Microhardness testing procedure applied to blended cement based matrix

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MICROHARDNESS TESTING PROCEDURE APPLIED TO BLENDED CEMENT BASED MATRIX

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ABSTRACT

In the paper a new method of determination of cement paste microhardness is presented. It includes the procedure of systematic indentation with a Vickers tip and a statistical processing of population of obtained results. The tested specimens were cast with different kinds of blended cements, containing high calcium fly ash (HCFA) as one of major components. Differences in values of microhardness obtained for six series of tested specimens mixes are discussed and compared with compressive strength of investigated materials.

Keywords: Microhardness, Blended cements, High calcium fly ash (HCFA), Porosity

INTRODUCTION

The evaluation of the hardness of concrete specimens is a method to determine the material ability to resist scaling and surface degradation when exposed to environmental aggressive agents. A variety of strategies is nowadays applied to estimate hardness because the mechanical properties of a concrete depend on its structural components: various origin and dimensions, [1]. Tremblay et al. [2] investigated the resistance of several concrete mixes to de-icer scaling processes. For characterization of the structural properties of tested concretes they used: air void content, compressive strength and indentation hardness. The hardness measurements were performed with application of Brinell indenter with 10 mm of diameter ball tip loaded with 5000 N. Indentation hardness of relatively large areas penetrated using this procedure was in close relation to the 28 - days compressive strength as presented in Table 1.

Table 1. Comparison of the 28 - days compressive strength versus Brinell hardness, Tremblay et al. [2]

| 28 - days compressive strength, [MPa] | 27.2 | 32.2 | 40.0 | 47.0 |
| indenter hardness HB, [MPa]         | 23.2 | 31.5 | 40.2 | 45.8 |
Sorelli et al. [2] applied a 'statistical nanoindentation' technique to identify the mechanical properties of different phases of an Ultra High Performance Concrete, made with a composition of minerals milled to very fine grain size. The authors used a three-sided pyramidal Berkovich indenter loaded with the maximal force of 500 mN. Table 2 summarizes the phase contents which were recognized during the investigation based on measurements of hardness in nanoscale range of tested area. The final value of nanohardness was estimated as a mean value of a large population of measurements, i.e. of seven groups with 100 traces each.

### Table 2. Estimated value of nanohardness of seven phases identified in Ultra High Performance Concrete, Sorelli et al. [3]

<table>
<thead>
<tr>
<th>Microstructure phase</th>
<th>low density C-S-H</th>
<th>high density C-S-H</th>
<th>residual cement clinker</th>
<th>pores &amp; air voids</th>
</tr>
</thead>
<tbody>
<tr>
<td>extracted value of nanohardness, MPa</td>
<td>550 ± 30</td>
<td>1360 ± 35</td>
<td>9120 ± 900</td>
<td>190 ± 30</td>
</tr>
<tr>
<td>Microstructure phase</td>
<td>quartz powder</td>
<td>quartz sand</td>
<td>steel fiber</td>
<td>-</td>
</tr>
<tr>
<td>extracted value of nanohardness, MPa</td>
<td>5140 ± 3080</td>
<td>5140 ± 3080</td>
<td>11990 ± 1970</td>
<td>-</td>
</tr>
</tbody>
</table>

Han [4] et al. have applied a similar technique to investigate the modification of the chemomechanical properties of hardened cement paste before and after carbonation. It was found that the mean elastic modulus and mean hardness obviously increased after the carbonation reaction.

The mean values mentioned above reflect the mechanical properties of all phases present in the tested samples. Specifically, these values decrease when the hardness was within 0.15–1.75 and 4.15–8.20 GPa and a remarkable increase when the hardness was in the range of 1.75–4.15 GPa. In addition, low density C-S-H was affected by the carbonation degradation more seriously than high density C-S-H. The carbonation reaction led to a distinct decrease in the number and size of unhydrated cement paste particles.

Since the method of statistical nanoindentation lets one to identify the mechanical properties of different phases by assessment the characteristic maxima on the distribution curve of the results of the measurements, the authors have reported the relative changes of the microhardness before and after carbonation as indicated in Table 3. The changes of nanohardness were determined in four phases of the microstructure. The tests were made on pastes prepared of Portland Cement of type CEM I 52.5 cement mixed with water, w/c = 0.53 (by mass).

