

SPECTROSCOPIC INVESTIGATIONS OF PHASE FORMATION IN CEMENT MORTARS WITH A HIGH CONTENT OF MINERAL FILLERS

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Keywords: cement mortars, mineral addition, IR spectroscopy, XRD, ecology

Abstract: One of the main approaches to reducing the environmental impacts of the construction industry is the use of mineral additives reducing quantity of cement used in mortars and concretes for construction. Solid industrial wastes, including the construction and demolition wastes, traditionally are used in conventional cement-based composites. Their application is limited by the application of compositions, requirements of desirable properties of fresh and hardened mortar/concrete, as well as the required durability and corrosion resistance to known exposure. White decorative mortars and concretes have restrictions on: white color of the binder and mineral additive, good workability, and a dense structure that does not have significant destructive processes at various atmospheric impacts.

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 phase composition (new formed phases as well as formation of C-S-H gels) are defined using X-Ray powder diffraction and Infra-Red Spectroscopy measurements. The experimental data show that the cement composites with higher water content exhibit variety of new-formed phases, like hydration products of C-S-H type. The use of marble as addition leads to creation of carbo-sulpho- aluminates.

Introduction

One of the main approaches to reducing the environmental impacts of the construction industry is the use of mineral additives reducing quantity of cement used in mortars and concretes for construction. Solid industrial wastes, including the construction and demolition wastes, traditionally are used in conventional cement-based composites. Their application is limited by the application of compositions, requirements of desirable properties of fresh and hardened mortar/concrete, as well as the required durability and corrosion resistance to known exposure. White decorative mortars and concretes have restrictions on: white colour of the binder and mineral additive, good workability, and a dense structure that does not have significant destructive processes at various atmospheric impacts.

The decorative cement mortars and concretes are an artificial imitation of the natural stones. Their main advantage is better workability, but the durability and stability are their key disadvantages [1-3]. The proper application of these cement-based stones in constructional works depends on physical, chemical and mechanical properties which are the result of the microstructure of new-formed hydrate phases. Here, it is of particular importance the correct choice of cement-substitutes additions (hydraulic, pozzolanic and almost inert filler, incl. technogenic wastes) and additives, which aim both reducing the cost of composite and improvement properties and durability in different environments [5-8].

The goal of this work is to study the influence of cement-water ratio and quantities of marble powder additive and polycarboxylate-based admixture on the hydration process. A major emphasis of the study is on the formation of hydrosulphate- and hydro-sulphonated calcium-silicate phases in white cement compositions and their effect on measured properties. The effect of the studied parameters is

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

Samples preparation

The chemical composition of used white Portland cement CEM I 52.5 N, produced by Devnya Cement (Bulgaria), was (in wt%): SiO₂ – 24.3; Al₂O₃ – 2.1; Fe₂O₃ – 0.2; CaO – 68.3; MgO – 0.3; Na₂O – 0.13; K₂O – 0.02; Free lime – 1.9. Thus the mineral composition, calculated by Bogue method was (in wt%): C₃S – 72.13; C₂S – 15.28; C₃A – 5.23; C₄AF – 0.61.

The mortars were prepared using two types of aggregate. For reference sample clean washed and dried river sand was used. The properties of sand were: fineness modulus $FM = 2.7$ (EN 12620:2002+A1:2008) and shape index – 4.6 % (EN 933-4:2008) i.e. spheroid particles, over 85.0 % content of SiO₂. The studied samples were prepared with marble powder, produced by AIAS S.A. White Marble Products (Greece) with chemical composition (in wt. %): CO₂ + H₂O – 45.7; SiO₂ – 0.12; Al₂O₃ – 0.38; Fe₂O₃ – 0.14; CaO – 32.9; MgO – 20.0; Na₂O – 0.05; K₂O – 0.19; MnO – 0.01. The decarbonization at 1000°C of this aggregate was divided to two stages (DTA peaks – 806.6°C and 821.2°C) with total mass loses of about 45% and, thus the mineral composition is Dolomite/Mg-rich Calcite. The polydispersity of aggregate was: maximal size of grains – 2 mm; grains with sizes < 0.125 mm – 50.0 wt %; grains with sizes < 0.063 mm – 35.0 wt %.

The polycarboxylate-based high range water reducer (HRWR) Sika ViscoCrete 5-800 was used and its dosage was 2.0% by weight of white cement. This HRWR was chloride-free, soluble in water, without any retarding effects and with density of 1.07 g/cm³ (at 20 °C).

