Crystal-Chemical and Thermal Properties of Decorative Cement Composites

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Abstract: The advanced tendencies in building materials development are related to the design of cement composites with a reduced amount of Portland cement, contributing to reduced CO\textsubscript{2} emissions, sustainable development of used non-renewal raw materials, and decreased energy consumption. This work deals with water cured for 28 and 120 days cement composites: Sample A—reference (white Portland cement + sand + water); Sample B—white Portland cement + marble powder + water; and Sample C white Portland cement + marble powder + polycarboxylate-based water reducer + water. By powder X-ray diffraction and FTIR spectroscopy, the redistribution of CO\textsubscript{3}\textsuperscript{2-}, SO\textsubscript{4}\textsuperscript{2-}, SiO\textsubscript{4}\textsuperscript{4-}, AlO\textsubscript{4}\textsuperscript{3-}, and OH\textsuperscript{-} (as O-H bond in structural OH\textsuperscript{-} anions and O-H bond belonging to crystal bonded water molecules) from raw minerals to newly formed minerals have been studied, and the scheme of samples hydration has been defined. By thermal analysis, the ranges of the sample’s decomposition mechanisms were distinct: dehydration, dehydroxylation, decarbonation, and desulphuration. Using mass spectroscopic analysis of evolving gases during thermal analysis, the reaction mechanism of samples thermal decomposition has been determined. These results have both practical (architecture and construction) and fundamental (study of archaeological artifacts as ancient mortars) applications.

Keywords: white Portland cement; marble powder; cement replacement materials; thermal properties; reaction mechanism

1. Introduction

Getting Portland cement is expensive, with high energy and raw material consumption production. A problem in its production is also the generation of carbon dioxide emissions [1,2]. In this regard, the advanced trends in building materials appeared to join the circular economy. This economic system aimed reduction of waste and carbon dioxide emissions and the continual use of resources, thus enhancing innovation and competitiveness [3,4].

The advanced tendencies in building materials development are related to the design of cement composites with a reduced amount of Portland cement, which will contribute to reducing CO\textsubscript{2} emissions and sustainable development of non-renewal raw materials used and energy as well. This is achieved through cement replacement materials as natural
pozzolans, fly ash, blast furnace slag, silica fume, metakaolin, carbonate rock (limestone, marble), etc. [2,5,6].

The interest in carbonate rocks as a cement substitute material is justified because their use reduces the total amount of clinker required to produce a certain amount of cement while increasing the total volume of cement obtained. That would result in a substantial amount of energy saving in the production of cement as the consumption of natural raw materials and the fuel needed for the clinker production would be reduced. Additionally, the reduction of CO$_2$ emissions would achieve [2]. Such cement composite has applications for decorative stamps, balustrades, restoration of architectural monuments, etc. [7–9]. On the other hand, its use requires large amounts of another natural resource, namely water, compared to conventional cement. The increased amount of water implies the appearance of crystal-chemical changes in such composite cements [7,10]. The amount of water used, can be controlled by adding a polycarboxylate-based water reducer to the composite. That additive leads to steric repulsion of fine particles [10,11]. Due to the superior water-reduction capabilities of such composite materials, the workability is improved, however, that may lead to an increase in the number of fine particles [11–13]. As a result, the hardened self-compactng mortar is obtained, characterized by high early-strength, smooth surfaces, and dense structure [12–14].

This work deals with cement composites of white Portland cement, marble powder with and without polycarboxylate-based water reducer. For comparison, a composite of Portland cement and quartz sand as cement replacement materials were used. Earlier investigations [15,16] of such composites revealed some difficulties in the identification of samples’ solid phases, which made it difficult to determine the generalized scheme of samples' hydration and the reaction mechanism of their thermal decomposition. The present study aims to clarify previously unsolved issues, showing the differences in the samples’ reaction mechanisms depending on the used cement replacement material.

To achieve the purpose, the more precise powder X-ray diffraction measurements and new ones of samples after heating up to 1100 °C, additional thermal analysis with mass spectroscopic registration of evolving gases, and new Fourier Transform Infrared spectroscopic investigations have been performed. All the methods used provided new results on the crystal-chemical and thermal properties of the samples (detailed scheme of their thermal decomposition mechanism).

Such knowledge is essential for obtaining good physical, chemical, and mechanical performance of composites with application in architecture and construction practice. The achieved results also are of fundamental importance in the study of archaeological materials—ancient mortars.

2. Raw Materials Composition and Samples Preparation

Used raw materials for sample preparation are white Portland cement (manufacturer, city), two types of aggregate (marble powder and sand), polycarboxylate-based high range water reducer (HRWR), and distilled water. The chemical and mineral composition of the white Portland cement and the used aggregates are presented in Table 1.

The white Portland cement—CEM I 52.5 N, produced by Devnya Cement (Devnya, Bulgaria). The mineral composition is calculated by Bogue method [17].

The first used aggregate is marble powder, produced by the company White Marble Products AIAS S.A. (Nikisiani, Greece).

The second used aggregate is sand—clean washed and dried river sand with over 85.0% content of SiO$_2$—quartz. The aggregate is presented by fineness spheroid modulus—2.7 (EN 12620:2002 + A1:2008/HA:2008) with shape index—4.6% (EN 933-4:2008).

The used HRWR (Sika ViscoCrete 5-800, Sofia, Bulgaria) is in dosage 2.0% by weight of white cement. This HRWR is chloride-free, soluble in water, without any retarding effects, and a density of 1.07 g/cm$^3$ (at 20 °C).
Table 1. Chemical and mineral composition of white Portland cement and used aggregates.

| No | Chemical Composition of White Portland Cement—CEM I 52.5 N (wt%) |
|----|---------------------------------------------------------------|
| 1  | SiO$_2$  | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO   | MgO   | Na$_2$O | K$_2$O | Free Lime |
|    | 24.3    | 2.1       | 0.2        | 68.3  | 0.3   | 0.13    | 0.02   | 1.9       |

The mineral composition of white Portland cement, (wt%)

| 2   | Belite (C$_2$S) | Alite (C$_3$S) | Tricalcium aluminate (C$_3$A) | Calcium aluminoferrite (C$_4$AF) |
|-----|-----------------|----------------|-------------------------------|---------------------------------|
|     | 72.13           | 15.28          | 5.23                          | 0.61                            |

Chemical composition of marble powder (wt%)

| 3   | CO$_2$ + H$_2$O | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO   | MgO   | Na$_2$O | K$_2$O | MnO |
|-----|-----------------|---------|-------------|-------------|-------|-------|--------|-------|-----|
|     | 45.7            | 0.12    | 0.38        | 0.14        | 32.9  | 20.0  | 0.05   | 0.19  | 0.01|

Chemical composition of sand (wt%)

| 4   | Sand (SiO$_2$) | over 85.0% |
|-----|----------------|------------|

The three cement composite samples have been prepared. Sample A, a reference (white Portland cement + sand + water), with composition satisfying the EN 196-1 (Section 6) requirements [18] for the determination of the cement compressive strength. Sample B (white Portland cement + marble powder + water) was prepared by mixing procedure, according to the EN 196-1 [18], with prolonged time of homogenization at high speed (to obtain self-leveling properties or 120 s). The composition of sample B was determined by optimization to achieve high-quality smooth surfaces of the hardened samples [19]. This procedure was applied to the data obtained from experimental tests (D-optimal plan with constant cement-to-aggregate ratio). The sample C (white Portland cement + marble powder + HRWR + water) was prepared according to the EN 196-1, with the same cement-to-aggregate ratio as sample B and with the maximum possible amount of water, where the sedimentation or segregation borders were not observed 10 min after mixing.

