DESIGN OF CONCRETE FOR RESTORATION INTERVENTIONS ON BUILDINGS OF BYZANTINE ERA - EVALUATION OF THEIR CHEMICAL AND MECHANICAL CHARACTERISTICS

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Abstract
In the present work, a preliminary approach is attempted in order to design and evaluate restoration concrete for restoration interventions of monuments thick joints brickwork masonries of Byzantine era. The design of these materials was based on the data obtained by the characterisation of historic concrete of typical Byzantine era monuments that presented a great

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durability in time. Therefore, traditional materials (aerial lime, hydraulic lime, pozzolana, sand and brick fragments) are used for the concrete production that was evaluated at the time of 1, 3 and 6 months using mechanical tests (compressive, flexural) for the determination of mechanical strength and ultrasonic technique for the determination of dynamic modulus of elasticity. Furthermore, thermal analyses (DTA-TG) were performed for the chemical evolution evaluation of these composite systems in time. The obtained results indicate that the lime/artificial pozzolana (metakaolin) concrete present sufficient mechanical behavior (ratio of $F_c/F_f$ and $E_d$ value), while natural pozzolana used presented a low reactivity in reacting with Ca(OH)$_2$. Several examined concrete seem to be in progress after 3 months of curing, fact that is confirmed by the evolution rate of mechanical characteristics and the Ca(OH)$_2$ conversion.

1. Introduction

The study of buildings behaviour of Byzantine era can become a valuable tool for the decoding of construction techniques and materials and the reproduce of materials with analogous behavior, that are addressed to the restoration interventions on buildings of that period. Characteristic monuments of Byzantine era that presented a great durability in time and in addition an excellent behavior under earthquake stresses are the Hagia Sophia in Istanbul, and the church of St. Michael in Kiev. A thorough study in the structural materials used revealed that they presented a similar nature and production technology.

In the case of Hagia Sophia [1,2], the dimensions of the bricks used are 30-36x3.5-4 cm and the mortar joint thickness is about 1-1.5 times the brick one. On the other hand, in the church of St. Michael in Kiev [3], the bricks were about 26-36cmx 2.5-3cm and the joint mortar was on average up to 5 cm. Thus, regarding the masonry structure type, in both monuments the structural materials were bricks and the mortar joint was about 1-1.5 times the brick thickness. Furthermore the mortars used presented of hydraulic nature. The aggregates were coarse and composed by a mixture of ceramic fragments and sand. Especially, in the case of Hagia Sophia, the aggregates
dimensions are in the range of 0-16mm and this is the reason that this kind of mortar is considered as concrete. Regarding their physicochemical and mechanical characteristics they both exhibited a high tensile strength, a low value of elasticity modulus, low values of density, high value of hydraulicity. At last, in both mortars were formed amorphous hydrated aluminosilicates compounds as gel phase in the binder that allows for greater energy absorption and shows self-healing effects, while the compatibility of the mortar to the original ones allows for continuous stresses and strains [1,2,3]. Various tests were performed to determine the mechanical properties of these materials, such as the tensile strength. Tensile strength tests performed on mortar samples show values between 1,25-2 MPa as compared to 0,7-1,5 MPa for Hagia Sophia [4].

The main goal if this research is a preliminary approach for the design, production and evaluation of concrete for restoration interventions of monuments thick joints brickwork masonries of Byzantine era. In addition, as secondary goals, the effect of aggregates and binder nature to the mechanical characteristics of concrete synthesis is, also, studied.

2. Materials and Methods

Traditional type of materials were used for the concrete production in order to assure the physico-chemical compatibility to authentic materials. Lime powder (Ca(OH)2:89%, CaCO3:5%) and natural hydraulic lime (NHL3.5-Z according to CEN prEN 459-1) were used as binding materials along with cement (I/45, Titan Cement Industry) for comparative reasons. The pozzolanic additions used were either earth of Milos (EM) – a natural pozzolan derived by the island of Milos in Greece, or an artificial high reactive pozzolane (Metakaolin – Imerys Minerals Ltd). Table 1 reports the chemical composition and the physical properties of the materials used for the concrete preparation. Furthermore, Fig.1 presents the grain size distribution of the pozzolans as they derived by laser CILAS 715 method. The metakaolin is the finest pozzolan with cumulative passing percentage at 64 µm of 100% and at 16 µm up to 95.6%. On the other hand, Earth of Milos presents a cumulative passing percentage from 64 µm up to 95.9%.