### Table 3. The estimated nanohardness of major phases after carbonation. [4]

<table>
<thead>
<tr>
<th>Microstructure phase</th>
<th>Pores</th>
<th>Low density C-S-H</th>
<th>High density C-S-H</th>
<th>Cement clinker</th>
</tr>
</thead>
<tbody>
<tr>
<td>estimated initial value of nanohardness, MPa</td>
<td>90 - 230</td>
<td>300 - 1000</td>
<td>1000 - 1710</td>
<td>4500 - 11000</td>
</tr>
<tr>
<td>relative change after carbonation</td>
<td>decrease 35.9 %</td>
<td>decrease 67.9 %</td>
<td>decrease 49.0 %</td>
<td>decrease 8.4 %</td>
</tr>
</tbody>
</table>

Tamimi and Ridgway [5] have compared two mixing methods in preparation of mortars in order to reduce bleeding and to increase strength of resulting compositions. They used the measurements of microhardness technique to characterize the properties of the interfacial
bond of artificially prepared aggregate and bulk paste. A Vickers micro-hardness tester was used with a maximum load of 20 N. Indentations were made across aggregate - cement paste interface in lines starting from the aggregate area and heading toward the bulk paste keeping the spacing of 1 micrometer. The values of microhardness corresponding with the consecutive indentation traces were evaluated manually by means of microscopic observations. The results revealed for the w/c ratio of 0.45 and 28 days aged mixes a falling tendency of the mean level of microhardness starting from 2000 MPa within the aggregate region and reaching a value of ca. 1000 MPa within the bulk paste region. These results remain in a good agreement with data reported in [4].

A modified procedure was designed to be applied in concrete specimens, for example - in cores drilled from constructions under service [6]. The presence of larger dimension aggregates implied the increase of applied loads and enlargement of indents. The procedure was aimed to evaluate the properties of cement matrix and to calculate the ratio of the material of degraded structure in respect to the total volume of matrix; here the microhardness of aggregate was neglected. According to the data presented in Tables 2 and 3, the microhardness of the bulk of cement matrix was estimated to the value about 1000 MPa, while the microhardness of the degraded regions - less than 300 MPa.

THE NOVEL PROCEDURE OF MEASURING THE MICROHARDNESS OF CEMENT MATRIX

The microhardness of concrete specimens was measured using standard Vickers indenter [7]. Its diamond pyramid has the angle of penetrating ending of 136°. Depth Sensing Indentation method was applied relying on continuous recording of loading force and penetration depth during the entire indentation process. The mechanical load was supplied with Lloyd EZ 50 test frame. The indentation load was measured with 50 N load cell and the indenter displacement $\delta$ into tested material was measured with the accuracy of 0.1 $\mu$m. The mechanical loading of the specimens was executed under control of the automatic software Ondio NEXYGEN, supplied by Lloyd Instruments. During the single test the indenter was penetrating the bulk of the sample until a force of 45 N was reached. To control the correctness of the indentation process the acoustic emission sensor was placed at the side of the sample. This enabled for optical monitoring of crushing of the bulk of the sample with means of an auxiliary system for presenting of emitted acoustic emission signal on a computer screen [7]. The indenter, the LVDT vertical displacement sensor, acoustic emission sensor and the sample under test are presented in Fig. 1.

![Image of the indenter and sensors](image.jpg)

Figure 1. The indenter and the sensors used by the authors to perform
Determination of the microhardness coefficient $HV$ after a single indent was done with 1% accuracy by the software with application of the following formula:

$$HV = 1.8544 \frac{P}{d^2}$$  \hspace{1cm} (1)

where:
- $P$ – load applied to the indenter [N],
- $d$ – average length of the pyramid trace diagonal, while $d = 7.0006 \delta$ [mm], and
- $\delta$ – penetration depth [mm].

Typical graph of the applied load versus extension of the indenter is presented in Fig. 2. Fig. 3 shows the shape of microindenter trace of 50 x 50 $\mu$m together with the path made on the polished surface of a concrete specimen.

