

# Application of cement replacement materials in phase formation in mortar as an ecological approach for reducing greenhouse gases

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## Introduction

The object of this research are different cement composites with high content of inert mineral fillers (marble and quartz sand) and low water-cement ratio, obtained after hydration of White Portland cement.

The aim of the work is to investigate the phase formation and to measure the density, compressive strength and porosity of the cement composites, where the research is made after 28 and 120 days of water curing.

The effect of the studied parameters is evaluated by the methods of powder X-ray diffraction, IR, SEM and physico-mechanical methods for obtaining properties: bulk density after immersion, adsorption after immersion, compressive strength and porosity.

## Methods

The bulk density after immersion and adsorption after immersion were measured according ASTM C642-13. Due to the different bulk densities of the samples, the values of adsorption were adjusted to comparable values. The compressive strengths at 28 and 120 days of water curing were measured according EN 196-1:2016. Broken parts sample with mass of  $2.0 \pm 0.3$  mg were used to measure the porosity by mercury intrusion porosimetry method using Carlo Erba, Porosimeter Mod. 1520, pressure range 1-150 atm corresponding to pore size range 50-15000 nm. The XRD patterns were performed on X-ray powder diffractometer D2 Phaser BrukerAXS, CuK $\alpha$  radiation ( $\lambda = 0.15418$  nm) from 5 to 80  $2\theta$  with a step of 0.05 $^\circ$ . The microstructures were observed with Philips PH Model 515, regime of secondary electron emission.

## Sample

Table 1. Compositions of the samples, \*all particles with sizes below 125  $\mu$ m

Mortar	Binder	Aggregate	Ratios (wt/wt)		
			cement/aggregate	water/cement	water/fines**
As – As028*, As120	White Portland cement	River sand	1:3	0.50	0.500
Mm – Mm028, Mm120	White Portland cement	Marble powder	1:2	0.60	0.353

## Results

Table 2. Physical mechanical properties of the samples

Sample	Bulk density after immersion	Adsorption after immersion	Compressive strength		Pore volume	
			28 days	120 days	28 days	120 days
	kg.m <sup>-3</sup>	mm <sup>3</sup> .cm <sup>-3</sup>	N.mm <sup>-2</sup>	N.mm <sup>-2</sup>	mm <sup>3</sup> .g <sup>-1</sup>	mm <sup>3</sup> .g <sup>-1</sup>
As	2126	173.8	56.3	60.6	44.98	41.91
Mm	2158	258.5	53.8	61.5	64.66	58.69

### Physical-mechanical Properties

The results show that the 28-day compressive strength of conventional cement mortar A is comparable to that given by the factory. The compressive strength increases by 7.6% at 120-day, due to the filling of porous space with new-formed hydrates (the pore volume increases by 6.8%).