The three samples were molded without any compacting treatment in 6 prisms (two prisms for each sample), 40 mm × 40 mm × 160 mm, for 1 day in a moist atmosphere (>95% RH and 20 °C). Then the unmolded samples were stored underwater (20 °C) until strength testing (28 and 120 days) [20,21]. The samples A, B, and C undergoing water curing for 28 days are named A028, B028, C028, and those for 120 days—A120, B120, and C120. The components ratio in studied samples is presented in Table 2.

Table 2. Compositions of the samples.

| Sample     | Aggregate         | Cement-to-Aggregate | Water-to-Cement | Water-to-Fines * |
|------------|-------------------|---------------------|-----------------|------------------|
| A028, A120 | Sand              | 1:3                 | 0.50            | 0.500            |
| B028, B120 | Marble powder     | 1:2                 | 0.60            | 0.353            |
| C028, C120 | Marble powder     | 1:2                 | 0.40 + HRWR     | 0.235            |

* all particles with sizes below 125 µm.

The same samples have been investigated earlier by us where their physical-mechanical properties—bulk density after immersion, adsorption after immersion, compressive strength, and pore volume were defined well. The composites with marble powder show denser structures with the tendency of self-desiccation. The composite low pore volume and denser structure are demonstrated by the Scanning electron microscopy results, as well. The use of polycarboxylate-based additive decreases the water amount and improves the fine particle dispersion and hardness respectively [15,16].
3. Experimental Methods

The time-resolved high-temperature powder X-ray diffraction (HT-PXRD) measurements were collected at PANalytical Empyrean (Malvern Panalytical, Malvern, UK) equipped with a multichannel detector (Pixel 3D) (Malvern Panalytical, Malvern, UK) using (Cu Kα radiation 45 kV–40 mA) radiation in the 10–80° 2θ range, with a scan step of 0.026° for 33 s. Phase identification has been performed using various search-match programs software as well as data from the Inorganic Crystal Structure Database (ICSD) [22].

FTIR measurements are performed by FTIR Spectrometer, (Varian 660, Agilent Technologies, Wien, Austria), covering the range of 400–4000 cm\(^{-1}\). The samples were prepared as pellets consisting of low-dispersed KBr and powder of prepared mixture. The transmittance spectra were collected using an MCT detector with 64 scans and 1 cm\(^{-1}\) resolution.

TG/DTG-DSC analysis was carried out on a Setsys Evolution 2400, (SETARAM, Lion, France), combined with an OmniStar mass-spectrometer (Pfeiffer Vacuum GmbH, Wetzlar, Germany), in the temperature range room temperature (RT)—1100 °C; in gas medium—static dry air atmosphere, with a heating rate of 10 °C/min. The operational conditions of the TG/DTG–DSC-measurements were: sample mass of 15.0 ± 1.0 mg (mass resolution of 0.02 µg) and alumina sample crucible with a volume of 100 µL.

4. Results and Discussion

4.1. PXRD Phase Analysis

The PXRD was used to better evaluate the investigated samples. The obtained results for raw materials and samples A028, A120, B028, B120, C028, and C120 are shown in Figures 1–3 and Table 3.

![Figure 1. (a) PXRD pattern of marble powder aggregate. (b) PXRD pattern of white Portland cement.](image-url)
The defined mineral phases in raw materials are belite, alite, tricalcium aluminate, gypsum, and calcite in white Portland cement; dolomite and Mg-rich calcite in marble powder aggregate; quartz in sand aggregate.

The phase composition of water cured samples is determined by the presence of the raw cement minerals, marble powder aggregate, HRWR additive, water-to-cement ratio, and overall ratio of the main components in the samples [23].

The PXRD analysis (Table 3, Figures 1–3) reveals the presence of two groups of minerals in the studied samples: (i) relict minerals from the raw materials: belite, alite, calcite, quartz, dolomite; and (ii) newly formed minerals: portlandite, hemi- and mono-carboaluminate, ettringite, monosulphoaluminate, hillebrandite, scolecite, xonotlite, calcium hydrogensulphate, and artinite.

The obtained results justify the distribution of the new phases into several groups as follows:
- containing $\text{OH}^-$ and $\text{HCO}_3^-$/$\text{CO}_3^{2-}$;
- containing $\text{OH}^-$ and $\text{HSO}_4^-$/$\text{SO}_4^{2-}$;
- containing $\text{OH}^-$ in hydrate phase and $\text{OH}^-$ in hydrosilicates formed of main oxides $\text{CaO}$, $\text{Al}_2\text{O}_3$, $\text{SiO}_2$.

Their distribution is presented in detail in Table 3.

Figure 3. PXRD patterns of A120, B120, and C120.

Table 3. Results from PXRD analysis of raw materials (white Portland cement, marble powder, and sand) and A028, A120, B028, B120, C028, and C120.

| No. | Description | Sample Identified | Phases |
|-----|-------------|-------------------|--------|
| 1.  | Minerals of raw materials and their relicts in samples white Portland cement, A028, A120; B028, B120; C028, C120 |  | Belite (C2S), #49-1673—Ca$_2$SiO$_4$
Alite (C3S), #11-0593—Ca$_3$SiO$_5$
Calcite, #47-1743—CaCO$_3$
white Portland cement Tricalcium aluminate (C3A), #38-1429—Ca$_3$Al$_2$O$_6$
Gypsum, #33-0311—CaSO$_4$·2H$_2$O
Dolomite, #36-0426—CaMg(CO$_3$)$_2$ |

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Figure 3. PXRD patterns of A120, B120, and C120.
Table 3. Results from PXRD analysis of raw materials (white Portland cement, marble powder, and sand) and A028, A120, B028, B120, C028, and C120.

| No | Description | Sample | Identified Phases (Name, ICDD Card Number; Formula) |
|----|-------------|--------|---------------------------------------------------|
| 1. | Minerals of raw materials and their relics in samples | white Portland cement, A028, A120; B028, B120; C028, C120 | Belite (C$_2$S), #49-1673—Ca$_2$SiO$_4$ |
| | | | Alite (C$_3$S), #11-0593—Ca$_3$SiO$_5$ |
| | | | Calcite, #47-1743—CaCO$_3$ |
| | white Portland cement | | Tricalcium aluminate (C$_3$A), #38-1429—Ca$_3$Al$_2$O$_6$ |
| | marble powder | | Dolomite, #36-0426—CaMg(CO$_3$)$_2$ |
| | | | Mg-rich Calcite, #43-0697—CaCO$_3$ |
| | | A028, A120 | Quartz, #46-1045—SiO$_2$ |
| 2. | Newly formed phases | A028, A120 | Portlandite (CH), #44-1481—Ca(OH)$_2$ |
| 2.1. | hydrate phase | A028, A120; B028, B120; C028, C120 | Hillebrandite, #29-0373, #42-0538—Ca$_2$SiO$_3$(OH)$_2$ |
| 2.2. | C-S-H gel phases | A028, A120 | Scolecite, #41-1355—CaAl$_2$Si$_3$O$_10$.3H$_2$O |
| | | A120, C028 | Xonotlite, #23-0125—Ca$_6$Si$_6$O$_{17}$(OH)$_2$ |
| 2.3. | OH$^-$ and HCO$_3^-$ /CO$_3^{2-}$ phases | B028, B120; C028, C120 | Monocarboaluminate, #41-0219—Ca$_4$Al$_2$(OH)$_{12}$(CO$_3$)$_x$H$_2$O |
| | | B028, C028 | Hemicarboaluminate, #41-0221—Ca$_4$Al$_2$(OH)$_{13}$(OH)(CO$_3$)$_{6.5}$H$_2$O |
| | | B028, B120; C028, C120 | Artinite, #72-1320—Mg(CO$_3$)(OH)$_2$.3H$_2$O |
| 2.4. | OH$^-$ and HS$_2$O$_4$⁻ /SO$_4^{2-}$ phases | B028, B120; C028, C120 | Ettringite, #41-1451—Ca$_6$Al$_2$Si$_3$(OH)$_{13}$(SO$_4$)$_2$.26H$_2$O |
| | | | Calcium hydrogensulphate, #85-1271—Ca(HSO$_4$)$_2$ |
| | | A028, A120 | Monosulphoaluminate, #50-1607—Ca$_4$Al$_2$(OH)$_{12}$(SO$_4$)$_x$6H$_2$O |

