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APPLICATION OF CEMENT REPLACEMENT MATERIALS IN PHASE FORMATION IN MORTAR AS AN ECOLOGICAL APPROACH FOR REDUCING GREENHOUSE GASES

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Abstract: *One of the main approaches to reducing the environmental impacts of the construction industry is the use of mineral additives to reduce the quantity of cement used in mortars and concrete for construction. Solid industrial wastes, including construction and demolition wastes, are traditionally used in conventional cement-based composites. Their application is limited by the application of compositions, the requirements of desirable properties of fresh and hardened mortar/concrete, as well as the required durability and corrosion resistance to known exposure.*

The objects of this research are different cement composites with a high content of inert mineral fillers (marble and quartz sand) and low water-to-cement ratio, obtained after the hydration of white Portland cement. The aim of the work is to investigate 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 (newly formed phases, as well as the formation of C-S-H gels) was defined using powder X-Ray diffraction and scanning electron microscopy. The experimental data show that the cement composites with higher water content exhibit a variety of newly formed phases, like hydration products of C-S-H gels. The use of marble as an additive lead to the creation of carbo-sulpho-aluminates. Testing of samples with a high content of inert mineral fillers showed that their structure is denser. Prolonged hardening of cement systems under constant access to water increases the compressive strength by 17.9%.

ПРИЛОЖЕНИЕ НА ЦИМЕНТОЗАМЕСТИТЕЛИ ВЪВ ФАЗООБРАЗУВАНЕТО НА ЦИМЕНТОВИ РАЗТВОРИ КАТО ЕКОЛОГИЧЕН ПОДХОД ЗА РЕДУЦИРАНЕ НА ПАРНИКОВИ ГАЗОВЕ

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Ключови думи: *циментови разтвори, минерални пълнители, прахова рентгенова дифракция, сканираща електронна микроскопия, екология*

Резюме: *Един от основните подходи за намаляване на въздействието на строителната индустрия върху околната среда е използването на минерални добавки за намаляване на количеството цимент, използван в строителните разтвори и бетона. Твърдите промишлени отпадъци, включително отпадъците от строителство и разрушаване, традиционно се използват в конвенционалните композити на циментова основа. Тяхното приложение е ограничено от прилагането на съставите, изискванията за желаните свойства на пресния и втвърдения*

разтвор/бетон, както и от необходимата трайност и устойчивост на корозия при известни експозиции.

Обект на това изследване са различни циментови композити с високо съдържание на инертни минерални пълнители (мраморно брашно и кварцов пясък) и ниско водоциментно съотношение, получени след хидратация на бял портландцимент. Целта на работата е да се изследва фазообразуването и да се измерят плътността, якостта на натиск и порьозността на циментовите композити, като изследванията са направени след 28 и 120 дни на втвърдяване с вода. Фазовият състав (новообразуваните фази, както и образуването на C-S-H гелове) е определен с помощта на рентгенова прахова дифракция, измервания с инфрачервена спектроскопия и сканираща електронна микроскопия. Експерименталните данни показват, че циментовите композити с по-високо съдържание на вода показват разнообразие от новообразувани фази, като хидратационни продукти на C-S-H гелове. Използването на мрамор като добавка води до създаването на карбо-сулфо-алуминати. Изпитването на образци с високо съдържание на инертни минерални пълнители показва

Използването на мраморното брашно като добавка води до формирането на карбосулфоалуминати. Изпитването на образци с високо съдържание на инертни минерални пълнители показва, че структурата им е по-плътна. Продължителното втвърдяване на циментовите системи при постоянен достъп на вода увеличава якостта на натиск със 17,9 %.

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 construction and demolition wastes, traditionally are used in conventional cement-based composites. Their use 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 [1, 2], good workability [3, 4], 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 key advantage is better workability, but durability and stability are their main disadvantages [5-7]. The proper application of these cement-based stones in construction works depends on their physical, chemical and mechanical properties, which are the result of the microstructure of newly formed hydrate phases. Here, of particular importance is the proper choice of cement replacement additives (hydraulic, pozzolanic, and almost inert fillers, incl. technogenic wastes) and additives, which aim both at reducing the cost of the composite and improving its properties and durability in different environments [8-12].

The goal of this work is to study the influence of the cement-to-water ratio, the amount of marble powder additive and the low water-to-cement ratio on the hydration process. A major emphasis of the study is on the formation of hydrosulphate- and hydrosulphonated calcium-silicate phases in white cement compositions and their effect on the measured properties. The effect of the studied parameters is evaluated by the methods of powder X-ray diffraction, SEM microscopy, and physical-mechanical methods for obtaining the following properties: bulk density after immersion, adsorption after immersion, compressive strength, and porosity.