## Results -

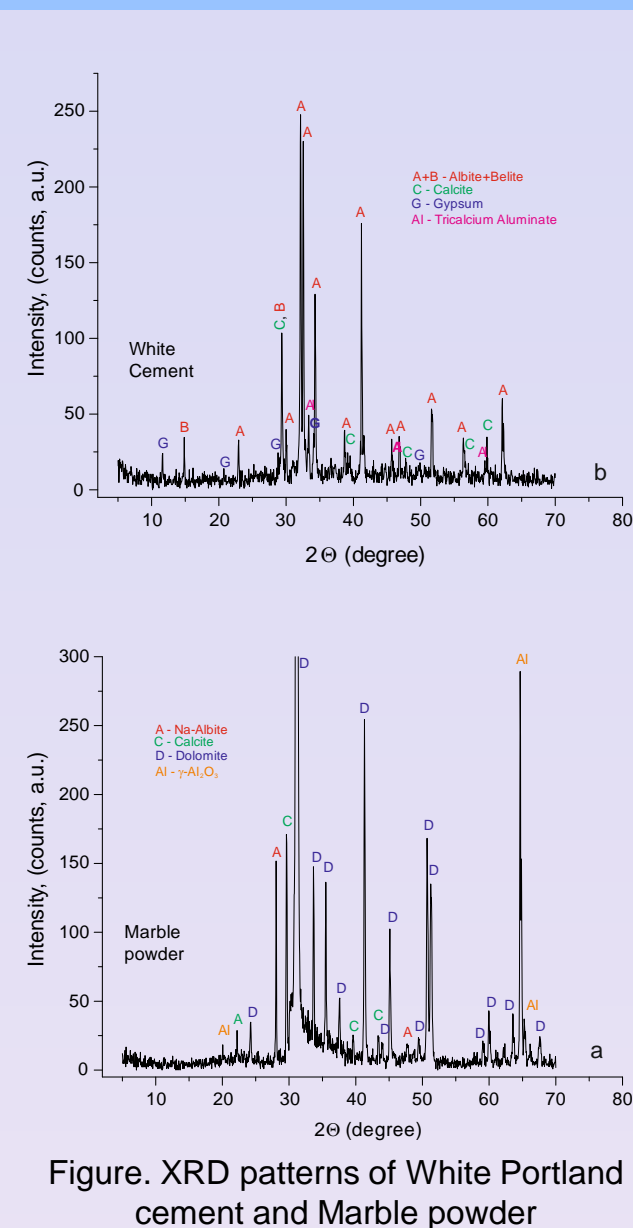


Figure. XRD patterns of White Portland cement and Marble powder

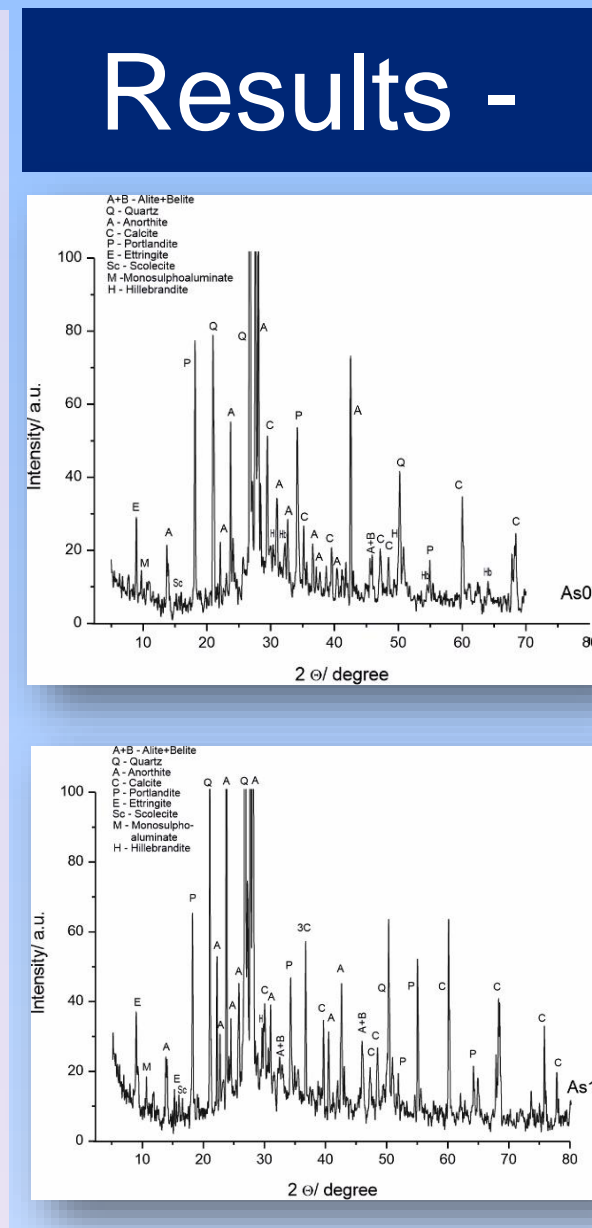
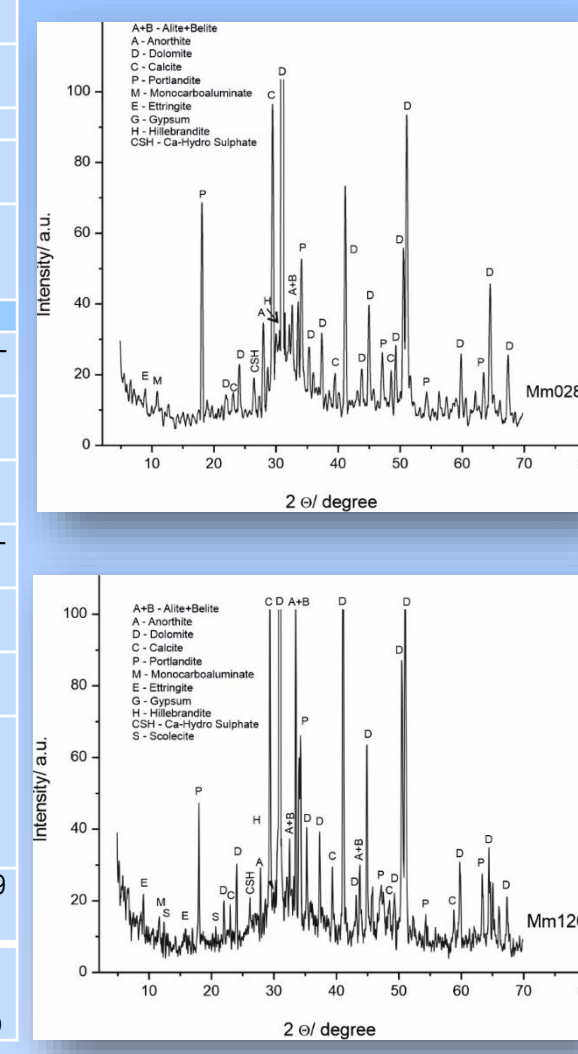