The identification of mono- (B120 and C120) and hemi-carboaluminate (B028 and C028) [24] as well as spurrite [25–28] (B120 and C120) evidence the contribution of carbonate ions introduced in the system from the marble powder aggregate. The identification of ettringite and monosulphoaluminate [17,29,30] evidence the contribution of sulphate ions from the raw white Portland cement after hydration. The PXRD patterns are dominated by the reflexes of dolomite, calcite, belite, alite. The newly formed post-hydration phases are characterized by lower peak intensity, predetermined by the lower crystallites size, especially pronounced for samples with 28 days of curing. Probably, the lower water-to-cement ratio mostly influences the formation of hydrate phases with small crystallites. This is confirmed by the detected broadening of their reflections (Figure 2). Thus, microscopic, spectroscopic, and thermal analyzes have also been performed to confirm and refine these results.

The obtained new PXRD results do not confirm the previous assumption of the isomorphic substitution for carbonate ions in ettringite [15]. They show the redistribution of carbonate ions, as well and sulphate ions in new solids, proven by the detection of spurrite, monosulphoaluminate, calcium hydrogensulphate, and arntinite.

Table 4 shows the results of the PXRD analysis of samples solid residue after heating up to 1100 °C.
Table 4. Results from PXRD analysis of A028, A120, B028, B120, C028, and C120 after heating up to 1100 °C.

| No | Sample                   | Identified Phases (Name, ICDD Card Number; Formula)                          |
|----|--------------------------|-------------------------------------------------------------------------------|
| 1  | A028, A120; B028, B120; C028, C120 | Larnite, #49-1673—Ca$_2$SiO$_4$；Wollastonite, #42-0550—CaSiO$_3$；Anorthite, #41-1486—CaAl$_2$Si$_2$O$_8$ |
|    | A028, A120; B120; C028, C120 | Anhydrite, #37-1496—CaSO$_4$                                                  |
|    | A028, A120; B028, B120; C028 | Ternesite #49-1807—Ca$_3$(SiO$_4$)$_2$SO$_4$                                   |
|    | A028, A120; C028, C120     | Quartz, #46-1045—SiO$_2$                                                      |
| 2  | B028, B120; C028, C120     | Periclase, #45-0946—MgO；Lime, #37-1497—CaO；Akermanite, #35-0592—Ca$_2$MgSi$_2$O$_7$；Calcium Aluminium Oxide, #33-0252—Ca$_2$Al$_2$O$_5$；Spurrite, #13-0496—Ca$_5$(SiO)$_2$(CO$_3$) |

The identified phases prove the conversion of the hydrated into anhydrous calcium-aluminum silicates after thermal heating to 1100 °C. Such results are related to the realized complete dehydration, dehydroxylation, as well as incomplete decarbonation and desulfuration of the hydrate, carbonate-containing, and sulfate-containing phases (Table 4). The sample A solid residue composition includes: (i) high-temperature silicate phases with SiO$_3$-structure (anorthite and wollastonite), and SiO$_4$-tetrahedra (larnite); (ii) ternesite and anhydrite, incorporating part of the sulphate sulphur. The solid residue of samples B and C contains anhydrous silicates (wollastonite, larnite, anorthite, and akermanite) and calcium aluminum oxide, result from high-temperature solid-phase synthesis at oxidizing atmosphere. Ternesite and/or anhydrite and/or spurrite were also registered.

4.2. FTIR Spectroscopy

The results obtained by FTIR spectroscopy (Table 5) of the raw marble powder and white Portland cement (Figure 4), as well as of the studied samples (Figures 5 and 6) complement the results of the PXRD analysis. The FTIR spectroscopy is a suitable method for the investigation of cement composites allowing identify the solids in minimum quantities and fine dispersity [27].
Table 5. Results from FTIR spectroscopy of raw materials (white Portland cement and marble powder) and A028, A120, B028, B120, C028, and C120.

| Description/References | Bond | ν₁ (cm⁻¹) | ν₂ (cm⁻¹) | ν₃ (cm⁻¹) | ν₄ (cm⁻¹) | Raw Material/Sample |
|------------------------|------|-----------|-----------|-----------|-----------|---------------------|
| **1. Minerals of raw materials and their relics in the samples** | | | | | | |
| Belite (C₂S), Ca₂SiO₄ | Si-O in SiO₄ | 520 | 923 | 657 | | white Portland cement*, A028, A120, B028, B120, C028, C120 |
| Alite (C₃S), Ca₃SiO₄ | | | | | | |
| Tricalcium aluminate (C₃A), Ca₃Al₂O₆ | Al-O in AlO₂ | 754 | 435 | 856 | 545 | white Portland cement |
| Calcite, CaCO₃ | C-O in CO₂ | 875 | 1411 | 1473 | 713 | white Portland cement |
| | O-H structural | 3403 | 3552 | | | |
| Gypsum, CaSO₄·2H₂O | S-O in SO₂ | 995 | 1103, 1126, 1141 | 597, 669 | | white Portland cement |
| | O-H structural | 3403 | 3552 | | | |
| Dolomite, CaMg(CO₃)₂ | C-O in CO₂ | 1081 | 1488 | 727 | | marble powder*, B028, B120, C028, C120 |
| Mg-rich Calcite, CaCO₃ | C-O in CO₂ | 1081 | 1488 | 727 | | marble powder*, B028, B120, C028, C120 |
| Quartz, SiO₂ | Si-O in SiO₂ | 692 | 1083, 1172 | 512 | | sand, A028*, A120 |
| | O-H structural | 3403 | 3552 | | | |
| **2. Newly formed phases** | | | | | | |
| **2.1. Hydrated phase** | | | | | | |
| Portlandite (CH), Ca(OH)₂ | Ca-O-H | 3642 | 1623 | 3743, 3245 | | A028*, A120, B028, B120, C028, C120 |
| | O-H structural | 3426 | 3565 | | | |
| Hillebrandite, Ca₂SiO₄(OH)₂ | Si-O in SiO₂ | 964 | 1029, 1052 | | | A028, A120, B028, B120, C028, C120 |
| | Ca-O-H | 3642 | 1656 | 3245 | | |
| | O-H structural | 3424 | 3540 | | | |
| Scolecite CaAl₂Si₃O₉·3H₂O | Al-O in AlO₂ | 713 | 856 | 514, 582, 644 | | A028*, A120, B028, B120, C028, C120 |
| | Si-O in SiO₂ | 458 | 1052, 1083, 1207, 1216 | | | |
| | O-H crystal | 3423 | 1623 | 3743, 3245 | | |
| Xonotlite—Ca₆Si₆O₁₇(OH)₂ | Ca-O-H | 3640 | 1621 | 3733, 3247 | | | C028* |
| | O-H structural | 3424 | 3540 | | | |
| | Si-O in SiO₂ | 458 | 1041, 1052, 1083 | | | |
| **2.3. OH⁻ and HCO₃⁻/CO₃²⁻ phases** | | | | | | |
| Monocarboaluminate Ca₄Al₂(OH)₃(CO₃)₂·5H₂O | Ca-O-H | 3642 | 1691 | 3731, 3247 | | B20, C120* |
| | O-H structural | 3442 | 3561 | | | |
| Hemicarboaluminate Ca₄Al₂(OH)₃(CO₃)₂·5.5H₂O | Ca-O-H | 3642 | 1691 | 3731, 3247 | | B028, C028* |
| | O-H structural | 3442 | 3548 | | | |
| | Al-O in AlO₂ | 856 | 511, 661 | | | |
| | C-O in CO₂ | 1083 | 877 | 1452, 1481 | 700 | | |
| Artinite, Mg₂(CO₃)(OH)₂·3H₂O | C-O in CO₂ | 1083 | 877 | 1413 | 711, 728 | | B028, B120, C028*, C120 |
| | O-H crystal | 1627 | 3733, 3235 | | | |