Samples preparation

This work investigates cement solutions with different ratios of the main components – cement, aggregate and binder. The components of these mixes are: white Portland cement (binder) type CEM I 52.5 N (Devnya Cement, Bulgaria), clinoptilolite (0-0.8 mm, Beli Plast deposit, Bulgaria), and clean washed and dried river sand as an aggregate.

The chemical composition of the used white Portland cement CEM I 52.5 N, produced by Devnya Cement (Bulgaria), is (in wt%): SiO_2 – 24.3; Al_2O_3 – 2.1; Fe_2O_3 – 0.2; CaO – 68.3; MgO – 0.3; Na_2O – 0.13; K_2O – 0.02; Free lime – 1.9. The mineral composition was calculated via the Bogue method (wt %): C_3S – 72.13; C_2S – 15.28; C_3A – 5.23; C_4AF – 0.61.

Two mortars were prepared using two types of aggregate – river sand (sample, named As) and marble powder (sample, named Mm). The first type of aggregate, river sand, was cleaned, washed and dried. The properties of sand were defined as: 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 SiO_2. The second aggregate, marble powder, was produced by AIAS S.A. White Marble Products (Greece) with the following chemical composition wt %): CO_2 + H_2O – 45.7; SiO_2 – 0.12; Al_2O_3 – 0.38; Fe_2O_3 – 0.14; CaO – 32.9; MgO – 20.0; Na_2O – 0.05; K_2O – 0.19; and MnO – 0.01**.**

The polydispersity of the aggregate is: 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 prepared mortar specimens (6 prisms, 40×40×160 mm) were stored in the moulds for 1 day in a moist atmosphere (> 95% RH and 20 °C). Then the demoulded samples were stored under water (20 ºC) until strength testing for 28 and 120 days – the obtained samples were named As028, As120, Mm028, and Mm120, respectively).

Table 1 shows the samples' composition: sample As: binder (white Portland cement) + aggregate (river sand) + water, and sample Mm: binder (white Portland cement) + aggregate (marble powder) + water. All samples were mixed with distilled water.

Table 1. Composition of mortars

Sample	Binder	Aggregate	Ratio		
			cement/ aggregate	water/ cement	water/ fines*
As028, As120	white Portland cement	river sand	1:3	0.50	0.500
Mm028, Mm120	white Portland cement	marble powder	1:2	0.60	0.353

* all particles with sizes below 125 μm

Experimental Methods

The bulk density after immersion and adsorption after immersion were measured according to ASTM C642-13 [13, 14]. Due to the different bulk densities of the samples, the adsorption values were adjusted to comparable values. The compressive strength at 28 and 120 days of water curing was measured according to EN 196-1:2016 [15].

A broken part of a sample with a mass of 2.0±0.3 mg was used to measure the porosity by the method of mercury intrusion porosimetry using the Carlo Erba, Porosimeter Mod. 1520, pressure range 1-150 atm, corresponding to the pore size range 50-15000 nm.

Powder X-ray diffraction (PXRD) analysis was performed with an X-ray powder diffractometer D2 Phaser BrukerAXS, CuKα radiation (λ = 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). Phase identification and peak fitting were carried out using the computer program for qualitative analysis QualX (v. 2.24) with the indexed Powder Diffraction File database [16].

Scanning electron microscopy (SEM) was performed with a microscope Philips PH, Model 515, regime of secondary electron emission. The fracture fragments of the samples with an approximately flat surface of about 10×10 mm were dried for 12 hours at 60 ± 5ºC, then coated with a thin layer of gold.

Results and Analysis

Physical-mechanical properties

The results show that the compressive strength of the conventional cement mortar As028 is comparable to that given by the factory (Table 2). This indicates that the sand used is similar to the CEN Standard sand, EN 196-1. The compressive strength increases by 7.6% at day 120 (As120), due to the filling of the porous space with newly formed hydrates (the pore volume decreases by 6.8%).

The values for the measured parameters indicate the formation of a thin structure of hardened samples Mm, which are characterized by a higher 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%, which is greater than the decrease in the total pore volume by 9.3% (Table 2).