![Graph of applied load versus indenter penetration depth at the microhardness measurement](image1)

**Figure 2.** Graph of applied load versus indenter penetration depth at the microhardness measurement

![Two traces of microindenter (50 X 50 $\mu$m), made in epoxy resin (left), the trace path made in concrete specimen, magnified ten times (right). The matrix was dyed darker and the aggregates remain with more bright shades of the blue dye.](image2)

**Figure 3.** Two traces of microindenter (50 X 50 $\mu$m), made in epoxy resin (left), the trace path made in concrete specimen, magnified ten times (right). The matrix was dyed darker and the aggregates remain with more bright shades of the blue dye.
During the preliminary tests the indents into the surface of concrete specimens were observed by the stereomicroscope Nikon SMZ800 in order to assign them to the area of aggregate grains, to hardened cement paste or to low density area. The latter were mostly the damaged regions of low density. Such manual recognition data were later used for verification of the elaborated computer-aided procedure. The assumed simplified partition of the indents into three groups (structural areas) was based on earlier results, published in [8], showing a relationship between concrete resistance to aggression of XF4 environment and microhardness of hardened cement paste. Assuming 100 % of indents, the following occurrence frequency of areas was recognized:

- aggregates: 50 - 58 %,
- cement matrix: 40 %,
- low density area: 2 - 10 %.

Moreover it was found that in most cases the microhardness of low density areas falls in the range between 0 and 299 MPa, the microhardness of cement matrix represents the microhardness of 300 - 1300 MPa, while values for the ordinary aggregates fall above 1300 MPa (up to 5000 MPa). Because the indentations were executed on a highly heterogeneous material the analysis of a large set of indents needs to be carried out statistically. Typically a number of 150 indents was chosen to guarantee a convergence on the measured microhardness values to the characteristic value being a mean level in the tested sample. A population of indents done on aggregates, cement matrix and low density areas, can be therefore understood as a sum of three normal distribution of measured values, i.e. assumed to be spread around the mean level in accordance with the formula:

$$P_j = \frac{2}{\sqrt{2\pi}S_j} \exp\left(-\frac{(x-\mu_j)^2}{2S_j^2}\right)$$

(2)

where $P_j$ is a probability distribution function of member of a population indexed with $j$, $\mu_j$ and $S_j$ are the mean and standard deviation and $y_j$ is a member of a population of the measured value of the microhardness. Moreover, as in [3], a two - dimensional projection of the population of indents was constructed as a frequency distribution depended on the measured microhardness. The interval by which the distribution was discretized was set to 100 MPa. Fig. 4 presents a frequency distribution of microhardness measured in concrete made on cement CEM I 42.5, with quartz sand, amphibolite aggregate and water mixed in proportions of 350/630/1350/158 (by mass).

The graph was analyzed in three areas with respect to the range of measured microhardness. The procedure of determination of microhardness of cement matrix was performed in such a way that within the population of all results of the measurements a group falling into a range of 300 - 1300 MPa was selected and their average was estimated as a final result. Additionally, the ratio of the number of indents with microhardness lower than 300 MPa and those lower than 1300 MPa can be treated as a measure of structural tightness and was labeled as low density area ratio (LDR).

The single results of microhardness measurement were obtained with the accuracy of 1 %. Within the population of ca. 60 results falling into a range denoted as cement matrix area the standard deviation of the results was 35 % and thus according to the statistical rules the value of microhardness for that concrete was estimated as $719 \pm 252$ MPa. 7 results of
microhardness testing had values less than 130 MPa thus LDR parameter for the tested sample could be calculated as 10%.

![Graph](image)

**Figure 4. Example of frequency distribution of microhardness of a concrete specimen**

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**MATERIALS AND SPECIMENS**

The microhardness of cement matrix of various concrete mixes was estimated for concrete specimens intentionally different because of binder composition and different kinds of blended cements. Six concrete compositions were prepared with w/c = 0.45 and labeled A45, B45, C45, D45, E45, F45 and six compositions were prepared with w/c = 0.55, using the same cement blends as above, and the latter were labeled A55, B55, C55, D55, E55, F55, respectively. To obtain suitable plasticity the superplasticizer of type Gramium SKY 591 was added. In some cases the influence of the plasticizer admixture to the final tightness of the hardened concrete was observed. The mixes were prepared with a laboratory mixer.

The procedure of determining the microhardness of cement matrix required two specimens to get appropriate number of indents (2 x 75). The mix proportions are listed in
Table 4. The compressive strength of concrete at 28 days determined on cube specimens is given in Table 5.

