Glazing effect for producing environmentally friendly ceramics for cladding applications

Elizaveta A. Pavlycheva, Evgeniy S. Pikalov and Oleg G. Selivanov

Vladimir State University, Vladimir, Russia

Abstract

This paper presents results of comparative studies of environmental safety of ceramic materials, based on a low-plasticity clay with the introduction of galvanic sludge, boric acid and titanium dioxide in 3 different combinations. The experimental samples were manufactured under 15 MPa pressing pressure and at the maximum firing temperature of 1050 °C. Prior to the toxicological experiments, diurnal extracts of the materials into the model neutral and acidic media were obtained. The toxicological safety was determined by using the *Daphnia* mortality method, and by comparing the maximum permissible concentrations of heavy metals for drinking and household water with the heavy metals' concentrations in diurnal extracts. The presented data show that the combined introduction of all the investigated additives results in the glazing effect of ceramic particles surfaces so that an environmentally safe material can be produced that exhibits sufficiently high-performance properties. The use of low-plastic clay and electroplating sludge expands the raw material base for producing ceramics and allows the disposal of environmentally hazardous compounds of heavy metals contained in electroplating sludge. Ceramic materials based on the developed charge composition can be used for producing items for external cladding for buildings and structures.

Keywords: environmental safety; vitrification; low-plasticity clay; electroplating sludge; heavy metals.

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1. INTRODUCTION

Technologies for utilization of various waste types in production of construction materials are simple and provide disposal of considerable amounts of waste. Such waste utilization stimulates savings of primary natural resources, while simultaneously reducing the production cost and environmental pollution by waste [1-3].

However, in most cases, the use of waste reduces the quality and operational properties of the manufactured materials and products and is also associated with the necessity to ensure their environmental safety, since waste components and substances, formed during their disposal, often belong to fourth hazard class substances at best. In this regard, it is required not only to determine the waste content, ensuring the regulatory requirements compliance for the materials and products performance, but it is also necessary to provide the environmental safety assessment. Besides, in production of building materials waste is in most cases used only as a cheap filler, not utilizing all possible valuable properties of substances and component, contained in waste.

We have previously studied the use of various wastes as functional additives for improving the quality and performance properties of construction materials. In one of the studies, the combined introduction of electroplating sludge, boric acid and titanium dioxide provided production of ceramics with a self-glazing effect on the sample surfaces, which reduced water absorption and increased frost resistance [4].

Corresponding author: Oleg G. Selivanov, Vladimir State University, Vladimir, Russia
E-mail: selivanov6003@mail.ru

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Recycling of electroplating sludge is up to date, since it is classified in 2-3 hazard waste classes and its processing by using other methods is time and resource consuming [5-7]. The application of the obtained composition is relatively simple and allows galvanic sludge utilization as a pore-forming agent and vitreous phase modifier.

The research objective was to study the impact of the vitrification effect, obtained during combined introduction of electroplating sludge, boric acid and titanium dioxide, on environmental safety of the resulting ceramics aimed for cladding applications.

2. MATERIALS AND METHODS

2. 1. Sample production

In this research we consider the ceramic material produced from the clay of Suvorotskoye Deposit in the Vladimir region (Russia) of the following composition (wt.%): 67.5 SiO_2; 10.75 Al_2O_3; 5.85 Fe_2O_3; 2.8 CaO; 1.7 MgO; 2.4 K_2O; 0.7 Na_2O [8,9]. The clay plasticity index was determined by the standard method as 5.2. Therefore, according to the standard GOST 9169-75, this clay belongs to the low-plasticity grade, so that the resulting manufactured items are low quality products *i.e*. of low strength and high water absorption. Thus, the effective application of this clay requires the introduction of modifying additives.

Boric acid (BA) grade B (ProfSnab LLC, Russia) 2nd class (GOST 18704-78) was used as the first additive, being a strong fluxing agent and providing liquid-phase sintering, which increases ceramics strength and reduces its water absorption [10].