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Table 1. Chemical composition and physical properties of the materials used for the concrete syntheses preparation

<table>
<thead>
<tr>
<th>MT</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>K₂O (%)</th>
<th>Na₂O (%)</th>
<th>SO₃ (%)</th>
<th>LOI (%)</th>
<th>d* (g/cm³)</th>
<th>Tot. Sil. (%)</th>
<th>Reac. Sil. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK</td>
<td>51.70</td>
<td>40.60</td>
<td>0.64</td>
<td>0.71</td>
<td>0.96</td>
<td>2.00</td>
<td>0.31</td>
<td>0.11</td>
<td>1.19</td>
<td>2.52</td>
<td>54.19</td>
<td>44.59</td>
</tr>
<tr>
<td>EM</td>
<td>69.66</td>
<td>12.21</td>
<td>2.34</td>
<td>2.01</td>
<td>0.70</td>
<td>3.28</td>
<td>0.62</td>
<td>-</td>
<td>7.35</td>
<td>2.36</td>
<td>70.15</td>
<td>52.89</td>
</tr>
<tr>
<td>L</td>
<td>0.17</td>
<td>0.18</td>
<td>0.07</td>
<td>70.06</td>
<td>2.35</td>
<td>-</td>
<td>0.77</td>
<td>25.60</td>
<td>2.34</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

MT: Material, L: Aerial Lime, MK: Metakaolin, EM: Earth of Milos, *Density determination according to ASTM C-188-95, #: Total and reactive silica % determination according to EN 196-2

Fig.1 Grain size distribution of pozzolanic additions

The aggregate materials were a mixture of sand (calcitic and quartz origin) and ceramic fragments. The former has already been detected in historic mortars/concrete samples with the effect of

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producing lightweight materials, due to its lower bulk density in respect to the sand aggregates, along with lower modulus of elasticity that it provides [5]. In order to achieve an analogous grain size distribution with the one to Hagia Sophia 5 types of aggregates were mixed:

- Sand of quartz origin in 4 grain size distributions (S1-0.063/0.5, S2-0.5/1, S3-1/2, S4-3/6 mm)
- Sand of calcitic origin (S5-2/4 mm)
- Coarse calcitic gravel (G1-1/16 mm)
- Ceramic Fragments (C1), disposed in several grain size fractions: 0.063, 0.125, 0.25, 0.5, 1, 2, 4, 8, 16 mm.
- Ceramic Fragments (C2) in two grain size distributions (0/8, 2/16 mm)

Table 2 reports the materials mixing proportions as percentage per weight (% p.w.) for the concrete synthesis preparation.

<table>
<thead>
<tr>
<th>Code</th>
<th>L</th>
<th>EM</th>
<th>MK</th>
<th>C</th>
<th>NHL</th>
<th>Aggregates</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10</td>
<td>20</td>
<td></td>
<td></td>
<td>70</td>
<td>sand/gravel</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>20</td>
<td></td>
<td>70</td>
<td>sand/ceramic fragments:35/35</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>15</td>
<td>15</td>
<td></td>
<td>70</td>
<td>sand/gravel</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>15</td>
<td>15</td>
<td></td>
<td>70</td>
<td>sand/ceramic fragments:35/35</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>15</td>
<td>15</td>
<td></td>
<td>70</td>
<td>ceramic fragments</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>20</td>
<td>10</td>
<td></td>
<td>70</td>
<td>sand/ceramic fragments:35/35</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>15</td>
<td>15</td>
<td></td>
<td>70</td>
<td>sand/ceramic fragments:35/35</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>70</td>
<td>sand/ceramic fragments:35/35</td>
</tr>
</tbody>
</table>

L: Aerial Lime, EM: Earth of Milos, MK: Metakaolin, C: Cement, NHL: Natural Hydraulic Lime
In order to study the effect of aggregates nature to the concrete mechanical characteristics, syntheses I to V were produced with the same binder and aggregates of different nature with the same grain size distribution (Curve 1-Fig. 2). Moreover, in order to study the effect of binder nature to the concrete mechanical characteristics, syntheses VI to VIII were produced with the same aggregates (grain size distribution - Curve 2- Fig.2), and with binders of different nature.

Fig.2: Grain size distribution of aggregates mixes compared to the Hagia Sofia Historic Concrete

The amount of water that was added in the syntheses was determined through the criteria of slump cone in the range of 10-40 mm, according to EN 12350-2, testing Fresh Mortar – Part 2: Slump Test. In that way, the amount of water was the minimum that could be added and the syntheses presented almost the same consistency.
Once the synthesis was prepared was molded in two layers and each layer was compacted by using a vibrator table. The dimensions of the moulds used were 10x10x50cm for the evaluation of concrete flexural strength. The specimens of LMK, NHLZ, LC were stored at a moist curing chamber of relative humidity RH>95% and temperature T=20±2°C for the first seven days after their preparation, the seventh day were removed from the moulds and consequently were stored till the testing day in a chamber of standard conditions (RH=50±1%, T=20±2°C). On the other hand the specimens of LEM could be removed from the moulds the 14th day after their preparation and therefore they were stored in the moist curing chamber for fourteen days.

