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PHYSICAL–CHEMICAL PROCESSES AT HARDENING OF SOME LIME–LIMESTONE–VOLCANIC TUFF COMPOSITES

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Lucrarea aduce informații cu privire la procesele care au loc la întărirea unor compozite liante din sistemul var-calcar-tuf vulcanic, realizate pentru lucrări de restaurare. Compozițiile, preparate cu var hidratat, material puzzolanic și calcar de diferite tipuri, au fost investigate din punct de vedere al procesului de întărire. Analiza de difracție de raze X, analize termice complexe și microscopia electronică au fost utilizate pentru investigarea întăririi probelor până la termenul de 56 zile.

The paper brings information regarding to processes taking place at hardening of some composite masses in the lime–limestone–volcanic tuff system, especially formulated for restoration work. The compositions made with hydrated lime, pozzolanic material and limestone of various sorts were investigated with respect to the hardening process. X-ray diffraction, complex thermal analysis and electronic microscopy were used to investigate some of the samples hardened up to 56 days.

Keywords: Composite masses, Lime, Pozzolanic material, Limestone, Hardening

1. Introduction

At hardening of binder composites based on hydrated lime and pozzolana, the carbonation reaction of portlandite ($Ca(OH)_2$) competes with the pozzolanic reaction between portlandite and the reactive silica from pozzolana—which, in this case, is volcanic tuff.

When exposed to air, the lime reacts with carbon dioxide from the atmosphere in order to form calcium carbonate,—with the carbonation process being responsible for the hardening of composite masses of the type mortar based on lime. In literature, five stages of the carbonation process are mentioned [1–4] as follows:

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a. Diffusion of CO_2 gas through mortar pores
b. Dissolution of portlandite ($Ca(OH)_2$) in the water from pores

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^{-} \qquad (1)$$

c. Dissolution of CO_2 in the water from pores

$$CO_2 + OH^{-} \leftrightarrow HCO_3^{-} \qquad (2)$$

d. Development of an equilibrium at the dissolution of CO_2 in the water existing in pores

$$HCO_3^{-} + OH^{-} \rightarrow CO_3^{2-} + H_2O \qquad (3)$$

e. Precipitation of $CaCO_3$

$$Ca^{2+} + CO3^{2-} \rightarrow CaCO_3 \qquad (4)$$

In lime and pozzolana based mortars, the reaction of carbonation is accompanied by the pozzolanic reaction, which is a reaction taking place between calcium hydroxide and reactive silica from pozzolanic materials with formation of hydro-silicates which contribute at hardening. The pozzolanic reaction is based on acid-base reactions between portlandite ($Ca(OH)_2$) and silicic acid (H_4SiO_4 or $Si(OH)_4$). For simplification, this reaction may be represented schematically as follows:

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2H_2O \rightarrow CaH_2SiO_4 \cdot 2\,H_2O \qquad (5)$$

In the present paper the hardening process of some composites from the lime–limestone–volcanic tuff system was studied, with limestone playing the role of aggregate. Several types of limestone of various colour and certain compositional differences, such as the content of calcite ($CaCO_3$) and of quartz (SiO_2), were used.

2. Experimental

2.1 Materials

The raw materials used in performing the composites were hydrated calcium lime, volcanic tuff and limestone. They were all characterized chemically in terms of oxide composition (according to SR EN 196–2), and, in the case of limestone, in terms of clay content (according to SR EN 933–9) and total organic carbon or TOC (according to SR EN 13639). Table 1 presents the compositional characteristics of the materials.

Table 1

The oxide composition of the raw materials

Characteristics (%)	**Raw material**					
	Calcium hydrated lime	**Volcanic tuff**	**Limestone**			
			C_1 - white	**C_2 - ochre**	**C_3 - red**	**C_4 - black**
L.O.I	29.74	7.75	43.58	24.54	36.67	42.44
SiO_2	0.13	69.46	0.30	41.59	13.08	3.13
Al_2O_3	0.43	11.91	0.41	2.14	3.28	0.63
Fe_2O_3	0.39	1.60	0.12	0.41	0.30	0.02
CaO	68.04	2.80	54.43	29.66	38.62	53.02
MgO	0.77	0.30	0.49	0.59	5.55	0.59
SO_3	0.04	0.05	0.03	0.06	0.10	0.16
Na_2O	0.23	2.81	0.16	0.26	0.43	0.32
K_2O	0.02	1.84	0.04	0.42	1.08	0.10
Clay content	-	-	nd	0.84	0.36	0.20
TOC	-	-	0.04	0.03	0.03	0.07
$CaCO_3$	-	-	97.20	52.96	68.96	94.68
Reactive SiO_2	-	62.41	-	-	-	-

The X-ray diffraction analysis revealed that the hydrated lime contains preponderantly $Ca(OH)_2$ along with $CaCO_3$.