The second additive was galvanic sludge (GS) formed as a result of reagent treatment of waste water at the Avtopribor plant (Vladimir, Russia), and is characterized by the following composition (wt.%): $Zn(OH)_2$ ≈ 11.3 %; SiO_2 ≈ 7.08 %; $Ca(OH)_2$ ≈ 16.52 %; $Cr(OH)_3$ ≈ 9.31 %; $(Fe^{2+})Cr_2S_4$ ≈ 4.17 %; $CaCO_3$ ≈40.25 %; CaO ≈ 3.45 %; ZnO ≈ 2.41 %; $Cu(OH)_2$ ≈ 2.38 %; $Ni(OH)_2$ ≈ 2.62 %; $Mn(OH)_2$ ≈ 0.64 %; $Pb(OH)_2$ ≈ 0.14 % [11].

In this study, titanium dioxide (TiO_2, NEO Chemical, Russia) of R-02 brand (GOST 9808-84) was considered as an additional additive affecting composition and structure of crystallization products and providing together with the other specified additives the vitrification effect in the depth of the samples.

Samples of the obtained material were made by using semi-dry pressing technology. The pre-crushed clay and electroplating sludge with the fraction of max 0.63 mm particle size were selected and dried to a constant mass. The choice of the fraction particle size, as well as the choice of subsequent parameters for manufacturing the ceramic samples, were based on the previous experiments in which the best results for mixing, compacting and sintering of ceramics, based on the used clay, were obtained at these parameters values. Next, all the charge components were initially mixed dry in accordance with the studied charge compositions, followed by mixing with water at the concentration of 8 wt.% in order to achieve uniform molding mass. The mixing period at each stage lasted 5 min. The ceramic samples were made from the molding mass by one-side pressing under the pressure of 15 MPa, followed by firing in the oxidizing atmosphere at the heating rate of 5 °C min^{-1} with the exposure at the temperature of 1050 °C during 30 min. The samples were made cube shaped of 50 mm side in three sample series for each charge composition, followed by averaging of the experimental results for each series.

2. 2. Characterization of the obtained ceramic samples

2. 2. 1. Compressive strength

The compressive strength was determined by continuous and uniform load application to the sample to reach its destruction with the maximum load fixation using hydraulic press P6326B (JSC "Gidropress", Russia).

2. 2. 2. Water absorption

Water absorption has been determined by the sample dry mass increase after saturation with water at the atmospheric pressure during 48 h.

2. 2. 3. Frost resistance

Frost resistance of the sample has been determined after the water absorption experiment. For this purpose the water-saturated sample has been kept during 4 h at the temperature in the range from -15 °C to -20 °C, and afterwards placed in water at room temperature for 2 h and examined for cracks. In the case that cracks were not found, a new freeze-thaw cycle was performed for the sample.

2. 3. Toxicological studies

Toxicological studies of the considered compositions containing additives were performed for the ceramic samples, using the biotesting method of *Daphnia magna Straus* mortality under the influence of the substances present in diurnal water extracts from the samples of the studied materials. To account for possible mechanical product damage and wear, the whole samples were slightly chipped and placed in 500 cm^3 of distilled water each for 24 h. Next, three samples (100 cm^3 each) were taken from the resulting extract. Separately, the control 100 cm^3 sample of the cultivation water was made. 10 daphnia from the pre-staged synchronized culture, grown in cultivation water were placed in each sample. The number of live and dead daphnia was counted once a day during 96 h. Daphnia were considered dead in the case of absence of movements within 15 s after a light shake of the glass with the sample. The experiment was considered reliable when at least 9 daphnia survived in the control sample.

To account for the likely effects of acid rain and soil acidity, chemical testing concerning the degree of heavy metals migration into the diurnal water (pH 7.2) and ammonium acetate (pH 4.8) from the samples of the studied materials has been performed. Zinc, chromium, copper, and nickel ions were chosen for assessment, since electroplating sludge contains the largest amount of these heavy metals' compounds. The extracts were prepared by placing the slightly chipped samples into 500 cm^3 of distilled water and 500 cm^3 of ammonium acetate solution, each. The acetate-ammonium buffer was prepared by adding 108 cm^3 of glacial acetic acid into 500-600 cm^3 of distilled water (ch. p, Lenreactive PLC, Russia) of 99.8 wt.% CH3COOH and 75 cm^3 of 25 % aqueous technical ammonia solution $NH_3 \cdot H_2O$ (brand A, PLC KuibyshevAzot, Russia). Quantitative detection of heavy metals in water extract from the samples has been performed by using an atomic-absorption spectrometer Quant-Z.ETA-T (NEO Chemical, Russia). The ceramics structure was studied by using Quanta 200 3D scanning electron microscope (FEI Company, USA).

