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Nano-modified cementing composites for self-cleaning building materials

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Abstract: This paper is devoted to the development of nano-modified cementing composites in the field of self-cleaning building materials. Particle-size distributions of the main constituents such as ultra-fine zeolite and limestone of multicomponent cements, and titanium dioxide and kaolin additives are given. The degree of the interphase of the active surface in Portland cement and supplementary cementitious materials is calculated. It has been shown that due to the synergistic effect, anatase and rutile mixtures can be included in cementing composites to improve the properties of self-cleaning plasters. The influence of titanium dioxide and kaolin additives on the mechanical properties of nano-modified multicomponent cement was investigated using the method of mathematical planning for the experiment. The results obtained using the XRD and SEM methods showed that the addition of high-surface-area nano-scale particles of TiO_2 to the cement paste leads to the formation of a denser microstructure in the cementing matrix.

Keywords: nano-modified cementing composites, titanium dioxide, kaolin, mechanical properties, self-cleaning plasters

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Introduction

Developing technology opens up the possibility of creating new housing formats such as Active House – multi-comfort houses that combine innovative energy-efficient, environmental, and building solutions. The main criteria for such buildings are the maximum use of natural heat and light sources, efficient operation of roofs and windows for the accumulation and conservation of energy, and a number of other integrated solutions to ensure maximum economic and environmental efficiency (Mlecnik, 2013).

In the process of building multi-comfortable houses, modern construction and finishing materials are being developed using nanotechnologies (Rao et al., 2015). One such nano-modified material is tiocement – a high-tech cement with photocatalytic properties. The main modifier in this cement is nanoparticles of titanium dioxide, which give the cement an ability to self-purify by adsorbing harmful environmental components (smoke, organic matter, oils, carbon monoxide, nitrogen, etc.) and through ultraviolet and visible light, neutralize them (Boonen & Beeldens, 2014).

Over the years, a wide range of TiO_2 nanoparticles with different phase compositions, crystallinities, and surface areas have been used. The photocatalytic additive (titanium dioxide) can be added to mortars prepared with aerial lime, cement and gypsum binders (Lucas et al., 2013). As shown in the study (Sikora et al., 2017), nanocomposite silica-titania ($mSiO_2/TiO_2$) core-shell improves the mechanical and bactericidal properties of cement mortars. Due to the synergistic effect of the anatase/rutile mixture, the recombination rate of photogenerated electron-hole pairs slows down. In this case, the photocatalytic activity was increased with the anatase/rutile mixture TiO_2 nanoparticles (Siah et al., 2016).

Nowadays, in the building industry, nanocomposites are widely applied, however, cement-based composites are mainly modified with a single type of nanostructures. Therefore, it is important to investigate the effect of the anatase/rutile mixture on the properties of multicomponent cementing composites. These include multimodal Portland-composite cements which exhibits the positive properties of the main constituents and minor additives, while diminishing the negative impacts of each of the components applied separately. Thus, this cementing composite refers to so-called "multifunctional materials" (Kryvenko et al., 2014; Sanytsky et al., 2018). The goal of the presented work is to develop new innovative nano-modified cementing composites for self-cleaning plasters – "multimodal, multicomponent tiocement, containing the nano-sized anatase/rutile mixture".

1. Experiment

1.1. Materials

Ordinary Portland cement (OPC) CEM I 42.5R manufactured by PJSC "Ivano-Frankivskcement" and composed of C_3S: 61.35, C_2S: 13.52, C_3A: 6.75, C_4AF: 12.02, wt.% was used in the investigation. Natural pozzolan – zeolite tuff with 70.50, wt.% SiO_2 was obtained from the Sokyrnytsky quarry. The zeolite mineral clinoptilolite $[(Na_4K_4)\ (Al_8Si_{40}O_{96})\cdot 24H_2O]$ contained in the tuff was 58% (Si/Al = 6.5). Limestone powder with 95 wt.% $CaCO_3$ was used as a micro filler. The multimodal Portland-composite cement type CEM II/B-M was produced by mixing CEM I 42,5 R and supplementary cementitious materials (SCMs). The main non-clinker constituents of such binders are zeolite (15 wt.%) and limestone (7 wt.%). Minor ultrafine additives – kaolin and titanium dioxide – were added to the cementing composites.