<table>
<thead>
<tr>
<th>Mix.</th>
<th>Cement type</th>
<th>Cement</th>
<th>River sand 0 - 2 mm</th>
<th>Crushed aggregate</th>
<th>Superplasticizer</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kg/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A45</td>
<td>CEM I 42.5</td>
<td>336</td>
<td>696</td>
<td>667</td>
<td>629</td>
<td>0.88</td>
</tr>
<tr>
<td>B45</td>
<td>CEM II/AW</td>
<td>335</td>
<td>605</td>
<td>666</td>
<td>628</td>
<td>1.66</td>
</tr>
<tr>
<td>C45</td>
<td>CEM II/B-W</td>
<td>336</td>
<td>605</td>
<td>666</td>
<td>628</td>
<td>2.09</td>
</tr>
<tr>
<td>D45</td>
<td>CEM II/B-M(V-W)</td>
<td>336</td>
<td>604</td>
<td>665</td>
<td>628</td>
<td>1.64</td>
</tr>
<tr>
<td>E45</td>
<td>CEM II/B-M(S-W)</td>
<td>340</td>
<td>612</td>
<td>674</td>
<td>637</td>
<td>1.36</td>
</tr>
<tr>
<td>F45</td>
<td>CEM V/A (S-W)</td>
<td>337</td>
<td>606</td>
<td>657</td>
<td>628</td>
<td>1.79</td>
</tr>
<tr>
<td>A55</td>
<td>CEM I 42.5</td>
<td>313</td>
<td>617</td>
<td>661</td>
<td>636</td>
<td>0</td>
</tr>
<tr>
<td>B55</td>
<td>CEM II/AW</td>
<td>313</td>
<td>615</td>
<td>659</td>
<td>634</td>
<td>0.35</td>
</tr>
<tr>
<td>C55</td>
<td>CEM II/B-W</td>
<td>312</td>
<td>615</td>
<td>659</td>
<td>634</td>
<td>0.70</td>
</tr>
<tr>
<td>D55</td>
<td>CEM II/B-M(V-W)</td>
<td>312</td>
<td>614</td>
<td>658</td>
<td>633</td>
<td>0.56</td>
</tr>
<tr>
<td>E55</td>
<td>CEM II/B-M(S-W)</td>
<td>313</td>
<td>617</td>
<td>661</td>
<td>637</td>
<td>0.50</td>
</tr>
<tr>
<td>F55</td>
<td>CEM V/A (S-W)</td>
<td>312</td>
<td>615</td>
<td>659</td>
<td>634</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The 150 mm cubes were stored for 28 days at high humidity of RH >95% and constant temperature of 20±2 ºC according to standard requirements. After curing the small block 40x120x20 mm were cut out of cube specimens as it was required for microindentation tests. The upper surface of these blocks was thoroughly polished using diamond powders to comply with the requirements of the microindentation procedure.

**EXPERIMENTAL RESULTS**

The experimental results have revealed that the mixes prepared with CEM I Portland cement presented the highest value of microhardness and that parameter was higher for w/c = 0.45 than for w/c = 0.55. The histograms of microhardness probability of two CEM I mixes are presented in Fig 5.
Figure 5. The histograms of the microhardness probability of two concrete mixes with CEM I (A45 and A55).

Blended cements generally have higher fineness due to low-diameter particle fly ash/slag addition than CEM I of the same class and that property is reflected in the results of the indentation of some compositions presented below. Low density area ratio (LDR) calculated for concrete mix made with CEM I was 10%, while LDR calculated for blended cements was in the range of 3 - 8%. Two histograms of the hardness probability of mixes prepared with use of blended cement of type CEM II/A-W versus type CEM II/B-W are shown in Figs. 6 and 7. The code letter 'W' stands for the experimental high calcium fly ash admixture. The microhardness of those mixes was lower than of those made of Portland cement and that feature was in a good agreement with results of compressive strength measurements listed further. The microhardness of ‘A type’ blends was higher than those of type ‘B’. The microhardness of the mixes made with the water to cement ratio of 0.55 was lower than the microhardness of the mixes made with w/c ratio 0.45. It was also found that compressive strength at 28 days of the mixes made with w/c ratio 0.55 was lower than compressive strength of the mixes made with w/c ratio 0.45.