3. RESULTS AND DISCUSSION

In this research the comparative studies of compositions not containing and containing the considered additives have been carried out (Table 1).

Table 1. Compositions and properties of the studied ceramic materials

№	Additive amount, wt.%)			Compressive strength, MPa	Water absorption, %	Frost resistance (cycles)
	GS	BA	TiO_2			
1	-	-	-	14.3±0.7	7.5±0.5	39±2.0
2	5	-	-	11.6±0.6	12.7±0.7	30±2.0
3	5	5	-	21.3±0.9	7.2±0.4	42±2.0
4	5	5	10	21.0±0.9	3.2±0.2	51±3.0

Toxicological studies have shown (Fig. 1) that the composition 2, containing only galvanic sludge, caused 100 % *Daphnia* mortality on the second day of the experiment, while the composition 3 containing galvanic sludge and boric acid caused *Daphnia* mortality not exceeding the critical value of 50 % throughout the experiment, although approaching it in 96 h.

Data concerning the composition without additives (composition 1) and the composition containing all the considered additives (composition 4) are not shown in Figure 1 as during 96 h all investigated planktonic organisms survived in the corresponding diurnal water extracts, indicating the material environmental safety.

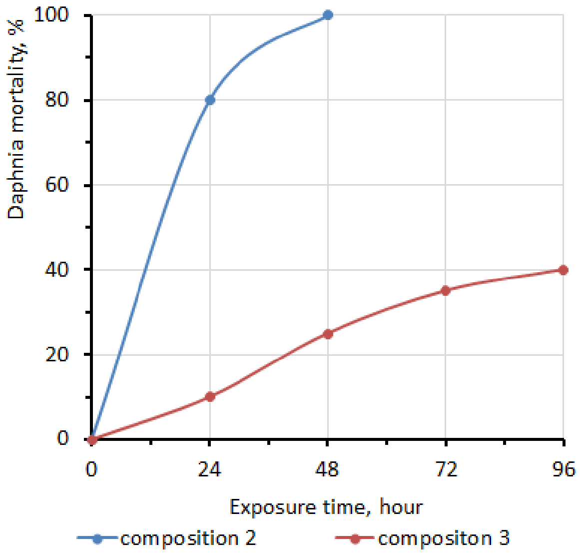

Figure 1. Dependence of Daphnia mortality on exposure time and sample composition

The obtained results can be explained by structural features of the studied ceramic materials. The initial ceramic material without any additives constitutes the sintered ceramic grains (Fig. 2a), while the galvanic sludge, introduced into the charge, caused the grain debonding and porosity increase (Fig. 2b), which is confirmed by the increase in water absorption (see Table 1).