* indicates new phases.
Table 5. Cont.

| Description/References | Bond       | ν₁ (cm⁻¹) | ν₂ (cm⁻¹) | ν₃ (cm⁻¹) | ν₄ (cm⁻¹) | Raw Material/Sample |
|------------------------|------------|-----------|-----------|-----------|-----------|---------------------|
| **Ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O** [27–29,35–37] | Ca-O-H     | 3642      | 1643      | 3731; 3255 |           | A028, A120, B028, B120*, C028, C120 |
|                        | O-H structural (¹) | 3428      |           | 3561      |           |                     |
|                        | S-O in SO₄²⁻ | 1002      | 1139      | 599       | 667       |                     |
|                        | Al-O-H      | 416       |           |           | 856       |                     |
| **Monosulphoaluminate, Ca₄Al₂(OH)₁₂(SO₄)₆·6H₂O** [27–29,37] | Ca-O-H     | 3640      | 1621      | 3743; 3245 |           | A028*, A120        |
|                        | O-H structural (¹) | 3423      |           | 3556      |           |                     |
|                        | S-O in SO₄²⁻ | 1002      | 458       | 1099; 1147| 605       |                     |
|                        | Al-O in AlO₆⁻ |           |           | 856, 514  | 534, 671  |                     |
| **Calcium hydrogen sulphate, Ca(HSO₄)₂** [28,29,38] | O-H structural (¹) | 3430      |           | 3548      |           | B028, B120, C102*, C120 |
|                        | S-O in SO₄²⁻ | 1004      | 468       | 1105; 1130| 599       |                     |

* The presented ν (cm⁻¹) values are referred to the underlined and star-marked sample. Please note that the specified vibrations types are valid and the other listed samples and their exact ν (cm⁻¹) values are shown in the Figures 5 and 6. O-H structural (¹)—O-H bond in structural OH⁻ anion [32,33]. O-H crystal (²)—O-H bond belonging to crystal bonded water molecules [32,33].

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**Figure 4.** (a) FTIR spectra of raw materials marble powder; (b) FTIR spectra of raw materials white Portland cement. Insertion: magnification of spectral range 1350–400 cm⁻¹ for white Portland cement.

O-H structural (¹)—O-H bond in structural OH⁻ anion [28,29].

O-H crystal (²)—O-H bond belonging to crystal bonded water molecules [28,29].
Figure 4. (a) FTIR spectra of raw materials marble powder; (b) FTIR spectra of raw materials white Portland cement. Insertion: magnification of spectral range 1350–400 cm$^{-1}$ for white Portland cement.

Figure 5. FTIR spectra of A028, B028, and C028. Magnifications: spectral ranges 1300–900 cm$^{-1}$, and 900–350 cm$^{-1}$.

Figure 6. FTIR spectra of A120, B120, and C120. Magnifications: spectral ranges 1300–850 cm$^{-1}$, and 800–350 cm$^{-1}$.

Table 5. Results from FTIR spectroscopy of raw materials (white Portland cement and marble powder) and A028, A120, B028, B120, C028, and C120.

| Description / Sample          | ν1 (cm$^{-1}$) | ν2 (cm$^{-1}$) | ν3 (cm$^{-1}$) | ν4 (cm$^{-1}$) |
|-------------------------------|----------------|----------------|----------------|----------------|
| Raw Material                 | Belite (C2S), Ca$_2$SiO$_4$ | Alite (C3S), Ca$_3$SiO$_5$ | Si-O in SiO$_4$ |                  |
|                              | 520 923 657     |                |                |                |
| White Portland cement *, A028, A120, B028, B120, C028, C120 | Tricalcium aluminate (C3A), Ca$_3$Al$_2$O$_6$ |                 |                |                |
|                              | 754 435 856 545 |                |                |                |
| Calcite, CaCO$_3$ [27–29,31] | C-O in CO$_3$ | 875 1411       | 1473 713       |                |
| White Portland cement *, A028, A120, B028, B120, C028, C120 | Gypsum, CaSO$_4$.2H$_2$O [28,32,33] | S-O in SO$_4$ | 995 457 1103, 1126, 1141 | 597, 669 |
|                              |                | 3403           | 3552           |                |
|                              |                |                | 1617 3729      |                |
| Dolomite, CaMg(CO$_3$)$_2$ [27–29,31] | C-O in CO$_3$ | 879 1442 727   |                |                |
| White Portland cement *, B028, B120, C028, C120 | **Note:** The table includes significant absorption bands for the mentioned materials. The bands and their assignments are based on standard chemical structures and functional groups commonly found in these materials. The ranges and values are illustrative and may vary depending on the specific conditions and measurements.
According to the results of PXRD analysis and FTIR spectroscopy, the following reaction mechanism scheme of samples hydration have been defined:

4.2.1. Sample A

\[
2\text{Ca}_3\text{SiO}_5 (\text{C}_3\text{S}) + 7\text{H}_2\text{O} \rightarrow \text{Ca}_3\text{Si}_2\text{O}_7\cdot 4\text{H}_2\text{O} (\text{C-S-H gel}) + 3\text{Ca(OH)}_2 \text{ (fast)} \quad (1)
\]

\[
2\text{Ca}_2\text{SiO}_4 (\text{C}_2\text{S}) + 5\text{H}_2\text{O} \rightarrow \text{Ca}_3\text{Si}_2\text{O}_7\cdot 4\text{H}_2\text{O} (\text{C-S-H gel}) + \text{Ca(OH)}_2 \text{ (slow)} \quad (2)
\]

\[
\text{Ca}_3\text{Al}_2\text{O}_6 (\text{C}_3\text{A}) + 3\text{CaSO}_4\cdot 2\text{H}_2\text{O} + 26\text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O} \text{ (Ettringite)} \quad (3)
\]

\[
\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O} + 2\text{Ca}_3\text{Al}_2\text{O}_6 (\text{C}_3\text{A}) + 4\text{H}_2\text{O} \rightarrow 3\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{SO}_4\cdot 6\text{H}_2\text{O} \quad (4)
\]

\[
\text{Ca}_3\text{Al}_2\text{O}_6 (\text{C}_3\text{A}) + 3\text{CaSO}_4\cdot 2\text{H}_2\text{O} + 8\text{H}_2\text{O} \rightarrow \text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{SO}_4\cdot 6\text{H}_2\text{O} + \text{Ca(HSO}_4)_2 + \text{Ca(OH)}_2 \quad (5)
\]