Kaolin is used to improve the decorative properties of mortars. For kaolin, the sum of oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ is 93.77%. Kaolinite $Al_2Si_2O_5(OH)_4$ is a clay mineral (Si/Al = 1.2). Kaolinite is characterized by fine crystalline aggregates, which consist of crystals in the size of 1-5 µm. This produces a leafy structure of kaolin formed by layers of silicate and gibbsite, which are stacked one after the other. Kaolin has a high coefficient of reflection, which creates conditions for obtaining coatings with the necessary decorative qualities.

TIOXIDE® R-FC5 pigment (fine crystal rutile pigment) was used, which has excellent brightness, a blue undertone and high opacity. Its siloxane treatment ensures both low moisture pickup and outstanding dispersion properties and self-cleaning via chalking. Nano photocatalytic titanium dioxide powder (PC-Series) with an anatase crystalline structure and average particle size of about 10/20 nm^2 was chosen for obtaining the self-cleaning coating with a combination of super-hydrophilic, photocatalytic and anti-static features.

1.2. Research methods

Chemical compositions of materials were determined by an X-ray spectrometer (ARL 9800 XP). The particle size distribution (PSD) was measured by a laser analyzer (Mastersizer 3000). The coefficient of reflection of the decorative cements was determined using a FB-2 whiteness meter. A scanning electron microscope (Philips XL30 ESEM-FEG) was used for studying the morphology of the cement paste surface.

The evaluation of the properties of the nano-modified multicomponent cements was carried out through flowing and compressive strength tests. The consistency of the fresh cement mortars was tested in accordance with EN 1015-3. The prepared mortars were poured into oiled molds to form samples with a size of 40x40x160 mm, in accordance with the requirements of EN 196-1: 2005 (EN, 2005). The water to cement (W/C) ratio was fixed at 0.50 to get reasonable cement mortar workability. Fresh specimens were compacted on a vibration table (40 Hz) for 60 seconds. The samples were demolded after 24 h and then cured for 28 days in a standard water bath at a temperature of 20±2°C.

Effects of additives on the properties of the nano-modified cementing composites were determined with the help of a two-factor three-level mathematical modeling experiment according to the following methodology (Dvorkin et al., 2012).

2. Results and discussions

The Blaine specific surface areas (SSA) of OPC, zeolite, limestone powder, kaolin and TiO_2 rutile pigment were 3450, 12000, 9600, 15800 and 13350 cm^2/g

respectively. The particle size distributions of OPC, zeolite, limestone, kaolin and TiO_2 pigment are presented in Table 1. It is shown that an ultra-fine particle fraction of less than 0.5 μm for OPC and the mineral additives is in the range of 0.96-1.18%, while for TiO_2 pigment its content is increased to 3.42%. The volume mean diameter D[4;3] for OPC corresponds to 24.8 μm, and for the mineral additives it is in the range of 5.82-48.7 μm. At the same time, the surface area mean diameter D[3;2] for OPC corresponds to 5.21 μm, but for the non-clinker constituents the range of D[3;2] is 3.87-7.08 μm.

Table 1. Particle size distribution of the main constituents (*own research*)

Materials	Ø < 0.5 μm [%]	Ø < 1 μm [%]	Ø < 5 μm [%]	Ø < 10 μm [%]	Ø < 20 μm [%]	D[3;2] [μm]	D[4;3] [μm]
OPC	1.18	4.92	24.46	43.41	66.33	5.21	24.8
Zeolite	1.16	5.96	35.18	48.86	65.31	4.24	21.2
Limestone	0.96	3.97	28.71	39.72	51.05	7.08	48.7
Kaolin	0.0	0.0	62.26	90.51	97.35	3.87	5.82
TiO_2 pigment	3.42	43.78	100.0	100.0	100.0	1.06	1.36