The concrete mechanical and chemical characteristics were evaluated at the time of 1, 3, 6 months using the following techniques:

- Flexural strength (ASTM C 78-00) [AVERY – DENISON 7122, maximum Load: 2.000KN]
- Compressive strength tests using portions of beams broken in flexure (ASTM C 116) [TONI TECHNIK INSTRUMENT, maximum Load: 3000 KN, load rate: 0.5-1KN/sec]
- Fiber Optics Microscopy for the evaluation of the adhesion of aggregates to the binder matrix and the homogeneity of the binder
- Ultrasonic techniques (CNS Farnell-Pundit 5, transducers frequency: 54 KHz) for the dynamic modulus of elasticity (Ed) evaluation
- Differential thermal analysis and thermogravimetric analysis [DTA/TG, Netzsch 409EP), in a static air atmosphere with heating rate of 10°C/min from 25-1000°C was employed in order to investigate the binder chemical evolution.

3. Results and Discussion

3.1. Fiber Optics Microscopy
Photograph 1 present the a beam core of the concrete V where it could be observed the uniform distribution of the aggregates in the whole concrete mass. Photographs 2 and 3 are obtained by

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FOM for the concrete V and III, respectively where one could notice that a better adhesion of the binder matrix to the aggregates is occurred in the case of ceramic aggregates than to the gravels/sand aggregates.

3.2 Strength
Figures 3 and 4 report the flexural and compressive strength data for concrete at the time of 1, 3, and 6 months of curing. Regarding the effect of binder nature to the concrete mechanical strength it could be noticed that in the case of using EM the concrete presents low values of compressive and flexural strength, that is an indicator of the low reactivity of this pozzolanic addition in reacting with lime. Moreover, by the time of 6 months the system is not stabilized, yet. On the other hand, the MK concrete present high values of mechanical strength and the system seemed to be stabilised by the time of 3 months (comparison to the DTA/TG results), when this type of concrete gain the maximum strength (compressive and flexural). Furthermore, by the time of 1 month these mortars gain the 85-93% of the final compressive strength and the 70-85% of the final flexural strength. In addition, a higher ratio of lime/metakaolin results to a mechanical strength reduction. Therefore, by comparing the two pozzolans, it could be said that metakaolin present a much higher reactivity in reacting with lime compared to the natural pozzolan one, fact that is resulted to a total increase on the compressive the flexural strength up to 500%. This fact could be
attributed to the metakaolin fine grain size distribution, chemical composition, high specific surface area. Thus, metakaolin could be used as a pozzolanic addition for restoration mortars production in order to ameliorate the early strength of lime mortars. A good ratio $f_c/f_t$ ($\sim 8.8$) is presented for concrete prepared by mixing lime/metakaolin/ceramic fragment/sand:20/10/35/35 (in %p.w.), (Concrete VI) and it is estimated that in a concrete produced by higher ratio of lime/metakaolin the $f_c/f_t$ could be decreased more as far as the $f_t$ value.

On the other hand the LC concrete exhibits extremely high compressive strength and sufficient flexural one while the NHL concrete presents sufficient compressive strength (=10 MPa) for a brickwork masonry but a low flexural one. Nevertheless, it seems to be still in chemical evolution (DTA/TG results), therefore, the mechanical characteristics should be estimated, also, in 3 and 6 months.

Regarding the effect of aggregates nature to the concrete mechanical strength it could be noticed that the aggregates nature influence more the flexural strength and less the compressive one. Thus, addition of ceramic fragments decreases the flexural strength.

3.3 Ultrasonic Technique

The concrete dynamic modulus of elasticity ($E_d$) was evaluated by using the ultrasonic technique. Obtained data are reported in figure 5. In general, it could be said that the $E_d$ data are in accordance with the acquisition rate of mechanical strengths, meaning that concrete that present high mechanical strength present, also, high dynamic modulus of elasticity. Moreover, the $E_d$ values decreases on time for the most concrete synthesizes.

Regarding the effect of aggregates nature to the $E_d$, it could be observed that the gravel/sand aggregates present the highest value of $E_d$ while the use of ceramic fragments as aggregates

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decreases the Ed. In addition, use of ceramic fragments up to 50% to the total decreases the Ed up to 25%, while use only of ceramic fragments as aggregates decreases the Ed up to 40%.