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
	$kg.m^{-3}$	$mm^3.cm^{-3}$	$N.mm^{-2}$	$N.mm^{-2}$	$mm^3.g^{-1}$	$mm^3.g^{-1}$
As	2126	173.8	56.3	60.6	44.98	41.91
Mm	2158	258.5	53.8	61.5	64.66	58.69

PXRD analysis

PXRD analysis was used to confirm the previously obtained results and to better evaluate the investigated samples. The PXRD analysis (Table 3, Fig. 1 and Fig. 2) shows the presence of two

groups of minerals in the studied samples: (i) relict minerals from the initial composition: belite, albite, anorthite, Mg-rich calcite, quartz, dolomite and (ii) newly formed minerals: tobermorit, hillebrandite, and scolecite for CSH/CSAH gel minerals, ettringite and monosulphoaluminate for sulphoaluminates, hemi- and monocarboaluminate for carboaluminates and portlandite.

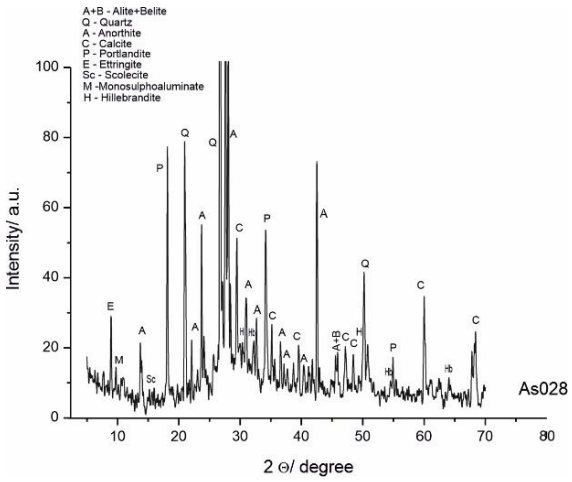

Fig. 1a. PXRD pattern of sample As028

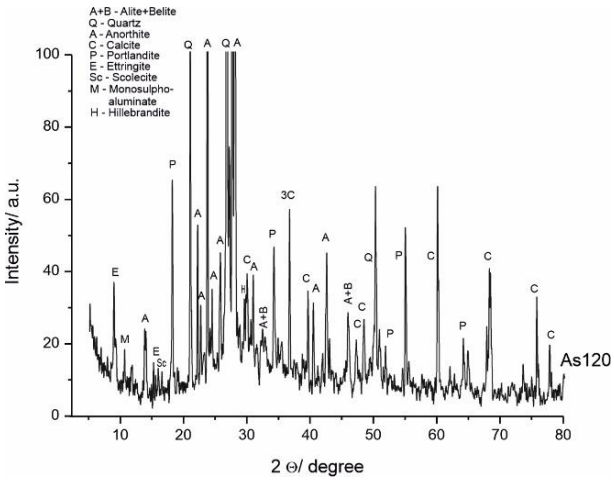

Fig. 1b. PXRD pattern of sample As120

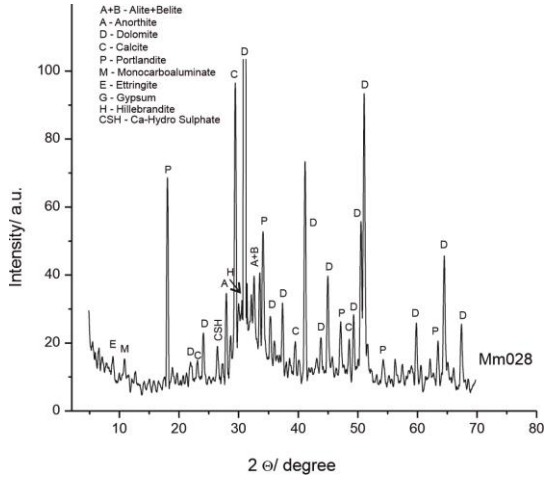

Fig. 2a. PXRD pattern of sample Mm028

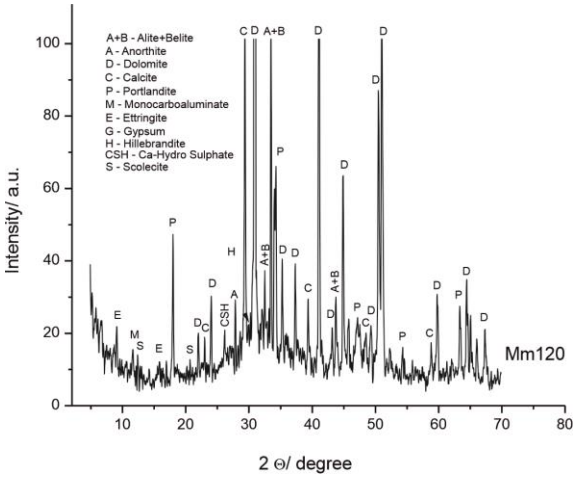

Fig. 2b. PXRD pattern of sample Mm120

The identification of relict minerals in the samples' compositions is associated with insufficient water in the systems, which results in an incomplete hydration of the raw minerals.