Volcanic tuff presents good pozzolanic characteristics, well highlighted by both the high content of chemically-determined reactive silica (about 62%) and its particularly vitreous character deduced by way of optical microscopy analysis.

The limestone was chosen after its hue, which is crucial in terms of its application in such composite masses designed for restoration of historical monuments. The chosen limestone sorts differ not only in colour, but also in their compositional characteristics: the content of calcite ($CaCO_3$) and silica (SiO_2). The larger proportion of calcite appears in limestone C_1 (54.43%) and limestone C_4 (53.02%). On the other hand, limestone C_2 has the highest content of silica (41.59%).

The colour of limestone varied from white to black as follow: limestone C_1 was white, limestone C_2 ochre, limestone C_3 red and limestone C_4 black. The hue in both the ochre and the red limestone comes from iron compounds (identified by optical microscopy), namely, hematite which was in a ratio of 0.5-1% in the micritic component of limestone C2, and hematite and limonite which were in a ratio of 2-5% and respectively, 5-10%, in limestone C3. The black hue in limestone C_4 is given by the existence of an amorphous phase of an organic substance, present as micro-granules (0.02–0.1 mm) dispersed in the microcrystalline fundamental mass. The amorphous phase is in proportion of 2-5%, and is reported also by chemical analysis by the highest content of total organic carbon (i.e., 0.07%).

2.2 Experimental conditions

Six composite masses in the lime–limestone–tuff system (Table 2) were developed. The ratio lime/tuff was kept constant at a ratio of 1/0.6 gravimetric parts. The masses from 1 to 4 had the same ratio of limestone with respect to the amount of lime and tuff. Moreover, the ratio of limestone was varied, with maintaining the same type of limestone and ratio lime/tuff (in masses 5 and 6).

Table 2

The composition of the lime–limestone–tuff composite masses

Components	**Composition (gravimetric) per composite masses**					
	1	**2**	**3**	**4**	**5**	**6**
Limestone (V)	1	1	1	1	1	1
White limestone (C_1)	0.9					
Ochre limestone (C_2)		0.9			1.3	
Red limestone (C_3)			0.9			1.3
Black limestone (C_4)				0,9		
Tuff (TA)	0.6	0.6	0.6	0,6	0.6	0.6

The limestone and tuff were grinded up to a fineness corresponding to a residue of about 6% on a sieve with 90 μm meshes. Table 3 presents the analysis of the grain size distribution for the limestone and the volcanic tuff.

Table 3

Laser grain size distribution of the limestone and volcanic tuff

Raw materials	**Grain size distribution (%)**			
	< 3 μm	**< 6 μm**	**< 16 μm**	**< 32 μm**
Limestone C_1	53.1	68.7	79.5	85.0
Limestone C_2	47.0	61.8	71.6	79.0
Limestone C_3	33.4	52.0	71.7	79.6
Limestone C_4	37.6	55.8	75.3	83.0
Volcanic tuff	18.3	33.2	62.4	77.2

The grain size distribution performed on the limestone presented a large spectrum of variation in all the cases, with an asymmetric distribution. This pointed out the effect of fine granular material (the cumulative passing reached a value of 50% for all the sorts of limestone at an average particle diameter of 6μm). The volcanic tuff revealed an almost uniform, unimodal spectrum, similar to a Gaussian distribution.

2.3 Testing methods

The processes taking place at hardening were investigated by using X-ray diffraction analysis and complex thermal analysis, performed on slurries with a water/binder ratio of 0.4 and hardened for 2, 7, 28 and 56 days.

The samples were kept for hardening in a humidity-saturated atmosphere (on water), in a sealed dessicator at a relative humidity of the air of about 95%. At the terms of testing, the hydration process was stpped by means of washing with acetone followed by drying at a temperature of 60°C.