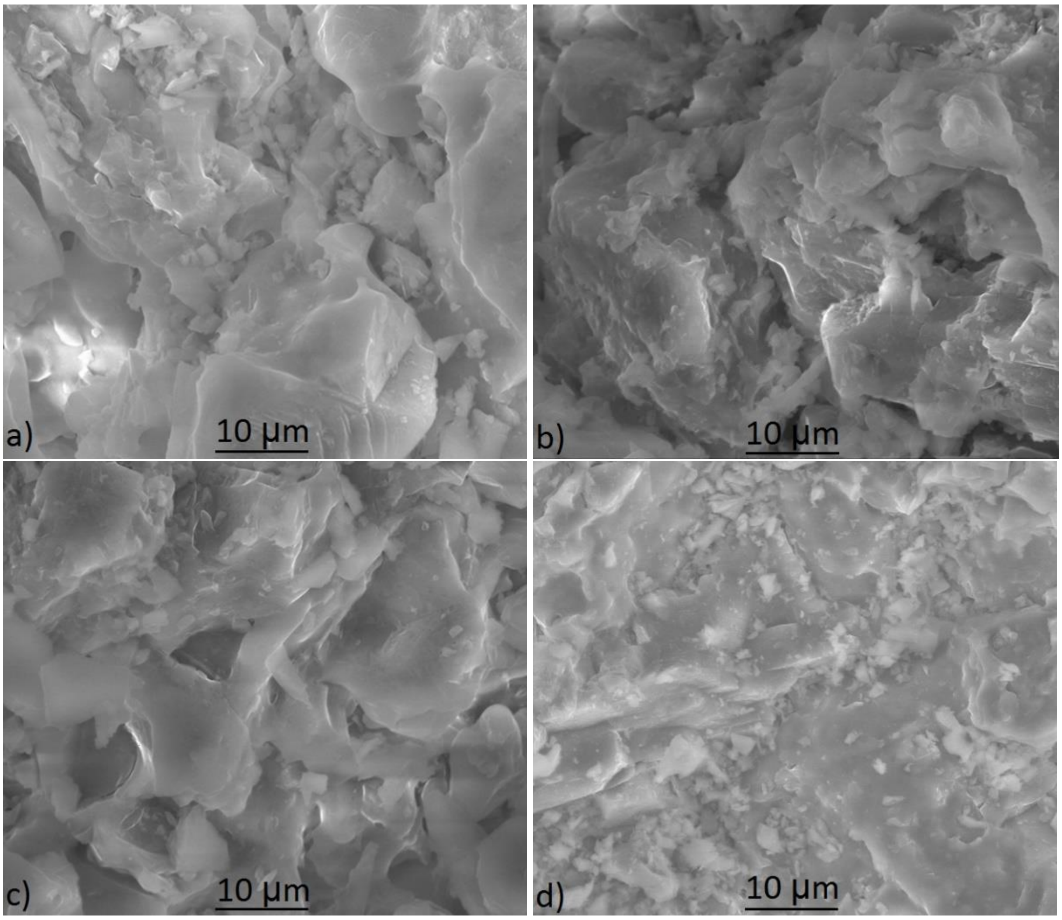

Figure 2. Scanning electron micrographs showing structure of the resulting ceramic materials: a) composition 1; b) composition 2; c) composition 3; d) composition 4

In addition to the porosity increase, the surface area of ceramic particles that is in contact with the aqueous medium also increases, which promotes heavy metal ions migration into the medium. Boric acid introduction along with the electroplating sludge causes vitreous phase formation in the ceramic structure (Fig. 2c), which partially fills pores and voids, thus reducing water absorption and heavy metal ions migration into the aqueous medium. When all three additives are used, the ceramic particles surface is vitrified, causing further increase in the vitreous phase content, covering most of the surfaces of ceramic particles with layers of different thicknesses and closing most of the open pores (Fig. 2d).

The extraction experiments (Table 2) demonstrated that samples containing electroplating sludge without the additional additives (composition 2), release the highest concentrations of all the considered metals in acidic media as compared to the other compositions. These concentrations are above the limits in the acidic extracts while although lower in the neutral medium (*i.e*. distilled water) still above the limits for chromium and nickel. The obtained concentrations , considering standard deviations from the average values, were compared to the maximum permissible concentrations (MPC) in water bodies used for domestic, drinking and recreational purposes [12].

Table 2. Determination of heavy metals concentrations in test media

Metal	Metal concentration, mg dm^{-3}		Metals MPC in water bodies*, mg dm^{-3} [12]
	In distilled water extract (pH 7.2)	In ammonium acetate extracts (pH 4.8)	
Composition 2			
Zinc	0.324±0.016	1.895±0.095	1
Chromium	0.058±0.003	0.295±0.015	0.05 for Cr^{3+}
Copper	0.012±0.001	1.514±0.076	1
Nickel	0.046±0.002	0.994±0.05	0.02
Composition 3			
Zinc	0.050±0.003	0.292±0.015	1
Chromium	0.009±0.001	0.045±0.002	0.05 for Cr^{3+}
Copper	0.002±0.001	0.233±0.012	1
Nickel	0.007±0.001	0.153±0.008	0.02
Composition 4			
Zinc	0.011±0.7	0.066±0.003	1
Chromium	0.002±0.001	0.01±0.001	0.05 for Cr^{3+}
Copper	0.000±0.001	0.052±0.003	1
Nickel	0.002±0.001	0.014±0.001	0.02