In addition, the binder nature influence also, the Ed values and it could be noticed that the EM concrete present the lowest values of Ed but also, low values in Fc and Ff. In the case of MK concrete, the lowest value of Ed in 3 months is detected for VI synthesis. Furthermore, it is observed that a decrease of 5% of metakaolin, decreases the Ed from 23.5 to 15.3 MPa. Therefore, a small further increase to the lime/metakaolin ratio will decrease more the Ed. At last, NHL and L/C concrete present high values of Ed. All the Ed should be determined also in 6 and 12 months, since these systems are not stabilised by the time of 3 months.

3.4 Thermal Analysis
The differential thermal analysis and thermogravimetric analysis [DTA/TG] data for concrete by the time of 1,3,6 months are reported in table 3. The EM concrete present a slow chemical reaction evolution and after 6 months of curing time, there is still unreacted Ca(OH)$_2$ in the concrete mass and therefore a further conversion of chemical compounds could be expected. The MK concrete of present a rapid chemical evolution and in 1 month time, all the Ca(OH)$_2$ seemed to be bounded by the pozzolan. The concrete of natural hydraulic lime and lime/cement are not stabilised chemically in one month of curing time.
Table 3. TG analysis of the compounds (% per weight) presented in mortars after 15 months of curing

<table>
<thead>
<tr>
<th>Code</th>
<th>Time</th>
<th>(350-450^\circ C)</th>
<th>&gt;600(^{\circ} C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\text{H}_2\text{O} - \text{Ca(OH)}_2)</td>
<td>(\text{Ca(OH)}_2)</td>
</tr>
<tr>
<td>I</td>
<td>1m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3m</td>
<td>0.60</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>6m</td>
<td>0.66</td>
<td>2.72</td>
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<tr>
<td>II</td>
<td>1m</td>
<td>1.90</td>
<td>7.81</td>
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<td>1.04</td>
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<td></td>
<td>6m</td>
<td>0.88</td>
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<td>III</td>
<td>1m</td>
<td>-</td>
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</tr>
<tr>
<td></td>
<td>3m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>6m</td>
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<td>IV</td>
<td>1m</td>
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<td></td>
<td>3m</td>
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<tr>
<td>V</td>
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<td></td>
<td>3m</td>
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<tr>
<td>VII</td>
<td>1m</td>
<td>3.35</td>
<td>13.77</td>
</tr>
<tr>
<td>VIII</td>
<td>1m</td>
<td>2.85</td>
<td>11.71</td>
</tr>
</tbody>
</table>
4. Conclusions
From the obtained results the following conclusive remarks can be point out, regarding:

1. The role of binder nature to the concrete mechanical characteristics
   • The natural pozzolanic addition-earth of milos present a low reactivity regarding the Ca(OH)$_2$ consumption resulted to low values of compressive and flexural strength
   • The artificial pozzolanic addition-metakaolin presents high reactivity regarding the Ca(OH)$_2$ consumption and could be used for restoration mortars production in order to ameliorate the early strength of lime mortars
   • Concrete prepared by mixing lime/metakaolin/ceramic fragment/sand:20/10/35/35 (in %p.w.), present a sufficient ratio of $F_c/F_f$ and $E_d$ value. Furthermore, it is estimated that by increasing the lime/metakaolin ratio, a decrease in $E_d$ and $F_c$ will be accomplished.
   • Concrete produced by NHL present a sufficient behavior regarding the compressive strength but high values of $E_d$ and low ones of $F_c$. Nevertheless, it seems to be still in chemical evolution (DTA/TG results) therefore, the mechanical characteristics should be estimated in 3 and 6 months.

2. The role of the aggregates nature to the concrete mechanical characteristics
   The use of ceramic fragments as aggregates influences mainly materials the $E_d$ values. Furthermore there is a slighter influence to the $F_f$ and an insignificant one to the $F_c$.

3. General
   Plenty of concrete synthesis are still in chemical and mechanical evolution, therefore their mechanical characteristics should be determined also, by the time of 3, 6 and 12 months.

4. Perspectives
   The concrete that will present the best performance should also, be tested in masonry wall scale under dynamic stresses and in a specific monument scale under dynamic stresses using finite element analysis.

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References

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Fig. 3 Compressive strength (MPa) of concrete in time
Fig. 4 Flexural strength (MPa) of concrete in time
Fig. 5 Dynamic Modulus of Elasticity (GPa) of concrete in time