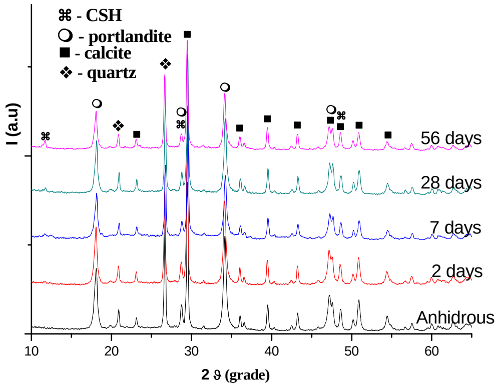
X-ray diffraction analysis was performed using a SHIMADZU XRD 6000 diffractometer, using Ni-filtered CuKa radiation, with scan step of 0.02° and couting time of 0.6 s/step, for diffraction angles 2 theta ranged between 10 and 65°, at room temperature.

The differential thermal analysis coupled with thermo gravimetric analysis (DTA/TG) was performed on a SHIMADZU DTG-TA- 50H, at a heating rate of 10°C /min, in static air.

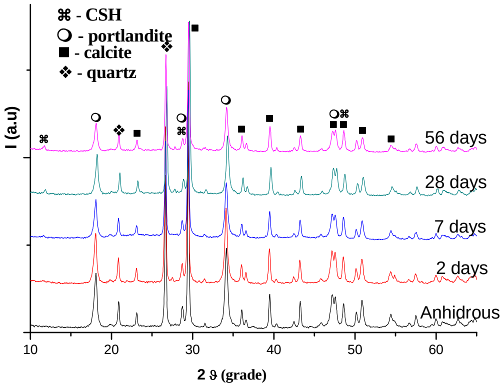
Moreover, electro-microscopic observations were performed on slurries of hardened composite masses at 2 and 7 days. SEM images were obtained by using a HITACHI S2600N equipment coupled with EDX probe, the samples being covered with a silver layer.

3 Results and discussions

The X-ray diffraction analyses led to obtaining similar spectrum patterns for both the anhydrous and the hydrated composite masses as can be seen in Fig. 1 for composite masses 2 and 5 with ochre limestone (C_2).



a.



b.

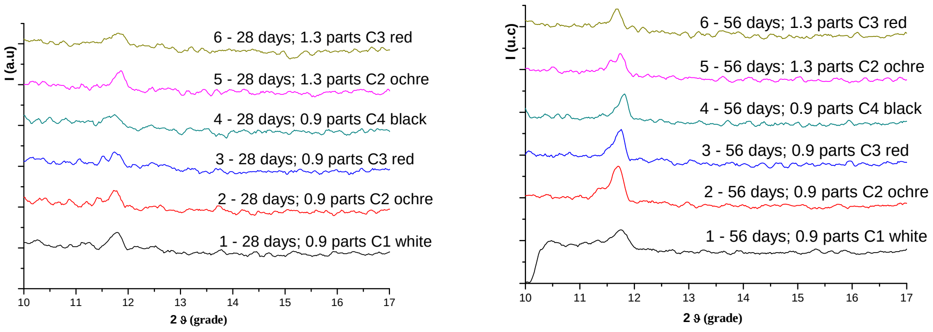
Fig. 1. Diffractograms of composite masses 2 (a) and 5 (b)—anhydrous and hydrated for 2, 7, 28 and 56 days

The diffractograms of the composite masses show decreases of portlandite-specific interferences with the hardening duration,—these being more significant at the term of 56 days. The fact has an explanation mainly in the partial carbonation of portlandite under CO_2 action inside the dessicator. Moreover, portlandite intensity decrease is also present for all the composite masses beginning with the term of 28 days. Portlandite intensity decrease is also due to portlandite consumption in the pozzolanic reaction (with SiO_2 from the volcanic tuff). In this respect, the diffractograms bring clues through the appearance of a small interference at $2\theta = 11.8°$ (7.57 Å), with an intensity which increased from 28 days to 56 days (Fig. 2a and 2b), thus suggesting the formation of some slightly crystallized calcium hydro-silicates, CSH.

Certain less important increases which may be observed for portlandite interferences may be explained through the increase in the crystallinity degree of portlandite and, possibly, through the hydration of some anhydrous, still existing, lime fractions

No changes in the intensity of the calcium carbonate interferences are noticed on the diffractograms. This may be due to the lower crystallinity degree of the calcite formed in the process of carbonation of the calcium hydroxide (portlandite) as opposed to the calcite brought in by the addition of limestone. It is also possible that, because of the more advanced fineness of the limestone, a small part of the calcite brought in by limestone to get dissolved only to get carbonated afterwards although in a rather poorer crystalline form. Besides, the hardening conditions—a humidity-saturated atmosphere (on water), in a sealed desiccator at a relative humidity of the air of about 95%—have the effect of stopping the carbonation process [5–7].