Two histograms of microhardness probability of mixes prepared with different blended cement CEM II A (V-W) versus CEM II A (S-W) are shown in Figs. 8 and 9. These cements were made of a mixture of clinker partly replaced by high calcium fly ash (W), low calcium fly ash (V), and ground granulated blast furnace slag (S). A minor differences were noticed between those two types of cements.
The results of estimated values of microhardness and low density area ratio confronted with measured compressive strength at 28 days are presented in Table 5. Some kind of proportionality between compressive strength and the estimated microhardness gathered together for mixes made on cements of type II is presented in Fig. 10.
Figure 8. The histograms of the hardness probability of two concrete mixes with blended cement CEM II A (V-W) versus CEM II A (S-W), both made with a constant w/c ratio, equal 0.45.

Figure 9. The histograms of the hardness probability of two concrete mixes with blended cement CEM II A (V-W) versus CEM II A (S-W), both made with a w/c ratio of 0.55.
Figure 10. The relation between compressive strength and the estimated microhardness gathered together for mixes made on cements of type II.

Table 5 The compressive strength of concrete at 28 days and estimated values of microhardness and low density area ratio

<table>
<thead>
<tr>
<th>Concrete mix.</th>
<th>Compressive strength at 28 days [MPa]</th>
<th>Estimated microhardness [MPa]</th>
<th>Low density area ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 45 (CEM I 42.5)</td>
<td>74.3</td>
<td>719</td>
<td>10</td>
</tr>
<tr>
<td>B 45 (CEM II/A-W)</td>
<td>78.0</td>
<td>702</td>
<td>6</td>
</tr>
<tr>
<td>C 45 (CEM II/B-W)</td>
<td>71.0</td>
<td>602</td>
<td>3</td>
</tr>
<tr>
<td>D 45 (CEM II/V-W)</td>
<td>67.4</td>
<td>599</td>
<td>6</td>
</tr>
<tr>
<td>E 45 (CEM II/S-W)</td>
<td>58.9</td>
<td>556</td>
<td>6</td>
</tr>
<tr>
<td>F 45 (CEM V/A(S-W))</td>
<td>48.9</td>
<td>497</td>
<td>20</td>
</tr>
<tr>
<td>A 55 (CEM I 42.5)</td>
<td>57.4</td>
<td>689</td>
<td>4</td>
</tr>
<tr>
<td>B 55 (CEM II/A-W)</td>
<td>58.5</td>
<td>647</td>
<td>7</td>
</tr>
<tr>
<td>C 55 (CEM II/B-W)</td>
<td>52.2</td>
<td>571</td>
<td>2</td>
</tr>
<tr>
<td>D 55 (CEM II/V-W)</td>
<td>53.4</td>
<td>591</td>
<td>6</td>
</tr>
<tr>
<td>E 55 (CEM II/S-W)</td>
<td>62.4</td>
<td>611</td>
<td>0</td>
</tr>
<tr>
<td>F 55 (CEM V/A(S-W))</td>
<td>54.0</td>
<td>551</td>
<td>8</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The results allow to formulate the following conclusions:

(1) The mixes made of Portland cement had a higher value of microhardness than the mixes made with blended cements. This can be explained by referencing the previously discussed conclusions of the authors [3] and [4] who wrote that clinker possesses a higher
value of hardness than most minerals constituting cement, and therefore substituting the clinker with them lowers the overall matrix property.

(2) The same effect is observed when comparing lower (ca. 15%) and higher (ca. 30%) substitution of Portland cement in mixes made of type A and of type B blends. In all cases the microhardness of A type blends was higher than those of type B.

(3) The decreased values of low density area ratio estimated in blended cements when compared with the LD parameter in Portland cement can be explained by general higher fineness of replacements added to blended cements than clinker particles in what is already reported in [8].

(4) The general tendency is proposed that a higher value of microhardness of 28-days concrete corresponds to its higher compressive strength. This was verified by all results presented in Table 5.

(5) One mix, labeled F45, made with CEM V/A(S-W) was characterized with remarkably low 28-days compressive strength, probably due to mixing inaccuracy. Both microhardness and low density area ratio of this mix lied behind the limits obtained for the other concretes and these measures reflected imperfection of the mix microstructure.

These conclusions allow to conclude that the proposed automatic method of estimation of two cement matrix microstructural parameters can be treated as a tool of investigation for properties of the concrete, especially to trace faults in component preparation and mixing.

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