Figure. XRD patterns of samples As and Mm – 28 and 120 days of curing

No	Description	Sample	Identified phases
1.	Non-hydrated phases of cement and aggregates	As (028, 120) Mm (028, 120)	Belite (C <sub>2</sub> S), 49-1673 – 2CaO.SiO <sub>2</sub> Alite (C <sub>3</sub> S), 11-0593 – (Na,Ca)Al(Si,Al) <sub>3</sub> O <sub>8</sub> Anorthite (CaSi <sub>2</sub> ), 41-1486 – CaO.Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub> Quartz, 46-1045 – SiO <sub>2</sub> Dolomite, #36-0426 – CaMg(CO <sub>3</sub> ) <sub>2</sub>
2.	Phases of the source components	As (028, 120) Mm (028, 120)	Mg-rich Calcite, #47-1743 – CaCO <sub>3</sub>
3.	New phases forming		
3.1.	- containing OH	As (028, 120) Mm (028, 120)	Portlandite (CH), #44-1481 – Ca(OH) <sub>2</sub> Ettringite, #41-1451 – Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> .26H <sub>2</sub> O
3.2.	- containing SO <sub>4</sub> <sup>2-</sup> , OH and crystal water H <sub>2</sub> O	As (028, 120) Mm (028, 120)	Monosulphoaluminate, #45-0158 – Ca <sub>4</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O Calcium hydrogensulphate, #85-1271 – Ca(HSO <sub>4</sub> ) <sub>2</sub>
3.3.	- hydrosilicates – CSH/CSAH, forming of main oxides CaO, SiO <sub>2</sub> , OH and/or crystal water H <sub>2</sub> O	As (028, 120) Mm (028, 120)	Hillebrandite, #42-0538 – Ca <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>2</sub> Tobermorite 11A, #45-1480 – Ca <sub>5</sub> Si <sub>4</sub> (O,OH) <sub>16</sub> .5H <sub>2</sub> O Scolecite, #41-1355 – CaAl <sub>2</sub> Si <sub>2</sub> O <sub>10</sub> .3H <sub>2</sub> O
3.4.	- OH- and HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup> phases	As (028, 120) Mm (028)	Monocarboaluminate, #41-0219 – Ca <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> (CO <sub>3</sub> ) <sub>0.5</sub> .5H <sub>2</sub> O Hemicarboaluminate, #41-0221 – Ca <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> (OH)(CO <sub>3</sub> ) <sub>0.5</sub> .4H <sub>2</sub> O