The diffractograms reveal a certain influence of the type of limestone on the formation of the reaction products (Fig. 2). Thus, in the composite masses with 35% limestone C_2–C_4, the intensity of the interference specific to the hydro-compounds of type CSH at 56 days is higher than in composite masses with limestone C_1 (Fig. 2b). Possibly, because of its advanced fineness, the silica in limestone C_2–C_4 is slightly activated and reacts with the portlandite in the system with formation of an additional amount of hydro-compounds of type CSH. Thus, it is clear that the intensity of the interference specific to the hydro-compounds CSH increases with increasing the silica content in the limestone from 3.13% in C_4 to 41.59% in C_2.



a. b.

Fig. 2. Diffractograms of the composite masses hardened for 28 days (a) and 56 days (b)

It is also clear that the increase in the ratio of limestone from 35% to 45% and the corresponding decrease in the ratio of lime and tuff (composite masses 5 and 6) led to a decrease in the amount of reaction products of type CSH, which was discernible due to the lower intensities of their interferences (Fig. 2b).

The complex thermal analyses carried out on composite masses 2 and 5 at the terms of 2 and 7 days brought additional information beside that obtained by X-ray diffraction. On the ATD and DTG curves, the presence of the following groups of effects along with mass losses (Fig. 3 and 4) was found:

- a strong endothermic effect at 450°C due to portlandite dehydration;
- effects with a peak varying from 690°C to 800°C, which may be assigned to the decarbonation processes of the $CaCO_3$ brought in by the limestone or resulted from the carbonation of calcium hydroxide. Depending on the origin of the $CaCO_3$ compound, the temperature at which an effect reaches a peak corresponding to decarbonation varies. Thus, the $CaCO_3$ compound formed by portlandite carbonation, with a poorer crystalline character, is decarbonated at a lower temperature, with a maximum between 600°C and 690°C, meanwhile the

calcium carbonate brought in by limestone is decomposed at higher temperatures, of about 720–800°C.

It must be mentioned that at short terms of hardening, there are no effects occurring along with mass losses at low temperatures (below 200°C) in any of the ATD and DTG diagrams, which could be due to the dehydration of gel-like calcium hydro-silicate.

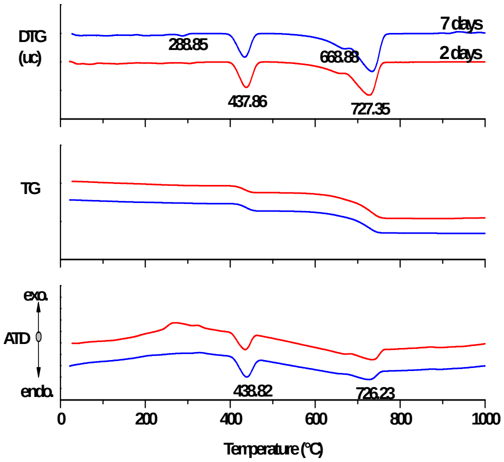


Fig. 3. Derivatograms of composite mass 2 at 2 and 7 days

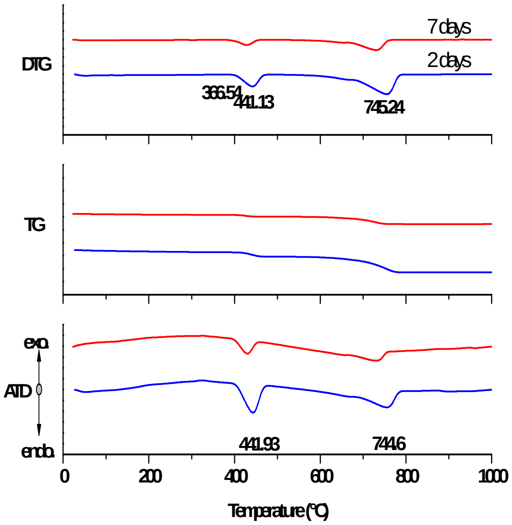


Fig. 4. Derivatograms of composite mass 5 at 2 and 7 days

Table 4 shows the mass losses registered on TG curves.