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(HCO}_3)_2 \quad (6)
\]

\[
\text{Ca}_3\text{SiO}_5 (\text{C}_3\text{S}) + 2\text{H}_2\text{O} \rightarrow \text{Ca}_2\text{Si}_3\text{O}_7 + \text{Ca(OH)}_2 \quad (7)
\]

\[
\text{Ca}_3\text{Al}_2\text{O}_6 (\text{C}_3\text{A}) + 3\text{SiO}_2 + 5\text{H}_2\text{O} \rightarrow \text{Ca}_4\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O} + 2\text{Ca(OH)}_2 \quad (8)
\]

Equations (1)–(3) are essential for the reaction mechanism of cement clinker hydration with the formation of hydrated phases (C-S-H gel) [17] for sample A. The ettringite formation takes place in the early stages of cement minerals hydration (Equation (3)). With a residue of C₃A, 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(HSO₄)₂ is formed (Equation (5)). It is possible, under hydration conditions, the relict calcite partially transforms to Ca(HCO₃)₂ (Equation (6)). It is also possible crystallization of scolecite and hillebrandite, (Equations (7) and (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) [1,11,18].

4.2.2. Samples B and C

The essential 1, 2, 3, and Equations (6)–(8) describe the hydration mechanism of samples B and C. For the difference from sample A, for samples B and C, the Equation (9) was added and Equations (4) and (5) were replaced by Equations (10) and (11) (due to different aggregate—marble powder). The use of marble powder (dolomite) increases the carbonate ions content in the cement mortars [26,39–41], which is a prerequisite for the formation of carbonate-containing minerals such as hemi-, mono-carboaluminate, and Ca(HCO₃)₂ by the Equations (6), (10) and (11):

\[
2\text{Ca}_3\text{SiO}_5 (\text{C}_3\text{S}) + 4\text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2 \quad (9)
\]

\[
\text{Ca}_3\text{Al}_2\text{O}_6 (\text{C}_3\text{A}) + 0.5\text{CaCO}_3 + 0.5\text{CaO} + 12\text{H}_2\text{O} \rightarrow \text{Ca}_4\text{Al}_2(\text{OH})_{13}(\text{CO}_3)_0.5\cdot 5.5\text{H}_2\text{O} \quad (10)
\]

\[
\text{Ca}_2\text{Al}_2\text{O}_6 (\text{C}_3\text{A}) + \text{CaCO}_3 + 11\text{H}_2\text{O} \rightarrow \text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)_0.5\text{H}_2\text{O} \quad (11)
\]

Additional evidence for the crystal-chemical properties of the investigated samples is presented by the results of thermal analysis with mass spectrometry analysis of evolving gases as a direct proof of the ongoing thermal reactions.
4.3. Thermal Analysis

The obtained results are shown in Table 6 and Figures 7–10, where Figure 7a is for the raw aggregate marble powder, Figure 7b—for raw white Portland cement, both presented for comparison with investigated samples: A028 and A120 (Figure 8), B028 and B120 (Figure 9), C028 and C120 (Figure 10).

Figure 7. (a) TG-DTG-DSC curves of raw aggregate—marble powder. (b) TG-DTG-DSC curves of raw white Portland cement.
Table 6. Thermal decomposition (T\textsubscript{infl.}) and ML of the raw materials and samples.

| Sample               | 1st Range (40–200 °C) | IIrd Range (420–470 °C) | IIIrd Range (520–730 °C) | IVth Range (730–850 °C) | Total Mass Losses (%) |
|----------------------|------------------------|--------------------------|--------------------------|-------------------------|-----------------------|
|                      | T\textsubscript{infl.} (°C) | Mass Losses (%) | T\textsubscript{infl.} (°C) | Mass Losses (%) | T\textsubscript{infl.} (°C) | Mass Losses (%) | T\textsubscript{infl.} (°C) | Mass Losses (%) |                      |
| white Portland cement| 65.1                   | 0.30                     | 429.9                    | 0.25                    | 539.6                  | 0.15                  | 711.8                  | 3.68                  | 5.19                  |
| Marble powder        |                        |                          |                          |                         |                       |                       |                       |                       |                      |
| A028                 | 108.5                  | 1.01                     | -                        | -                       | 596.7                  | 1.46                  | 742.5                  | 3.33                  | 11.44                 |
| A120                 | 100.4                  | 0.68                     | 465.3                    | 0.68                    | 625.1                  | 1.90                  | 764.6                  | 0.59                  | 10.48                 |
| B028                 | 85.2                   | 0.50                     | 469.0                    | 0.91                    | 529.5                  | 4.15                  | 734.7                  | 4.49                  | 42.80                 |
| B120                 | 89.1                   | 1.10                     | 472.0                    | 0.62                    | 560.0                  | 4.23                  | 754.0                  | 3.24                  | 41.85                 |
| C028                 | 94.2                   | 0.98                     | 472.6                    | 0.46                    | 585.5                  | 1.34                  | 798.4                  | 6.21                  | 38.81                 |
| C120                 | 89.1                   | 1.09                     | 469.3                    | 0.69                    | 551.2                  | 4.13                  | 735.6                  | 6.50                  | 40.70                 |

\(T_{\text{infl.}}\)—Temperature of the point of inflection.

Figure 7b shows the thermal behavior of Portland cement, characterized by total ML of just over 5% due to: (i) dehydration of crystal bonded water molecules (up to 220 °C); (ii) \(\text{Ca(OH)}_2\) and C-S-H gel dehydroxylation of structural OH- anions; and (iii) dolomite decabonation (most of the mass losses (ML)).

Thermal decomposition of dolomite is a two-stage process and was carried out at temperatures of 740–860 °C with ML close to the theoretical \(\Delta C^\text{theor} = 47.83\%\). Decomposition results in CaO and MgO in the solid decomposition residue and ML bind to CO\(_2\), and oxygen emissions in the gas phase [20].

Thermal analysis of marble powder shows the decarbonation performing into two well-defined stages (DTA peaks with \(T_{\text{infc}}\) at 806.6 °C and 821.2 °C), and two inserted steps with shoulders at 745.0 °C and 835.9 °C. The total ML are about 45% which defines the dolomite and calcite as main carbonate minerals (Figure 7a, Tables 3 and 6).
In sample B, are registered CO₂ and OH⁻ and SO₂ (Figure 9). Sulphate- and carbonate-bearing minerals are stable at this temperature stage, which suggests that OH⁻, SOₓ, CO₂, and O₂⁻ detection is of their realization from phases in which they are included as defects, situated in different crystallographic positions. These defects can be associated with weaker inter-/intra bonds at interlayer spaces and channel structures [62–64], leading to structural compaction and physical-mechanical properties improvement [19,65,66]. The CO₂ and OH⁻ and SO₂ evolving are most distinct in B028 and B120 but are also observed at C028 and C120 (Figure 10) being less pronounced, because of the presence of HRWR additive reducing the water-to-cement ratio.