Table 3. PXRD analysis results

No	Phase description	Sample	Identified phases
1.	***Relict minerals***		
1.1.	Non-hydrated phases of cement and aggregates	As028, As120 Mm028, Mm120	belite (C_2S), 49-1673– $2CaO.SiO_2$
			albite (C_3S), 11-0593 – $(Na,Ca)Al(Si,Al)_3O_8$
			anorthite (CAS_2), 41-1486– $CaO.Al_2O_3.2SiO_2$
			quartz, 46-1045 – SiO_2 – 3.34
		Mm028, Mm120	dolomite, #36-0426 – $CaMg(CO_3)_2$
1.2.	Phases of the source components	As028, As120 Mm028, Mm120	Mg-rich Calcite, #47-1743 – $CaCO_3$
2.	***Newly formed phases***		
2.1.	- containing OH^-	As028, As120 Mm028, Mm120	portlandite (CH), #44-1481 – $Ca(OH)_2$
2.2.	- containing SO_4^{2-}, OH^- and crystal water H_2O	As028, As120 Mm028, Mm120	ettringite, #41-1451 – $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$
		As028, As120	monosulphoaluminate, #45-0158 – $Ca_4Al_2SO_{10}.12H_2O$
		As028, As120 Mm028, Mm120	calcium hydrogensulphate, #85-1271 – $Ca(HSO_4)_2$

2.3.	- hydrosilicates – CSH/CSAH, forming of main oxides CaO, SiO_2, OH^- and/or crystal water H_2O	As028, As120 Mm028, Mm120	hillebrandite, #42-0538 - $Ca_6Si_3O_9(OH)_6$
		As028, As120	tobermorite 11A, #45-1480 - $Ca_5Si_6(O,OH)_{18}.5H_2O$
		As028, As120 Mm120	scolecite, #41-1355 - $CaAl_2Si_3O_{10}.3H_2O$
2.4.	- OH- and HCO_3^- /CO_3^{2-} phases	Mm028, Mm120	monocarboaluminate, #41-0219 – $Ca_4Al_2(OH)_{12}(CO_3).5H_2O$
		Mm028	hemicarboaluminate, #41-0221 – $Ca_4Al_2(OH)_{12}(OH)(CO_3)_{0.5}.4H_2O$

SEM

The surface structures of the studied samples are shown in Figures 3 and 4. The micrographs indicate the stable and dense structures, even at 28 days of curing, so there are no empty spaces for the growth of new minerals. The CSH/CSAH gel possibly forms a fine-grained crystal aggregate with structural parameters under the limit of PXRD detection. Additionally, the areas with self-desiccation drying cracks can be seen. Due to wall effects, different cement-to-water ratios, and empty spaces, these areas are filled with crystal hydrates of different morphologies: plate crystals (portlandite), needle crystals (ettringite), and fine crystal aggregates (CSH gel).