Table 4

Mass losses (%) registered on TG curves

Composite mass	**Mass losses (%) at temperatures of (°C)**									
	300–400		**400–490**		**490–690**		**690–800**		**800–1000**	
	L.O.I 2days	L.O.I 7days	L.O.I 2days	L.O.I 7days	L.O.I 2days	L.O.I 7days	L.O.I 2days	L.O.I 7days	L.O.I 2days	L.O.I 7days
2	2.705	2.962	5.432	4.305	5.359	6.187	10.791	10.507	0.287	0.296
5	2.336	2.689	4.764	3.964	3.361	4.562	13.897	13.269	0.091	0.044

The data in Table 4 reveal a decrease in the mass losses in the temperature range from 400°C to 490°C for the hardening time of 2 to 7 days, which is attributed to portlandite dehydration. The mass loss is higher for composite mass 2 (1.127%) than for composite mass 5 (0.8%), which is in correlation with the higher amount of lime in composite mass 2. The decrease of the mass losses in this range of temperature suggests a consumption of an amount of portlandite in the carbonation process and, to a lesser extent, even in a pozzolanic reaction with the reactive silica present in the volcanic tuff (Fig. 5).

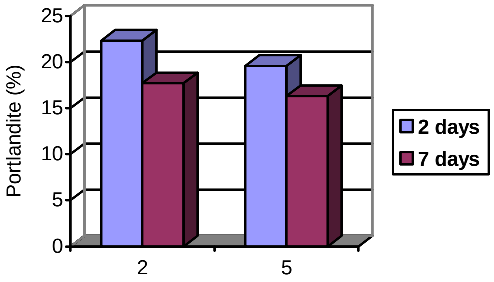


Fig. 5. Consumption of portlandite in composite masses 2 and 5 at 2 and 7 days

Considering that in the temperature range of 490–1000°C a decarbonation of the calcite from the two sources—carbonation of the portlandite from lime and the calcite from the raw materials (limestone)—takes place, a slight increase in the mass loss over time (from 2 to 7 days) was found,—of 0.553% for composite mass 2 and of 0.526% for composite mass 5. This means an increase in the amount of calcite in the system as a result of a partial carbonation of the portlandite (Fig. 6).

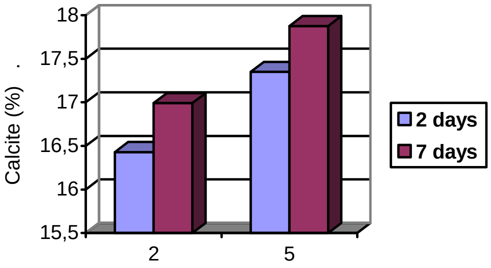
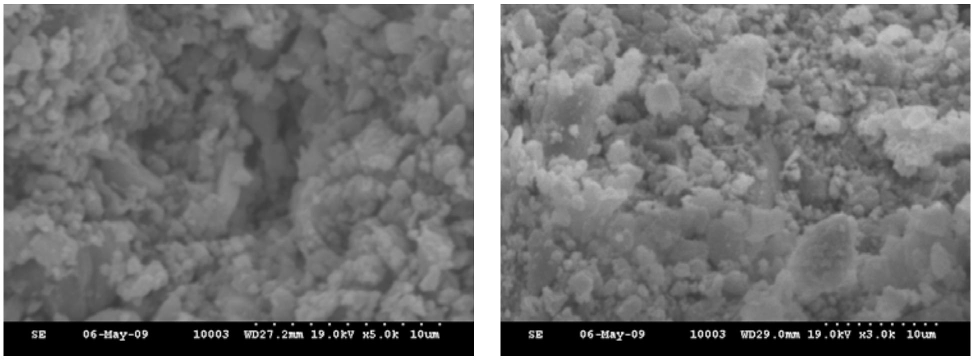