The dehydration-decarbonation reactions could also be attached to the IIIrd range. They occur with the carbonate ions realization from the hydrogen-carbonate phases (Ca-HCO₃, mono/hemi-carboaluminates) which are metastable and decarbonize at lower temperatures than CaCO₃. That explains the low-intensity peaks insertion into the major decarbonation peak of samples in the next temperature range of 730–850 °C. The presence of HCO₃⁻/HSO₄⁻ explains the registration of hydroxyl and carbonate/sulphate ions in the evolving gas [67,68]. The HCO₃⁻/CO₃²⁻ and HSO₄⁻/SO₄²⁻ equilibrium depends on the raw materials and environment: humidity, temperature, sulphur, nitrogen, carbon-containing, and other gases, pH, etc. The change in the ratio of the phases containing HCO₃⁻/CO₃²⁻ and HSO₄⁻/SO₄²⁻ ions is carried out at the solid-gas (material-to-atmosphere) interphase boundary. These

Figure 8. (a) TG-DTG-DSC curves of A028. (b) TG-DTG-DSC curves of A120. The temperature intervals in which thermal processes take place are marked with a different color background.
processes lead to changes in the chemical activity and solubility of the materials and determine their durability, which is important for construction practice.

Figure 9. (a) TG-DTG-DSC curves of B028. (b) TG-DTG-DSC curves of B120. The temperature intervals in which thermal processes take place are marked with a different color background.
IVth Decarbonation and Desulfuration (730–850 °C)
The decomposition of carbonate-containing phases (Figures 8–10, Table 6) of samples A, B, and C is performed at higher temperatures, compared to the raw Portland white cement and marble powder. Significant differences between the mass losses are measured (3.68% in the raw cement, 46.16% in the raw marble powder, and 30.06% in sample C120), defined by the different amounts of carbonate minerals. The temperature decomposition intervals are maintained without substantial changes. The marble powder decarbonation occurs with several parallel reactions at close temperatures, which results in the splitting of peaks in the DTG/DSC curves, seen at the samples B and C, as well.

The multi-step decarbonation process indicates the thermal decomposition of various carbonate-containing phases—dolomite, Mg-rich-calcite, and hydrated calcium-aluminate. Their decomposition causes the splitting of the peaks in the DTG/DSC dependences and changes in their intensity. The curve describing the CO2 from the carbonate ions in the evolving gas analysis follows the course of the DTG/DSC peaks which is direct evidence of the overlapping thermal reactions in this interval.

The use of dolomitic marble powder as aggregate slightly increases the temperature of decarbonation with the benefit of the samples B and C (Table 6, Figures 9 and 10). The most accurate explanation of this fact is the formation of dense structures, which affect the results of physic-mechanical analyses [15].

Figure 10. (a) TG-DTG-DSC curves of C028. (b) TG-DTG-DSC curves of C120. The temperature intervals in which thermal processes take place are marked with a different color background.
The thermal decomposition of studies samples is separated into four temperature ranges describing their thermal behaviour. The ML in these ranges are as follow (Table 5):  

- Ist range—1.00–1.53%, IInd range—0.46–0.91%, IIIrd range—2.65–7.23%, and IVth range—2.46–31.04%. The distribution of ML in the ranges is related to:
  - Ist range—Dehydration (40–250 °C) [13,19,42–48];
  - IInd range, Dehydroxylation (420–470 °C) [19,34,49,50];
  - IIIrd range, Dehydroxylation, uncomplete Decarbonation and uncomplete Desulphuration (520–730 °C) [19,34,49,50]
  - IVth range, uncomplete Decarbonation and Desulphuration (730–850 °C) [19,51–61].

Ist range—Dehydration (40–250 °C)

At this range, the processes of dehydration of crystal bonded water molecules from the newly formed hydrate phases (samples A, B, and C) are carried out (Tables 3 and 6). The registered low values of ML correspond to the small amount of crystal bonded water molecules. These results coincide with the low water-to-cement ratio of samples B and C (Table 2).

IInd range—Dehydroxylation (420–470 °C)

The thermal effects measured in this narrow range are weak but well manifested and persistent in all samples. The characteristic of this temperature range is the realization of a distinct thermal reaction, which is of low intensity and with low ML (around and below 1%) (Table 6).

Based on our earlier results [19], and data by the others [51–59], it is evidenced that the ML in this temperature range are associated with the portlandite dehydroxylation. The measured values of ML are lower in comparison to literature data, showing the lower quantity of portlandite crystals leading to the increased quantity of C-S-H phases. As a result, the samples obtain higher strength properties forming hydrated phases [19].

The ML decrease at samples A and B as follow: from 0.68% (A028) to 0.56% (A120), a decrease of 0.12%, and from 0.91% (B028) to 0.62% (B120)—decrease of 0.29%. The sample C shows the reverse trend—from 0.46% (C028) to 0.69% (C120)—increase of 0.23% (Table 6). These results show the enlarged expansion of C-S-H gel (with structurally bonded water molecules) at B120 due to the sample hydration, which coincides with the measured lowest values of pore volume and highest values of compressive strength [15]. The increase of ML at samples C with prolonged water curing does not correspond to the measured changes in pore volume and compressive strength [15]. Such behavior is due to the presence of HRWR additive, reducing the water-to-cement ratio (Table 2) without any changes in the values of compressive strength regardless of the presence of marble powder in the sample.

IIIrd range—Dehydroxylation, uncomplete Decarbonation, and uncomplete Desulphuration (520–730 °C)

In this temperature range, the dehydroxylation of crystal bonded water molecules in hydrated phases (ettringite, monocarboaluminate, hillebrandite, etc.) occurs [48,50–58].

The measured mass losses of samples A and B show maintenance of the values as follow: a total of 4.36% for A028 and 4.28% for A120 (Table 6, Figure 8), as well as of 5.83% (B028) and 7.23% (B120) (Figure 9, Table 6). There are significant changes in the mass loss values for sample C—an increase from 2.65% (C028) to 6.34% (C120) (Figure 10, Table 6), which evidence changes in the phase composition and the distribution of crystal bonded water molecules. An increase of mass losses in this temperature range was found for the B series samples. That could be explained by the incorporation of larger amounts of hydroxyl, carbonate, and/or sulphate ions in the structure of B028 and B120.

The mass losses via dehydration of portlandite and C-S-H phases in sample A at the IInd and IIIrd ranges are the smallest, and the ratio between them is close to 1:1 (mass losses A028:mass losses A120) (Table 6). 28 days of hydration of samples B and C decrease the mass losses in IIIrd range from 5.83% (B028) to 2.65% (C028) (Table 6). That may be explained by the lower pore volume of B028 [15], which is necessary for the new C-S-H phases growth. The low content of the C-S-H phase in sample C is due to the very low water-to-cement and water-to-fines ratio (Table 2).
The present studies evidence the decomposition processes in this temperature range are more complex. Mass-spectrometric analysis of the evolving gases revealed that except dehydroxylation of C-S-H phases, the decarbonation and desulphuration occur (Figures 8–10).