## XRD



## Results – IR, SEM

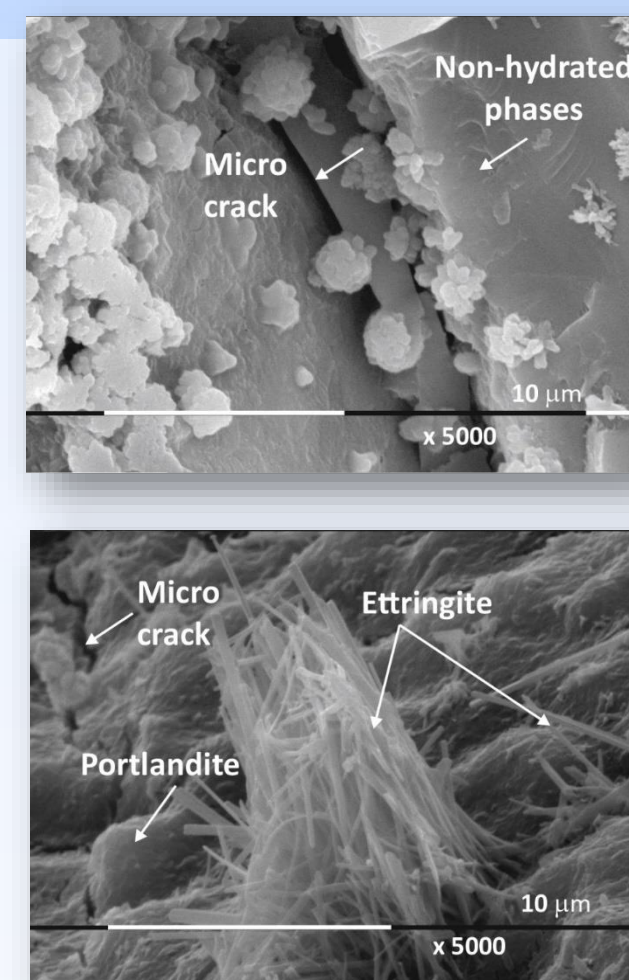


Figure. SEM of samples As – 28 and 120 days of curing

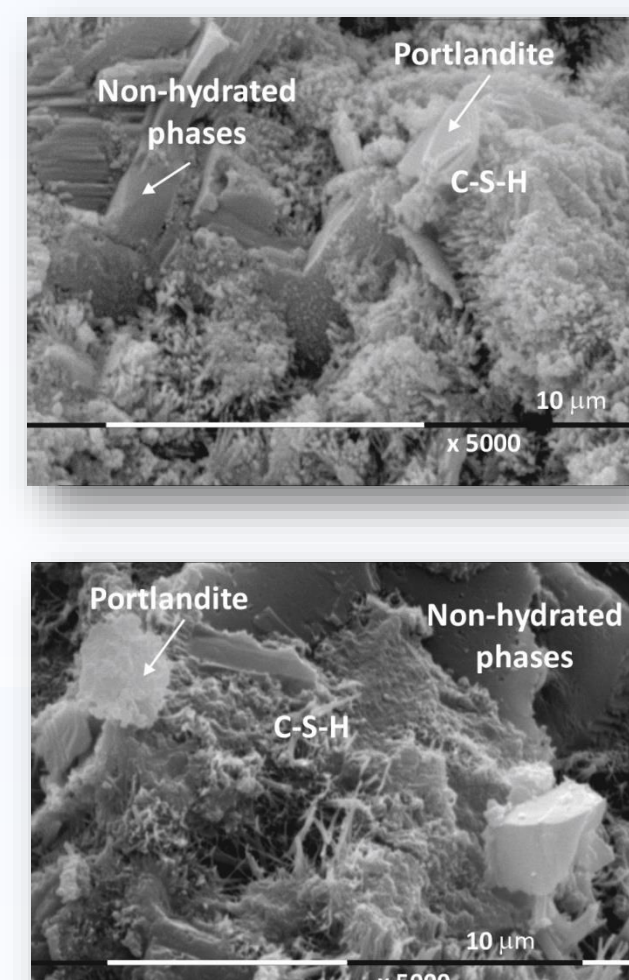


Figure. SEM of samples Mm – 28 and 120 days of curing

