OPC-1.
Figure 3. (continued).
Figure 3. (continued).
3.2.2. Sample VPC-1. The boundaries quartz-cement paste and fragment of granitoid-cement paste (figure 4a) were selected for study. Cluster analysis (figure 4b, c) and optical profilometry (figure 4d) were performed on the sample. In the Raman image, the ITZ isn’t as distinct as in the OPC-1 sample. Average Raman spectra for individual clusters in concrete VPC-1 are shown on figure 5. As in the case of the sample OPC-1, C-S-H is a major hydration product of Portland cement and is identified by bands at 331–334 and 638–646 cm$^{-1}$. The bands at 357–360 cm$^{-1}$ correspond to the Ca-O bond vibration in portlandite, which was detected in three clusters, but its intensity is weaker than that of the OPC-1 sample. It means that only small amount of this phase is formed in VPC-1. Weakly intense band of ettringite at 980 and 986 cm$^{-1}$ was detected in two clusters. A thin layer (1–5 µm) of calcite is formed around quartz grains (figure 4c), this can significantly reduce the strength of this zone.

![Figure 4](image_url)

**Figure 4.** Sample VPC-1 A) Bright-field image under the confocal optical microscope; B) Bright-field image of the sample underlain by Raman image in the studied area; C) Raman image of studied area of the sample; D) Sample profile analysed by optical profilometry.
Figure 5. Raman spectra for individual clusters from sample VPC-1.
Figure 5. (continued).
4. Discussion

Concrete doped with limestone powder and metakaolin has undoubtedly advantages in comparison with concrete, where the binder is only ordinary Portland cement. The ITZ in this concrete has lower thickness and contains fewer undesirable phases, mainly portlandite. Although this concrete has less carbonation resistance and a higher amount of calcite accumulates in the ITZ. Especially calcite forms layer around quartz, it causes that the strength of this zone may be lower.

Engineering properties of LC3 cement were studied by [e.g. 15, 16, 17, 18, 19], however it is not possible to compare the data of cements and the data of concrete prepared in this work, since the addition of the aggregate significantly affects the mechanical properties, mainly the strength characteristics.

Mechanical properties of concrete with LC3 cement were studied by fewer authors [e.g. 20, 21, 22]. In the research by Nguyen et al. [21] basalt was used as coarse-grained aggregate and samples were cured in lime-saturated water bath for 7 days at room temperature. Subsequently, the samples were stored for 21 days at room temperature and 50% relative humidity. In contrast, granitoid rock was used as coarse-grained aggregate in our research and only distilled water was used in curing for 28 days. Compressive strength of concrete with LC3 in the study by Nguyen et al. [21] reached up to 55 MPa after 28 days and thus had greater compressive strength than the reference sample.

In contrast, in the case of our prepared samples, the concrete with the addition of limestone powder and metakaolin had lower strength than the reference sample (see table 2).

As in our research, also in the research of Dhandapani et al. [22] granite was used as coarse aggregate. Compared to our research, in the study presented in [21] gypsum and the PCE superplasticizer were added to the mixture. It was found that concrete with LC3 binder has comparable compressive strength to concrete with conventional Portland cement. Moreover, compared to concrete with OPC, concrete with LC3 has higher resistance to chloride penetration [22]. Compared to our data, concrete samples from the work of Dhandapani et al. [22] have higher compressive strength.

Raman spectroscopy in comparison with other methods (XRD, WDX) represents a non-destructive research method. The laser beam is directed at a specific point in the sample and is also possible to analyse different layers of the sample, which is great advantage of this method in comparison with e.g. XRD [23]. It is possible to analyse aqueous solutions or gaseous phases that can be closed in pores of concrete using Raman spectroscopy [23, 24]. Amorphous phases can also be analysed using Raman spectroscopy [25, 26], as was also verified in this work, when C-S-H gel was identified in ITZ (figure 3.
and 5). This method is used to study the hydration of cement paste in situ [27, 28]. The problem in the study of OPC using Raman spectroscopy is the background fluorescence signals and weak Raman signals [29, 30], which can also be seen in the spectra of samples in our work (figure 3 and 5). Fluorescence in OPC is most often caused by organic impurities or contamination during grinding and polishing of the samples [31, 32]. Raman bands of C₃S and C₂S in OPC are in many cases shifted against pure standards [29, 33]. From this perspective, Raman spectroscopy is more suitable for studying mixtures without OPC, e.g. sulfoaluminate cements [34] or lime mortars [35].

5. Conclusion
Raman spectroscopy and mechanics properties study of concrete with ordinary Portland cement and concrete with the addition of metakaolin and limestone powder were presented. The results show the following:

- C-S-H is the main hydration product of Portland cement in both samples.
- In concrete with ordinary Portland cement, the interfacial transition zone has higher thickness and more portlandite is formed in this zone.
- In concrete with the addition of metakaolin and limestone powder, a thin rim of calcite is formed around quartz particles.
- Concrete OPC-1 has higher compressive and tensile strength and lower density and absorptability compared to concrete VPC-1.

Further research will be focused on the study of interfacial transition zone using electron microprobe and deepening the study using Raman spectroscopy on other concrete samples with the addition of supplementary cementitious materials.

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