The particle size of the complex cementing composite was reduced to ultra-size by adding nano-TiO_2 and kaolin. The volume mean diameter D[4;3] for TiO_2 pigment is 1.36 μm and the maximum of the surface area mean diameter D[3;2] is 1.06 μm. The particle size distribution of ultrafine additives such as kaolin (a) and TiO_2 rutile pigment (b) are given in Figure 1.

a) b)

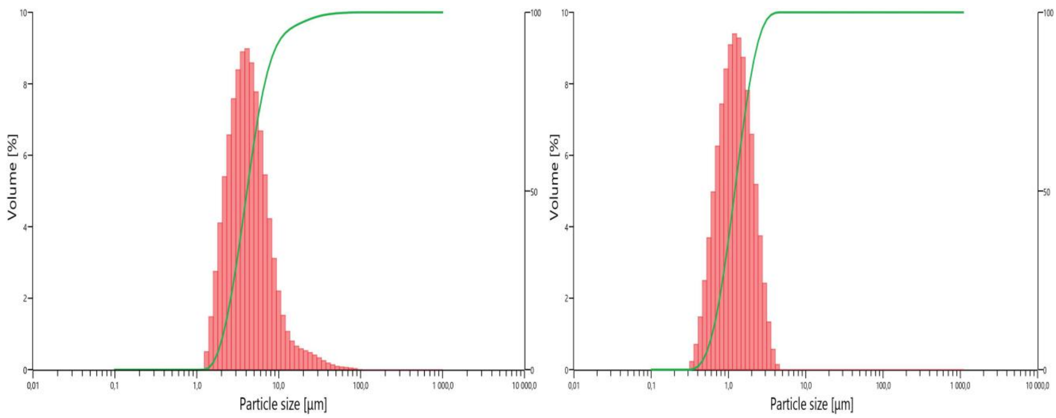


Fig. 1. Particle size distribution of kaolin (a) and TiO_2 rutile pigment (b) (*own research*)

The degree of additional interfacial active surface of OPC and SCMs could be obtained by the determination of the ratio between specific surface of particles and their volume (coefficient $K_{A/V}$). With the decrease of the particle size, their "excess surface energy" significantly increases. To assess the contribution of individual particles into the total specific surface area, an incremental coefficient of surface area (K_{isa}) was calculated, which is determined by multiplying the coefficient $K_{A/V}$ by the incremental volume of each fraction of the material (Siah et al., 2016). For OPC the maximum value of K_{isa} (5.57 μm^{-1}·vol.%) is achieved for a fraction 0.248 μm. For zeolite, limestone and kaolin the maximum value of K_{isa} is 5.11, 4.12 and 12.32 μm^{-1}·vol.% at particle sizes 0.89, 1.55 and 2.0 μm respectively.

The distributions of particle sizes by the surface area for kaolin and TiO_2 rutile pigment are shown in Figure 2. So, it follows that the TiO_2 rutile pigment is characterized by the very high incremental coefficient of surface area (K_{isa} = = 50.08 μm^{-1}·vol.%). For TiO_2 with an anatase crystalline structure and an average primary particle size 10/20 nm^2, the coefficient $K_{A/V}$ varies from 600 to 300 μm^{-1} and the value of K_{isa} is higher than for the TiO_2 rutile at 50-100 times. In this case, the calculated specific surface area (SSA) of the nano-TiO_2 anatase reaches 450-600 m^2/g and exceeds the surface area of OPC by 1500 times. Thus, in the initial period of the structure formation, the surface area of 0.1 wt.% nano-TiO_2 is an order of magnitude greater than the whole cementing system. This determines a significant contribution to the interphase surface of TiO_2 particles on a nanoscale 10/20 nm^2 and its self-cleaning properties. This indicates that just nano fraction is a significant contributor to the surface area of the cementing composite. The TiO_2 nanoparticles of the anatase/rutile mixture are characterized by a very high value of A/V and are extremely reactive relative to the particles of the OPC and main non-clinker constituents.