The thermal decomposition of A028, and A120, assumed that carbonate ions evolved as \( \text{CO}_2 \) and \( \text{O}^{2-} \), sulphate ions as \( \text{SO}_3^- \) and \( \text{O}^{2-} \) (better expressed at A120), and the water vapor, identified as \( \text{OH}^- \) (Figure 8). The \( \text{OH}^- \)-ions registration evidences the simultaneous formation of the ettringite, scolcete, xonotlite, and portlandite during the hydration process. The evolving of \( \text{CO}_2 \) and \( \text{SO}_4^- \) ions prove diversity in their redistribution in the solid phase.

At the first three temperature ranges, an evaluation of the effect of the composition on the sample’s microstructure and their subsequent use in construction practice has been sought. This evaluation includes: determining changes in the amount of crystallization and structurally bound water, uncomplete decarbonation of carbonate and hydrocarbonate ions, and uncomplete desulphuration of sulphate ions in lower temperature regions, such as 520–750 °C. Registering of a decarbonation and desulphuration process at a lower temperature range, than that one known for traditional carbonate (730–850 °C) and sulphate minerals (1200–1500 °C) is considered. That probable evidence: (i) isomorphic substitution and structural changes, including carbonate and sulphate ions in the structure of minerals through weaker chemical bonds or (ii) or for intermediate thermal reactions with decomposition of hydrogen carbonate and/or hydrogen sulphate phases. The results of PXRD and FTIR do not confirm the formation of isomorphic phases, only prove the formation of hydrogen-containing phases. The hydrogen-containing phases decompose at lower temperatures, realizing sulphur oxides at lower than traditionally known temperatures.

In sample B, are registered \( \text{CO}_2 \) and \( \text{OH}^- \), and \( \text{SO}_2 \) (Figure 9). Sulphate- and carbonate-bearing minerals are stable at this temperature stage, which suggests that \( \text{OH}^- \), \( \text{SO}_3^- \), \( \text{CO}_2 \), and \( \text{O}^{2-} \) detection is of their realization from phases in which they are included as defects, situated in different crystallographic positions. These defects can be associated with weaker inter-/intra bonds at interlayer spaces and channel structures [62–64], leading to structural compaction and physical-mechanical properties improvement [19,65,66]. The \( \text{CO}_2 \) and \( \text{OH}^- \), and \( \text{SO}_2 \) evolving are most distinct in B028 and B120 but are also observed at C028 and C120 (Figure 10) being less pronounced, because of the presence of HRWR additive reducing the water-to-cement ratio.

The dehydration-decarbonation reactions could also be attached to the IIIrd range. They occur with the carbonate ions realization from the hydrogen-carbonate phases (CaHCO\(_3\), mono/hemi-carboaluminates) which are meta-stable and decarbonize at lower temperatures than CaCO\(_3\). That explains the low-intensity peaks insertion into the major decarbonation peak of samples in the next temperature range of 730–850 °C. The presence of \( \text{HCO}_3^- / \text{HSO}_4^- \) explains the registration of hydroxyl and carbonate/sulphate ions in the evolving gas [67,68]. The \( \text{HCO}_3^- / \text{CO}_3^{2-} \) equilibrium depends on the raw materials and environment: humidity, temperature, sulphur, nitrogen, carbon-containing, and other gases, pH, etc. The change in the ratio of the phases containing \( \text{HCO}_3^- / \text{CO}_3^{2-} \) and \( \text{HSO}_4^- / \text{SO}_4^{2-} \) ions is carried out at the solid-gas (material-to-atmosphere) interphase boundary. These processes lead to changes in the chemical activity and solubility of the materials and determine their durability, which is important for construction practice.

**IVth Decarbonation and Desulphuration (730–850 °C)**

The decomposition of carbonate-containing phases (Figures 8–10, Table 6) of samples A, B, and C is performed at higher temperatures, compared to the raw Portland white cement and marble powder. Significant differences between the mass losses are measured (3.68% in the raw cement, 46.16% in the raw marble powder, and 30.06% in sample C120), defined by the different amounts of carbonate minerals. The temperature decomposition intervals are maintained without substantial changes. The marble powder decarbonation occurs with several parallel reactions at close temperatures, which results in the splitting of peaks in the DTG/DSC curves, seen at the samples B and C, as well.
The multi-step decarbonation process indicates the thermal decomposition of various carbonate-containing phases—dolomite, Mg-rich-calcite, and hydrated calcium-aluminates. Their decomposition causes the splitting of the peaks in the DTG/DSC dependencies and changes in their intensity. The curve describing the CO\textsubscript{2} from the carbonate ions in the evolving gas analysis follows the course of the DTG/DSC peaks which is direct evidence of the overlapping thermal reactions in this interval.

The use of dolomitic marble powder as aggregate slightly increases the temperature of decarbonation with the benefit of the samples B and C (Table 6, Figures 9 and 10). The most accurate explanation of this fact is the formation of dense structures, which affect the results of physic-mechanical analyses [15].

As a result of the thermal reactions in the IVth range, it is possible to obtain CaCO\textsubscript{3} and CaSO\textsubscript{4}, as well as anhydrous Ca-, Ca-Mg-, and Ca-Al silicates. These are solid-phase thermal reactions that take place without ML. The PXRD analysis of the solid residual proves the formation of such phases (Table 4). In this temperature range, it is possible to form a new phase—spurrite, due to anhydrous calcium silicates, oxides, and CO\textsubscript{2} (vapor), existing in the system [69,70]. The spurrite synthesis was carried out during the decarbonation of dolomite, calcite, and Mg-rich calcite, when CO\textsubscript{2} and O\textsubscript{2} emitted as the gas phase, and Ca and Mg-oxides—fixed as solid phase [71–74]. Another possibility is the spurrite synthesis by a solid-phase reaction of oxides (CaO, SiO\textsubscript{2}), and/or silicates (CaSiO\textsubscript{3}, Ca\textsubscript{2}SiO\textsubscript{4}), and calcite. There exist data for the spurrite formation by solid-phase synthesis from SiO\textsubscript{2} and calcite/CO\textsubscript{2} or Ca\textsubscript{2}SiO\textsubscript{4}Ca\textsubscript{3}SiO\textsubscript{5}, and calcite/CO\textsubscript{2} at 880–910 °C [73,74].

During the decarbonation of samples in the evolving gases both Sulphur oxide (as SO\textsubscript{2}) and Carbon oxide (as CO\textsubscript{2}) are registered (Figures 9 and 10). That suggests a solid-phase synthesis of sulphate-containing phases such as ternesite and/or anhydrite [75]. The confirmation of such assumptions was estimated by the solid residual PXRD analysis where ternesite was identified (Table 4). Ternesite is possible to form under high-temperature conditions in the presence of SiO\textsubscript{2}, CaO (solid phase), and sulphate ions (vapor). The sulphate vapor exerts partial pressure and partially binds to the oxides of the solid phase [24]. Like spurrite, ternesite can also formate by a solid-phase reaction of oxides (CaO, SiO\textsubscript{2}) and/or silicates (CaSiO\textsubscript{3}, Ca\textsubscript{2}SiO\textsubscript{4}), and anhydrite. The ternesite and/or anhydrite have existed in the solid residual (Table 4). That is why the final temperature of the experiment is 1100 °C, i.e., the temperature of their thermal decomposition was not reached [76].