The experiments were carried out with three types of cement composites, which codes, type of used aggregate and compositions are shown in Table 1. All samples were mixed with distilled water.

Table 1. Compositions of the samples

Sample	Aggregate	Ratios		
		Cement-to-aggregate	Water-to-cement	Water-to-fines*
A 28 & 120	Sand	1:3	0.50	0.500
B 28 & 120	Marble powder	1:2	0.60	0.353
C 28 & 120	Marble powder	1:2	0.40 + HRWR	0.235

*all particles with sizes below 125 μm

Experimental Methods

The bulk density after immersion and adsorption after immersion were measured according ASTM C642-13 [9-10]. 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 [11].

Brocken parts sample with mass of 2.0±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, CuKα radiation ($\lambda = 0.15418$ nm) (operating at 30 kV, 10 mA) from 5 to 80 °2θ with a step of 0.05° (grinded sample with weight – 1.0±0.1 mg and particle sizes below 0.075 mm).

Infrared spectroscopy was performed Infrared spectroscopy (FT-IR Spectrometer, Varian 660-IR, Austria, 2009) covering the range of 400-4000 cm⁻¹, KBr tableting.

Results and Analysis

Physico-mechanical Properties

The results show that the 28-day compressive strength of conventional cement mortar A is comparable to that given by the factory (Table 2). This indicates that the sand used is similar to CEN Standard sand, EN 196-1. 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 %).

The values for measured parameters indicate formation of thin structure of hardened samples B, which are characterized by high water-to-cement ratio. The presence of fine particles decreases the water-to-fines ratio, but does not increase the density of the structure. The prolonged water curing increases the compressive strength by 14.3%, whichever is greater than the decrease of total pore volume by 9.3 %. The same pattern is observed for samples C, where the increase of compressive strength (17.9 %) is greater than the decrease of the total volume of pore (9.8 %) with sizes in the studied range (Table 2).

The use of HRWR reduces water content by 33.3 % resulting in increased the bulk density and adsorption. The formed structure of samples C is very dense, which is detected when comparing the

pure volume of samples, recalculated from the measured value of pore volume and bulk density after immersion at 28 days of curing - 21.1 mm³/cm³ (Sample A); 17.6 mm³/cm³ (Sample C); 30.0 mm³/cm³ (Sample B). However, these samples have an open porosity, which allow penetration of the water through pores and capillaries, causing slow continuous hydration of cement grains. The high adsorption of samples with marble powder as aggregate can be explained by the high water absorption capacity of finest marble particles.

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 ⁻³	mm ³ .cm ⁻³	N.mm ⁻²	N.mm ⁻²	mm ³ .g ⁻¹	mm ³ .g ⁻¹
A	2126	173.8	56.3	60.6	44.98	41.91
B	2158	258.5	53.8	61.5	64.66	58.69
C	2348	192.5	90.1	106.2	41.30	37.26

X-Ray phase analysis

The X-ray powder diffraction was used to be proofed previously obtained results as well as to better evaluation of investigated samples. The obtained results from XRD analyses of phase composition, that contain new-formed products of hydration of basic cement minerals and the marble powder, are shown in Table 3.

The XRD analysis (Table 3) show the presence of two groups of minerals in studied samples: (i) relict minerals from the initial composition: Belite, Albite, Anorthite, Mg-rich Calcite, Quartz, Dolomite and (ii) new formed minerals: Portlandite, Mono- and Hemicarboaluminate, Thaumasite, Yugawaralite, Scolecite, Ettringite, Wollastonite and Tricalcium Silicate. The results of the complete analysis of the phase composition of the samples are presented in Table 3.