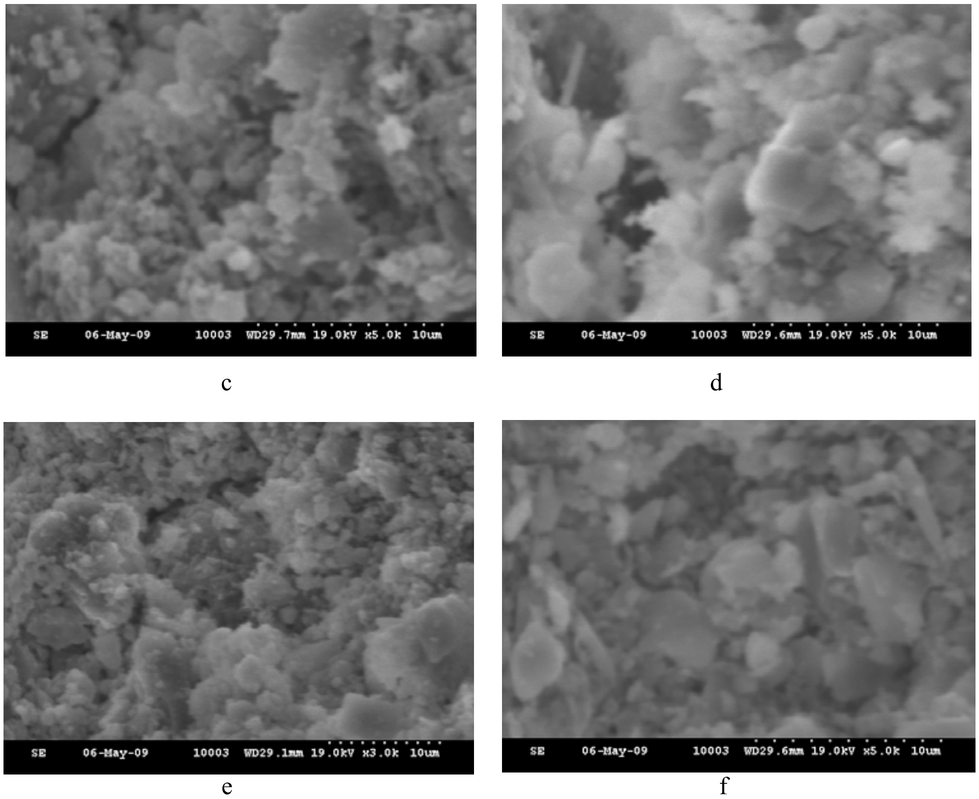
Fig. 6. The increase over time in the amount of calcite in composite masses 2 and 5

The Derivatograms of composite masses 2 and 5, which contain portlandite and volcanic tuff, lacked any effects attributable to the dehydration of any hydro-compounds of the type calcium hydro-silicates CSH. With the well-known low speed of the pozzolanic reaction, this is no surprise since the term of 7 days is too short for such compounds to form. Furthermore, the high content of fine limestone in the composite masses (which exceeds the content of $Ca(OH)_2$) stimulates portlandite carbonation by acting as centres of nucleation and crystallization of the newly formed calcite. Consequently, the availability of $Ca(OH)_2$ for the reaction with the active hydraulic material is affected.

The electronic microscopy pictures presented in Fig. 7 suggest the presence of $CaCO_3$ especially as agglomerated crystals with irregular contour, often deformed. In some pictures also visible are rhombohedral, better contoured crystals of calcite (Fig. 7b and 7f).



a b



c d

e f

Fig. 7. Images of electronic microscopy of the composites: a – 1; b – 2; c – 3; d – 4; e – 5; f – 6

Electronic microscopy could not detect any formations of the type CSH up until the hardening time of 7 days.

4 Conclusions

The paper aimed at the investigation of a series of composite masses obtained using hydrated lime, fine limestone and volcanic tuff in terms of the physical and chemical processes which take place at hardening.

Analyses based on X-ray diffraction corroborated with complex thermal analyses and electronic microscopy analyses revealed that the considered composite masses, which are designed for restoration work, get hardened by the following type of processes:

- Carbonation of $Ca(OH)_2$ with formation of slightly microcrystalline $CaCO_3$. The fine particles of limestone contained as a component in the composite masses favour this process by acting as centres of nucleation.

- Pozzolanic reactions between the reactive SiO_2 from the volcanic tuff and the $Ca(OH)_2$ brought in the system as a main component. The speed of reaction is rather slow, and so the formation of reaction products of the type CSH, slightly crystalline, was identified on the diffractograms of the samples hardened at 28 and 56 days in rounded, not too intense peaks.

As far as the composition is concerned, it was found that the type and ratio of limestone affect the hardening processes to a certain extent. Thus, the silica contained in certain sorts of limestone (C2–C4) becomes slightly more reactive after advanced grinding of the limestone, and reacts with the portlandite present in the system with formation of an additional amount of hydro-compounds of the type CSH.

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