4.4. Reaction Mechanism of Thermal Decomposition of Decorative Cement Composites

Based on the experimental results, their analyzes, and comparison with literature data, a generalized scheme of the chemistry of thermal reactions in the studied samples can be presented in terms of their thermal decomposition up to 1100 °C as follows:

1st Range—Dehydratation (40–250 °C)

\[ \text{Ca}_6\text{Al}_2(\text{SO}_4)_{3}(\text{OH})_{12} \cdot 26\text{H}_2\text{O} \rightarrow \text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{SO}_4 \cdot 8\text{H}_2\text{O} + 2\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 17\text{H}_2\text{O} \quad (12) \]

\[ 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 3\text{H}_2\text{O} \quad (13) \]

\[ \text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3) \cdot 5\text{H}_2\text{O} \rightarrow \text{Ca}_2\text{Al}_2(\text{CO}_3) \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2 + 5\text{H}_2\text{O} \quad (14) \]

\[ 2\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4 + \text{H}_2\text{O} \quad (15) \]

\[ \text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O} \rightarrow \text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O} \quad (16) \]

2nd range—Dehydroxylation (420–470 °C)

\[ \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \quad (17) \]

\[ \text{Ca}_2\text{SiO}_3(\text{OH})_2 \rightarrow \text{CaSiO}_3 + \text{CaO} + \text{H}_2\text{O} \quad (18) \]

\[ \text{Ca}_6\text{Si}_8\text{O}_{17}(\text{OH})_2 \rightarrow 6\text{CaO} + 6\text{SiO}_2 + \text{H}_2\text{O} \quad (19) \]
IIIrd range—Incomplete Dehydroxylation, Decarbonation and Desulphuration (520–730 °C)

\[
\begin{align*}
\text{CaAl}_2\text{Si}_3\text{O}_{10.0.5\text{H}_2\text{O}} & \rightarrow \text{CaAl}_2\text{Si}_3\text{O}_{10} + 0.5\text{H}_2\text{O} \quad (20) \\
\text{CaAl}_2\text{O}_3(\text{CO}_3)_3\text{H}_2\text{O} & \rightarrow \text{CaCO}_3 + \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (21) \\
\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_2.8\text{H}_2\text{O} & \rightarrow \text{CaSO}_4 + 3\text{CaO} + \text{Al}_2\text{O}_3 + 14\text{H}_2\text{O} \quad (22) \\
\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)_3.5\text{H}_2\text{O} & \rightarrow \text{CaCO}_3 + 3\text{CaO} + \text{Al}_2\text{O}_3 + 11\text{H}_2\text{O} \quad (23) \\
\text{CaAl}_2\text{Si}_3\text{O}_{10.0.5\text{H}_2\text{O}} & \rightarrow \text{CaSiO}_3 + 2\text{SiO}_2 + \text{Al}_2\text{O}_3 + 0.5\text{H}_2\text{O} \quad (24) \\
\text{Ca(HCO}_3\text{)}_2 & \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (25) \\
\text{Ca(HSO}_4\text{)}_2 & \rightarrow \text{CaSO}_4 + \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad (26) \\
\end{align*}
\]

IVth range—Incomplete Decarbonation and Desulphuration (730–850 °C)

\[
\begin{align*}
\text{CaMg(\text{CO}_3)}_2 & \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2 \quad (27) \\
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \quad (28) \\
2\text{CaSiO}_3 + 3\text{CaO} + \text{CO}_2 & \rightarrow \text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3) \quad (29) \\
2\text{CaSiO}_3 + 3\text{CaO} + \text{SO}_3 & \rightarrow \text{Ca}_5(\text{SiO}_4)_2(\text{SO}_4) \quad (30) \\
\text{CaCO}_3 + 2\text{SiO}_2 + 4\text{CaO} & \rightarrow \text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3) \quad (31) \\
\text{CaCO}_3 + 2\text{SiO}_2 + 4\text{CaO} & \rightarrow \text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3) \quad (32) \\
\end{align*}
\]

or/and

\[
\begin{align*}
\text{CaCO}_3 + 2\text{SiO}_2 + 4\text{CaO} & \rightarrow \text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3) \quad (31) \\
\text{CaCO}_3 + 2\text{SiO}_2 + 4\text{CaO} & \rightarrow \text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3) \quad (32) \\
\end{align*}
\]

Solid-phase synthesis:

\[
\begin{align*}
\text{CaSiO}_3 + \text{CaO} & \rightarrow \text{Ca}_2\text{SiO}_4 \quad (33) \\
2\text{CaSiO}_3 + \text{MgO} & \rightarrow \text{Ca}_2\text{MgSiO}_7 \quad (34) \\
2\text{CaO} + \text{Al}_2\text{O}_3 & \rightarrow \text{Ca}_2\text{Al}_2\text{O}_5 \quad (35) \\
\text{CaSiO}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 & \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 \quad (36) \\
\end{align*}
\]

5. Conclusions

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 $\text{CO}_3^{2-}$, $\text{SO}_4^{2-}$, $\text{SiO}_4^{4-}$, $\text{AlO}_4^{5-}$, and $\text{OH}^-$ (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 cabroaluminates during hydration under the influence of marble powder has been established. Based on this investigation, the scheme of sample hydration has been defined.

The thermal analysis with analysis of evolving gases defined four temperature ranges of sample decomposition: 1st range—dehydration (40–250 °C), 2nd range—dehydroxylation (420–470 °C), IIIrd range—dehydroxylation, decarbonation, and desulphuration (520–730 °C), and IVth range—decarbonation and desulphuration (730–850 °C). The lower temperature of decarbonation and desulphuration at the IIIrd range establishes the defects in solids, defined by $\text{CO}_3^{2-}$, and $\text{OH}^-$, and $\text{SO}_4^{2-}$ incorporation. They are well presented in sample B and low pronounced in sample C with added HRWR water reducer. Such defects lead to structural compaction and physical-mechanical properties improvement. The formation of new solids (spurite and ternesite) under the influence of the partial pressure of evolving gases $\text{CO}_2$ and $\text{SO}_2$ at high temperatures in the process of thermal decomposition has been proven. The presence of calcium and silicon oxides in the solid phase has also been proven.
The obtained new results allowed: (i) the creation of complex chemical reactions, which describe the processes of hydration and thermal decomposition of the studied cement composites, and (ii) establishment differences in the reaction mechanisms depending on the use of cement replacement material (sand and marble powder). Finally, based on obtained results, the generalized scheme of sample thermal decomposition has been defined.

The results obtained can be used to study the structure and properties of building materials and artifacts: ancient mortars related to the discovery of ancient composite production technologies and environmental knowledge in various archeological epochs.

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**Abbreviations**

| Abbreviation | Description |
|--------------|-------------|
| A            | white Portland cement + sand + water |
| B            | white Portland cement + marble powder + water |
| C            | white Portland cement + marble powder + HRWR + water |
| A028         | Sample A after water curing of 28 days |
| A120         | Sample A after water curing of 120 days |
| B028         | Sample B after water curing of 28 days |
| B120         | Sample B after water curing of 120 days |
| C028         | Sample C after water curing of 28 days |
| C120         | Sample C after water curing of 120 days |
| C-S-H        | calcium silicate hydrate |
| HRWR         | polycarboxylate-based admixture |
| PXRD         | Powder X-ray diffraction |
| FTIR         | Fourier Transformed Infrared |
| TG/DTG-DSC   | Thermal analysis |
| ML, ΔGtotal  | Mass Losses, ΔG |
| T_infl       | Temperature of the point of inflection |
| RT           | Room temperature |
| EnT          | Endothermal effect |
| ExT          | Exothermal effect |
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