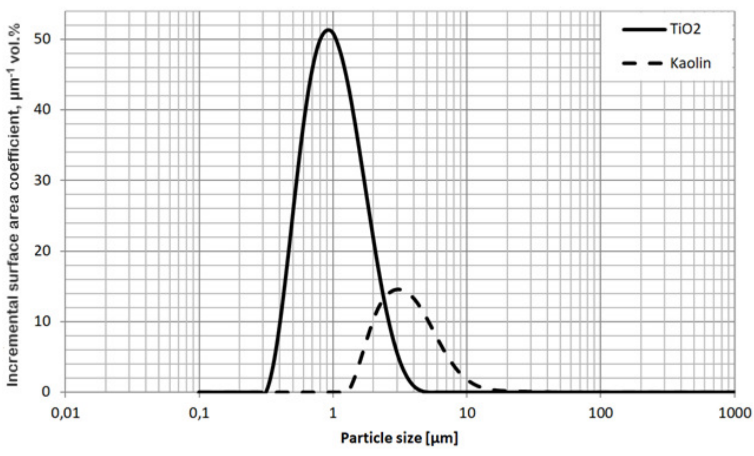


Fig. 2. Incremental surface area coefficient of kaolin and TiO_2 rutile pigment (*own research*)

Mineral additives with high whiteness were used to enhance the decorative properties of plasters. Kaolin and fine crystal rutile pigment TiO_2 are characterized by the higher coefficient of reflection (98 and 94% respectively), while for lime-stone it is 83% (Fig. 3). The high coefficient of reflection of such mineral additives provides the production of decorative cements for the finishing of facades.

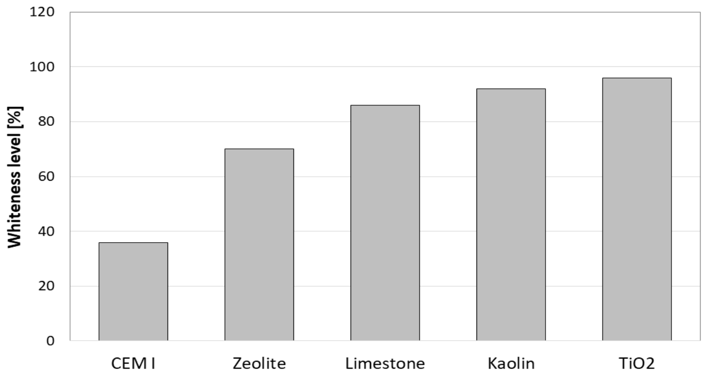


Fig. 3. Coefficient of reflection of cementing composites components (*own research*)

The optimization of nano-modified multicomponent cementing composites was determined due to a planned two-factor three-level experiment. The amount of kaolin (factor X1) was 0; 3; 6 wt.%, and the amount of anatase/rutile mixture TiO_2 (factor X2) was 0; 0.3; 0.5 wt.%. On the basis of the obtained coefficients, regression equations for the investigated strength functions of the nano-modified cementing composites were compiled after 28 days (Y):

$$Y_{R28} = 43.11 + 1.56X_1 + 2.51X_2 - 1.12X_1X_2 - 9.20X_{12} - 7.33X_2^2$$

According to the obtained mathematical dependencies of strength and the adequacy dispersion ($Sa_d^2 = 2.1$), a graphical interpretation (Fig. 4) was produced, which determines the optimal ratio between kaolin and the anatase/rutile mixture. In this case, the optimal balance between the multimodal Portland-composite cement type CEM II/B-M and the minor additives (3.0 wt.% kaolin and 0.3 wt.% TiO_2) ensures a 28-day compressive strength higher than 43.5 MPa. The physical and mechanical properties of the nano-modified multicomponent composite are presented in Table 2.