Table 3. Results from XRD analysis

No	Description	Sample	Identified phases
1.	Non-hydrated phases of cement	A (028, 120)	Belite (C ₂ S), 49-1673– 2CaO.SiO ₂
		B (028, 120)	Albite (C ₃ S), 11-0593– (Na,Ca)Al(Si,Al) ₃ O ₈
		C (028, 120)	Anorthite (CAS ₂), 41-1486– CaO.Al ₂ O ₃ .2SiO ₂
2.	Phases of the source components	B (028, 120)	Dolomite, 36-0426 – CaCO ₃ .MgCO ₃
		C (028, 120)	Mg-rich Calcite, 47-1743 – CaCO ₃
3.	New phases forming C-S-H gel: - containing OH ⁻	A (028, 120) B (028, 120) C (028, 120)	Portlandite (CH), 44-1481 – Ca(OH) ₂
3.1.	- containing CO ₃ ²⁻ , OH ⁻ and crystal water H ₂ O	B120 C120	Monocarboaluminate, 41-0219 - 3CaO.Al ₂ O ₃ .CaCO ₃ Ca(OH) ₂ .5H ₂ O,
		A120, B028	Hemicarboaluminate, 41-0221 – 3CaO.Al ₂ O ₃ .0.5CaCO ₃ .0.5Ca(OH) ₂ .5.5H ₂ O
3.2.	- containing SO ₄ ²⁻ , OH ⁻ and crystal water H ₂ O	A028, A120 C120	Ettringite, 41-1451 – 6Ca(OH) ₂ .Al ₂ (SO ₄) ₃ .26H ₂ O
		B028	Gypsum, 21-0167 - CaSO ₄ .xH ₂ O
3.3	- containing SO ₄ ²⁻ , CO ₃ ²⁻ , OH ⁻ and crystal water H ₂ O	B (028, 120)	Thaumasite, 46-1360 – Ca ₃ Si(OH) ₆ (CO ₃)(SO ₄).12H ₂ O
3.4.	- hydrosilicates forming of main oxides CaO, Al ₂ O ₃ , SiO ₂ , OH ⁻ and/or crystal water H ₂ O	B (028, 120) C120	Hydrogarnet, 84-1354, 76-0557 - CaSiO ₃ .Ca(OH) ₂
		B120	Yugawaralite, 39-1372 - CaO.Al ₂ O ₃ .6SiO ₂ .4H ₂ O
		B120 C120	Wairakite, 42-1451 - CaO.Al ₂ O ₃ .4SiO ₂ .2H ₂ O
		B120 C120	Scolecite, 41-1355 - CaO.Al ₂ O ₃ .3SiO ₂ .3H ₂ O
4.	Water free hydrated phases	A120 B (028, 120) C120	Wollastonite, 42-0550 - CaSiO ₃
		A (028, 120) -	Tricalcium Silicate, 74-0874 - 3CaO.3SiO ₂

FTIR Spectroscopy

The obtained results are presented on Fig. 3, 4 and Table 4.