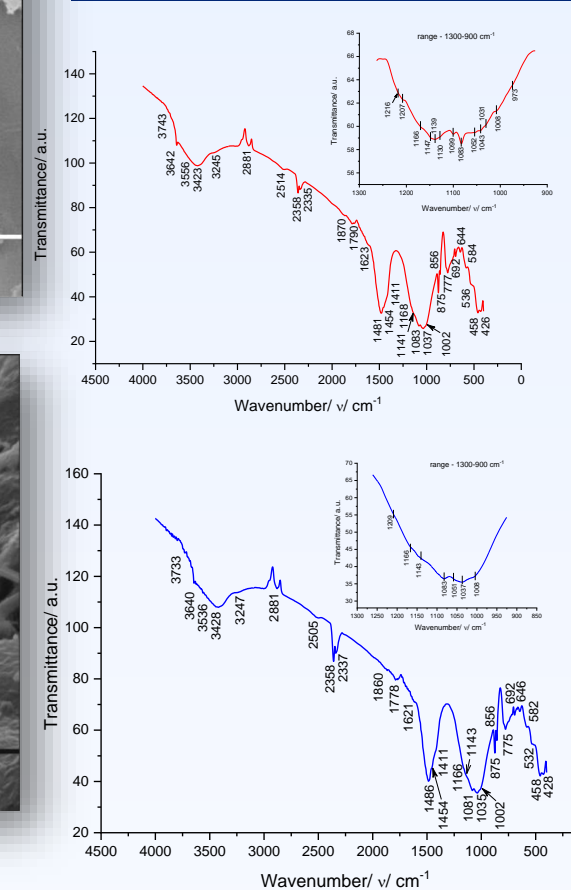


Figure. IR of samples As – 28 and 120 days of curing

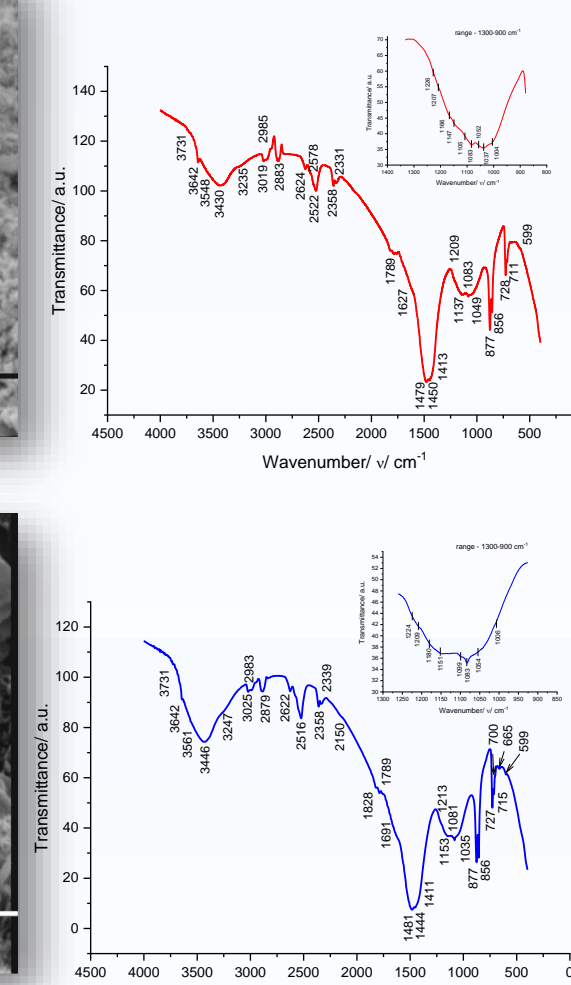
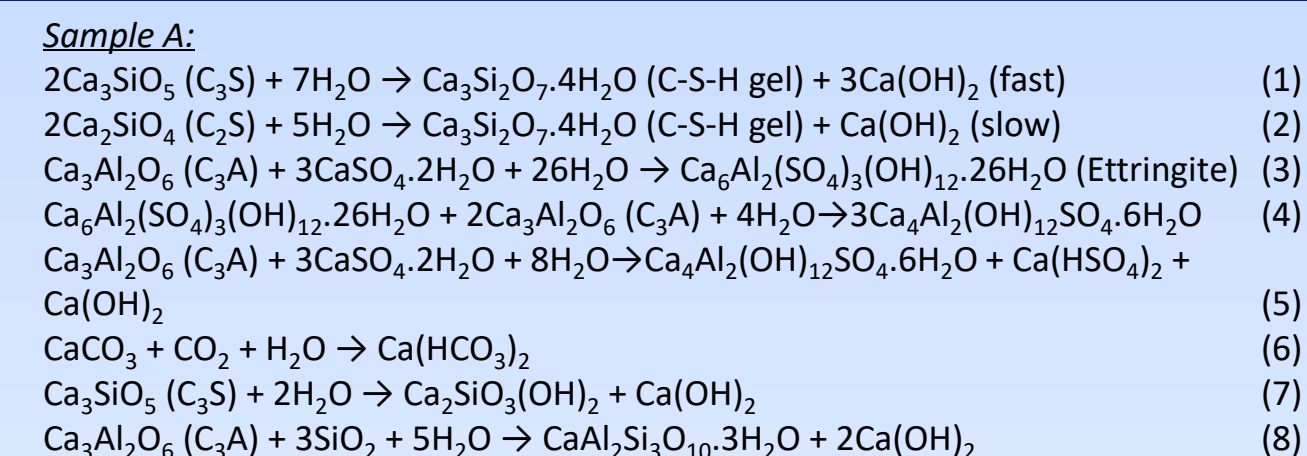
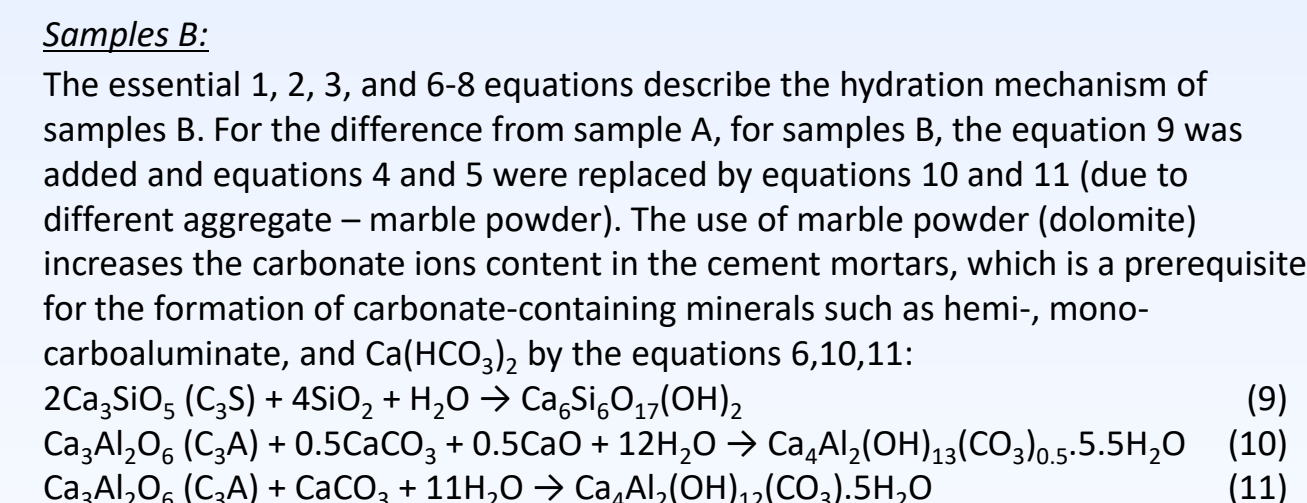