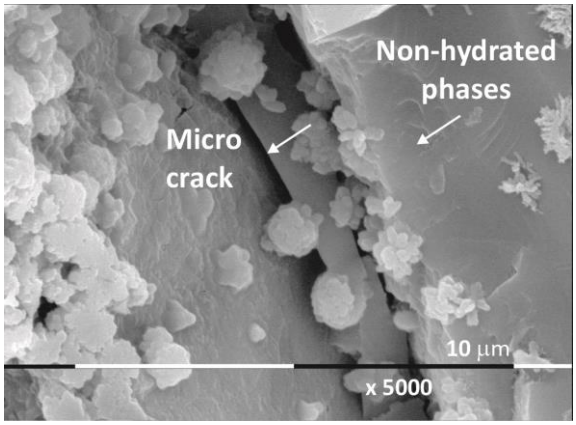

Fig. 3a. SEM micrograph of sample As028

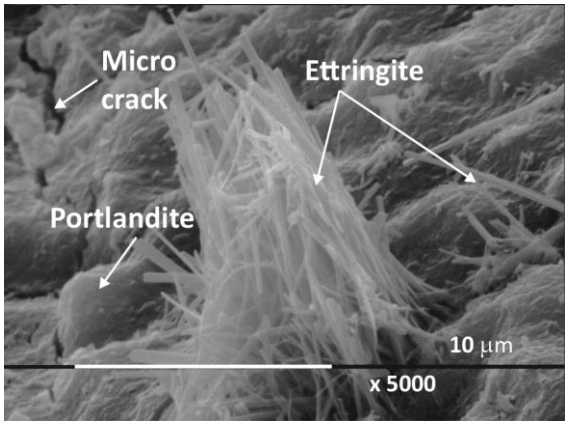

Fig. 3b. SEM micrograph of sample As120

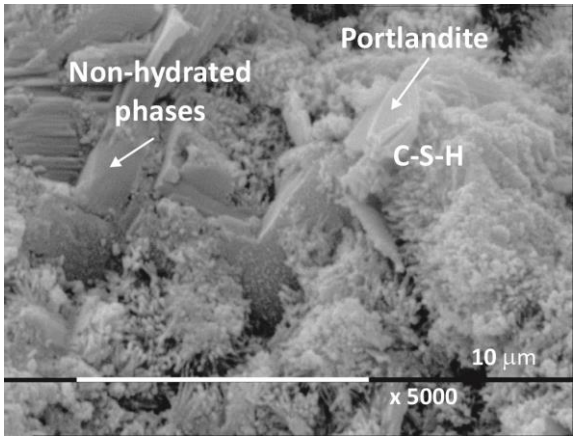

Fig. 4a. SEM micrograph of sample Mm028

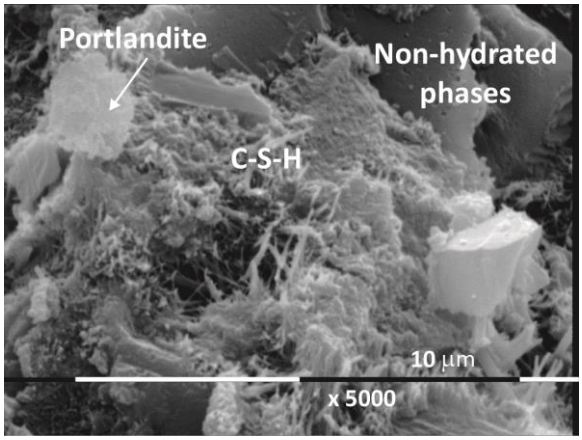

Fig. 4b. SEM micrograph of sample Mm120

According to the results of the PXRD analysis, the following reaction mechanism schemes for the hydration of the samples have been defined:

(1) $2Ca_3SiO_5$ (C_3S) + $7H_2O \rightarrow Ca_3Si_2O_7.4H_2O$ (C-S-H gel) + $3Ca(OH)_2$ (fast)

(2) $2Ca_2SiO_4$ (C_2S) + $5H_2O \rightarrow Ca_3Si_2O_7.4H_2O$ (C-S-H gel) + $Ca(OH)_2$ (slow)

Formation of ettringite

(3) $Ca_3Al_2O_6$ (C_3A) + $3CaSO_4.2H_2O$ + $26H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$

Formation of hillebrandite (CSH)

(4) Ca_2SiO_4 (C_2S) + $H_2O \rightarrow Ca_2SiO_3(OH)_2$

Formation of tobermorite (CSH) – only in compositions with sand

$2Ca_3SiO_5$ (C_3S) + $4SiO_2$ + $6H_2O$ → $Ca_5Si_6O_{16}(OH)_2.4H_2O$ (C-S-H gel) + $Ca(OH)_2$

$3Ca_2SiO_4$ (C_2S) + $3SiO_2$ + $6H_2O$ → $Ca_5Si_6O_{16}(OH)_2.4H_2O$ (C-S-H gel) + $Ca(OH)_2$

Formation of Scolecite (CSAH)

(5) $Ca_3Al_2O_6$ (C_3A) + $3SiO_2$ + $5H_2O$ → $CaAl_2Si_3O_{10}.3H_2O$

The use of marble white-powder (Mg-rich calcite) increases the content of CO_3-ions [17-19], which are involved in the formation of hydrated phases, verified by the presence of hemi-, and monocarboaluminate:

(6) $Ca_3Al_2O_6$ (C_3A) + $0.5CaCO_3$ + $0.5\ CaO$ + $12H_2O$ → $Ca_4Al_2(CO_3)_{0.5}(OH)_{12}.5.5H_2O$

(7) $Ca_3Al_2O_6$ (C_3A) + $CaCO_3$ + $11H_2O$ → $Ca_4Al_2(CO_3)(OH)_{12}.5H_2O$

Conclusions

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.

Regardless of the very dense structure, the samples have open and continuous porosity. Water penetrates through capillaries, thus making the processes of delayed hydration and pozzolanic reaction possible and reducing the amount of portlandite.

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