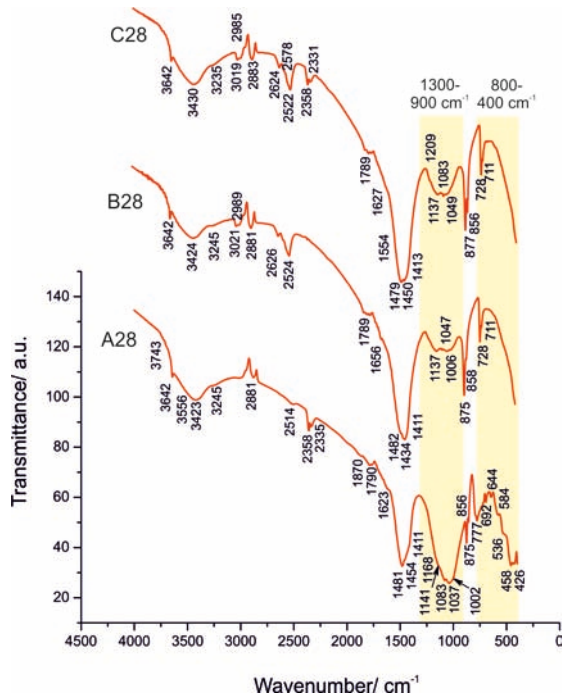


Fig. 3a. FTIR spectra of mortars of 28 days of water curing

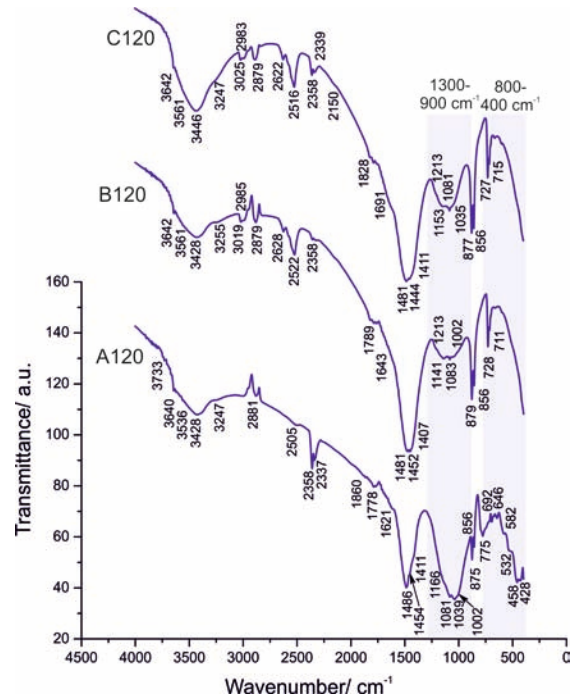


Fig. 3b. FTIR spectra of mortars of 120 days of water curing

The spectra, obtained by FTIR spectroscopy demonstrate a wide variety of streaks and are evidence of the formation of multiple hydrate phases in the samples (Fig. 3). This occurs in two areas – 1300-900 cm^{-1} and 800-400 cm^{-1} in which the overlap of the lines is strongly expressed. At these intervals the vibrational fluctuations of the functional groups which are essential for the identification of the cement hydration products are displayed. This is the reason why these intervals are presented in detail in Fig. 4, Fig. 5, and Table 4.

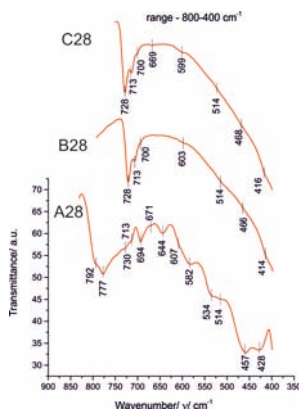


Fig. 4a. FTIR spectra of mortars of 28 days of water curing in the range 800-400 cm^{-1}

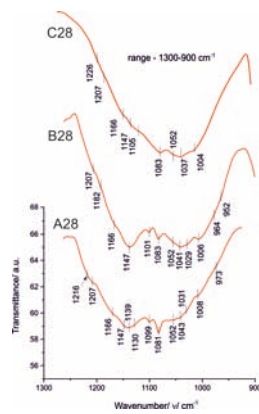


Fig. 4b. FTIR spectra of mortars of 120 days of water curing in the range 800-400 cm^{-1}

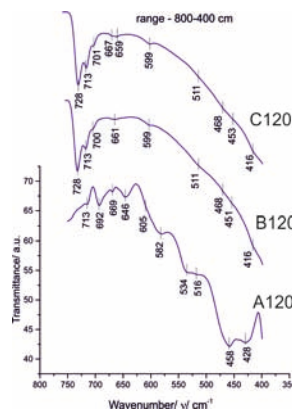


Fig. 4a. FTIR spectra of mortars of 28 days of water curing in the range 1300-900 cm^{-1}

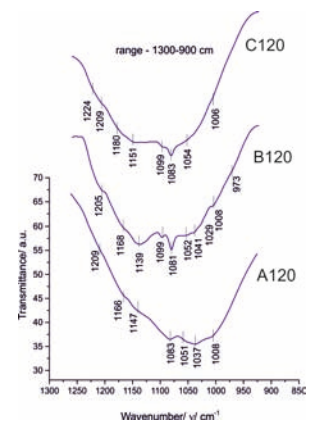


Fig. 4b. FTIR spectra of mortars of 120 days of water curing in the range 1300-900 cm^{-1}

Table 4.