Figure. IR of samples Mm – 28 and 120 days of curing



Equations 1-3 are essential for the reaction mechanism of cement clinker hydration with the formation of hydrated phases (C-S-H gel) for sample A. The ettringite formation takes place in the early stages of cement minerals hydration (equation 3). With a residue of C<sub>3</sub>A, ettringite participates in the crystallization of mono-sulphate aluminate (equation 4). It is assumed, together with the formation of mono-sulphate aluminate (equation 4), is a possible parallel reaction in which a certain amount of Ca(HSO<sub>4</sub>)<sub>2</sub> is formed (equation 5). It is possible, under hydration conditions, the relic calcite partially transforms to Ca(HCO<sub>3</sub>)<sub>2</sub> (equation 6). It is also possible crystallization of scolecite and hillebrandite, (equations 7, 8) when Ca, Al, and Si-ions content, with origin raw materials (cement clinker and quartz sand as aggregate – sample A). During most reactions, portlandite was also formed. The presentation of the hydration reaction mechanism was by a complex of equations 1-8.



## Conclusion

The micro-structural evolution, studied by physico-mechanical and structural analyses, shows the formation of a stable dense structure without any space for the growth of new crystals.

The investigations provide new results on crystal-chemical and thermal properties of cement composites with high content of marble powder aggregate and reduced water-cement ratio. Powder X-ray diffraction and Fourier transform infrared spectroscopy prove the redistribution of anionic groups CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, SiO<sub>4</sub><sup>4-</sup>, AlO<sub>4</sub><sup>5-</sup>, and OH<sup>-</sup> (as O-H bond in structural OH- anions and O-H bond belonging to crystal bonded water molecules) from raw minerals to newly formed. The formation of carboaluminates during hydration under the influence of marble powder has been established. Based on this investigation, the scheme of sample hydration has been defined.

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