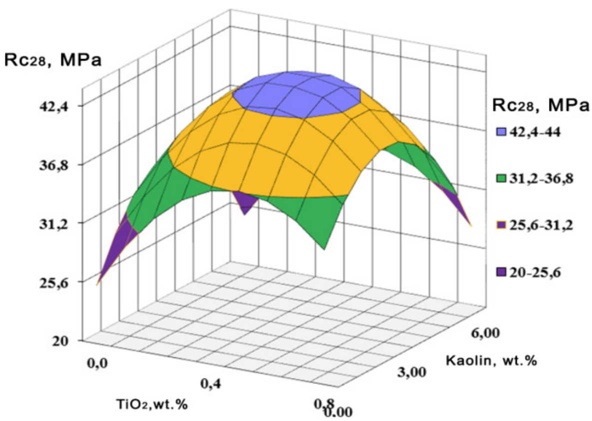


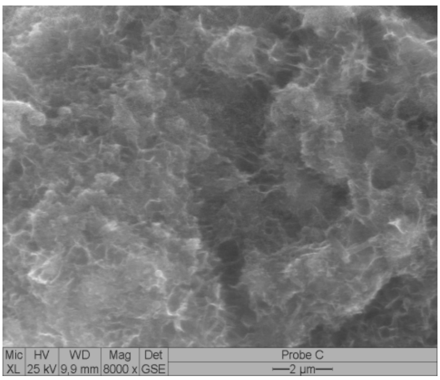
Fig. 4. The isoparametric lines of the 28-day compressive strength of the nano-modified multicomponent cementing composites (*own research*)

Table 2. Properties of nano-modified multimodal Portland-composite cement CEM II/B-M with 3.0 wt.% kaolin and 0.3 wt.% TiO_2 (*own research*)

Properties		Results
Water demand [%]		31.0
Coefficient of reflection [%]		68.0
Initial setting time [min]		185
Workability (flow value) [mm]		160
Bleeding [%]		8.7
Flexural /Compressive strength [MPa], after	2 d	3.9/21.6
	28 d	9.2/43.5
	180 d	12.6/55.7

According to the SEM data, after 28 days of hydration, the calcium hydrosilicates C-S-H form a dense microstructure of cement paste (Fig. 5a), which is confirmed by EDX (Fig. 5b). In the presence of TiO_2 there is a more intense formation of C-S-H, as evident from increased strength. Titanium dioxide is fairly stable. From the structural point of view, it serves as a micro filler in the cement, reducing the total porosity at an early stage of hardening.

a)



b)

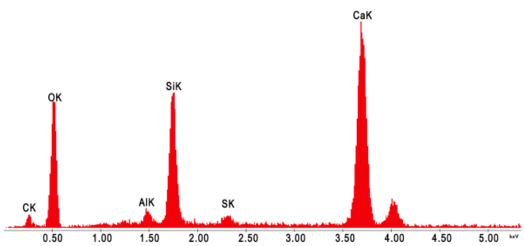


Fig. 5. SEM image (a) and EDX image (b) of paste based on nano-modified multicomponent tiocement after 28 days of hardening (*own research*)

A complex additive containing an ultrafine anatase/rutile titanium dioxide mixture and kaolin provides a higher uniformity of nanoparticle distribution in cementing composites, which can increase the service life and conserve the aesthetic appearance of facades over the long term. Such nano-modified multicomponent cementing composites for self-cleaning plasters can be used as smart materials in architecture, interior architecture and design.

Conclusions

The results of the study showed the effects of the anatase/rutile mixture TiO_2 and mineral additives on the performance of multicomponent cementing composites for self-cleaning building materials. The mechanical properties of the nano-modified multicomponent cement were investigated. The compressive strength of the cementing composite with nano-modified additives after 28 days was 43.5 MPa. Based on the laser granulometric data, it is calculated that the incremental coefficient of surface area for TiO_2 with the structure of crystalline anatase is higher than rutile, by 50-100 times; in addition, the mixture of anatase and rutile titanium dioxide crystalline forms with kaolin promotes the uniform distribution of nanoparticles in the cementing composites which produces plaster surfaces with the necessary decorative and self-cleaning properties.

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