FT-IR bands of cement mortars

No	Samples 28 days of water curing - Band positions, cm^{-1}			Samples 120 days of water curing - Band positions, cm^{-1}			Description
	A28	B28	C28	A120	B120	C120	
1	3743	3731		3743	3731	3731	(ν_3) stretching vib. mode of O-H in OH^- in H_2O capil., hydrate water
2	3642	3642	3642	3640	3642	3642	(ν_1) stretching vib. mode of OH^- directly bonded to Ca in $\text{Ca}(\text{OH})_2$
3	3552			3536	3561	3561	(ν_3) stretching vib. mode of O-H in bonded OH^-
4	3423 3245	3430 3235	3424 3245	3428 3247	3446 3247	3428 3255	(ν_1) stretching vib. mode of O-H in OH^- in capil. hydrate and crystal water [12]
5	2881	3019 2985 2883	3021 2989 2881		3025 2983 2879	2985 2879	(ν_1) stretching vib. mode of O-H in OH^- in H_2O capil. hydrate phase
6		2624 2578	2626		2622	2628	(ν_1) stretching vib. mode of C-O in CO_3^{2-} in Hemi/Monocarboaluminate, Thaumasite [13, 14]
9	2514 1623	2522 1627	2524 1656	2505 1621	2516 1691	2522 1643	(ν_2) bending vib. mode of O-H in OH^- in capil. hydrate and crystal water
11	1481 1454	1479 1450	1482 1434	1486 1454	1481 1444	1481 1452	(ν_3) stretching vib. mode of C-O in CO_3^{2-} in Calcite
12	1411	1413	1411	1411	1411	1407	(ν_3) stretching vib. mode of C-O in CO_3^{2-} and C-OH in HCO_3^- in Monocarboaluminate [15] and Asymmetric (ν_3) stretching vib. mode of S-O in SO_4^{2-} in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
14	1168	1137	1137	1166 1137	1185	1141	(ν_3) stretching vib. mode of S-O in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Monosulphoaluminate, Thaumasite
15	1083	1083		1081	1081	1083	(ν_3) stretching vib. mode of Si-O in SiO_6 in Thaumasite and Asymmetric (ν_3) stretching vib. mode of Si-OH in $[\text{Si}(\text{OH})_6]^{2-}$ in Thaumasite [16]
16	1037	1049	1047	1039	1035	1039	(ν_3) stretching vib. mode of Si-O in SiO_4 in Ettringite
17	1002	1005	1006	1002	994 967	1002 966	(ν_3) stretching vib. mode of S-C-O in Ettringite, Thaumasite and to C-O-H in HCO_3^- in hydrocarbonate phases
18	875	877	875	875	877	879	(ν_2) bending vib. mode O-C-O in CO_3^{2-} in CaCO_3
19	856	856	858	856	856	856	(ν_2) bending vib. mode of Al-OH in Aluminates
21	713 730	713 728	713 728	713	713 728	713 728	(ν_4) bending vib. mode of O-C-O in CO_3^{2-} in CaCO_3 and in Hemi/Monocarboaluminate, Thaumasite and (ν_4) bending vib. mode of O-Si-O in SiO_6^{8-} in Thaumasite
22	694	700	700	692	700	700	Si-O in SiO_6 in Thaumasite
23	671	669	-	669	665	667	(ν_4) bending vib. mode of O-Si-O in SiO_4^{2-} in C-S-H (colloidal gel; Ca/Si ratio \leq 1.5) and (ν_4) bending vib. mode of O-Si-O in SiO_6^{8-} in Thaumasite
24	644	-		646	-	-	(ν_4) bending vib. mode of Si-O in SiO_4^{2-} in C-S-H gel
25	607	599	603	605	599	599	(ν_4) bending vib. mode of S-O in SO_4^{2-} in Gypsum
26	584	-	-	582	-	-	Al-O in C_3A ($\text{Ca}_3\text{Al}_2\text{O}_6$)
27	514 534	514	514	516 534	511	511	(ν_4) S-O bending in Gypsum, Monosulphoaluminate and Thaumasite
28	458	468	466	458	453 468	451 468	(ν_2) bending vib. mode of S-O in SO_4^{2-} in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

The analysis of the results obtained from the infrared spectroscopy studies proves the vibration bands of the minerals formed by the hydration of the cement minerals. In the analysis, several groups of new-formed phases can be identified: (i) phases, containing chemically combined water (OH⁻); (ii) phases, containing carbonate ions (CO₃²⁻), structurally combined water (OH⁻) and chemically combined water-(H₂O); (iii) phases, containing sulphate (SO₄²⁻) ions, structurally combined water (OH⁻) and chemically combined water-(H₂O); (iv) phases, containing carbonate ions (CO₃²⁻) and sulphate ions (SO₄²⁻), structurally combined water (OH⁻) and chemically combined water (H₂O). The components, used for the production of cement-based composites, produce closely related new-formed hydrate phases, some of which are the same for all samples - Portlandite, Wollastonite, Mono/Hemicarboaluminate. In cement mortars (series B and C) in which marble powder and HRWR polycarboxylate additive were added, the new-formed calcium-aluminum silicates and aluminates are in a larger variety - Yugawaralite, Scolecite, Ettringite and Thaumassite.

Conclusion

The structures of the two types of white cement high workability mortars with relatively high content of marble powder containing fine particles are investigated. The comparison with cement-sand mortars shows that high content of fines make the structure denser, even prone to self-desiccation. The formed structure has open porosity, which allows water transport with slow continuous hydration resulting in growth of crystals and formation of variety products.

On the basis of the used methods the phase composition of the studied samples were determined. The effect of substitution of cement with marble powder was determined under limiting of the water-cement ratio. The formation of cement minerals such as thumasite, ettringite, mono and semi-carboaluminate, etc., has been proven. The composition of cement and marble powder has potential for further improvement the process of hydration.

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