*used for household, drinking and recreating purposes

The excess of nickel ions in acidic media is observed for the samples produced with the combined introduction of galvanic sludge and boric acid (composition 3), while in neutral media, *i.e*. under normal operating conditions, the material can be considered environmentally safe. The normal operating conditions for this material include standard weather conditions in contact with the materials, typical for temperate climate latitudes in cold and warm seasons, in case the products are for exterior usage for buildings and structures cladding. Non-standard operating conditions when the material is in contact with low-pH environments may include acid rain, soil and aggressive chemicals. According to the data presented in the table, such material (composition 3) can only be used for standard operating conditions. The heavy metal ions concentration does not exceed the maximum concentrations in both neutral and acidic environments, *i.e*., both are suitable for standard and non-standard operating conditions for the samples produced using all the considered additives (composition 4). In this case, environmental safety is ensured by the vitrification effect, created by the combined application of all additives: boric acid is the fluxing agent, titanium dioxide is the vitreous phase source, and galvanic sludge is the modifier of vitreous phase properties. Herewith most of heavy metal compounds are a part of the vitreous phase, migration from which is almost impossible at normal performance conditions and is insignificant in acidic media.

4. CONCLUSION

Based on the conducted research results it can be concluded that by the sole galvanic sludge introduction, it is impossible to produce an ecologically safe material. But in the case that both galvanic sludge and boric acid are used, environmentally friendly construction materials can be produced only for applications under standard conditions.

However, under the exposure in acidic media, migration of environmentally hazardous heavy metals ions from this material is potentially possible. It means that this material cannot be used for the constructional cladding.

At the same time, a combined introduction of electroplating sludge, boric acid and titanium dioxide provides the development of environmentally safe ceramic cladding materials that can be used in any environmental conditions. The resulting ceramics possessing a glazing effect has sufficiently good operational properties and can be used for the construction of environmentally friendly buildings and structures.

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SAŽETAK

Efekat glaziranja pri proizvodnji ekološki prihvatljivih keramičkih fasadnih obloga

Elizaveta A. Pavlycheva, Evgeniy S. Pikalov i Oleg G. Selivanov

Vladimir State University, Vladimir, Russia

(Stručni rad)

U ovom radu su predstavljeni rezultati uporednih studija na temu ekološki prihvatljivih keramičkih materijala na bazi nisko-plastičnih glina sa dodatkom tri različita odnosa galvanskog mulja, borne kiseline i titan-dioksida. Eksperimentalni uzorci su dobijeni presovanjem pri pritisku od 15 MPa i pri maksimalnoj temperaturi pečenja od 1050 °C. Pre toksikoloških analiza dobijeni su ekstrakti ispitivanih materijala u neutralnom i kiselom medijumu na dnevnom nivou. Toksikološka bezbednost materijala procenjena je primenom metode za određivanje mortaliteta po Dafniju i upoređivanjem maksimalno dozvoljenih koncentracija teških metala za pijaću vodu i vodu za domaćinstvo sa koncentracijama teških metala udobijenim ekstraktima. Dobijeni rezultati pokazuju da kombinovana primena korišćenih aditiva rezultira efektom glaziranja površine keramičkih čestica, tako da je opisanim postupkom moguće proizvesti ekološki prihvatljiv materijal koji se odlikuje visoko-kvalitetnim svojstvima. Upotreba nisko-plastične gline i galvanskog mulja proširuje sirovinsku bazu za proizvodnju keramike i omogućava odlaganje ekološki opasnih jedinjenja koja sadrže teške metale koji se nalaze u galvanskom mulju. Keramički materijali na bazi prikazanog sirovinskog sastava mogu se koristiti za proizvodnju obloga za spoljne zidove zgrada i građevina generalno.

Ključne reči: bezbednost životne sredine; vitrifikacija; glina niske plastičnosti; mulj za galvanizaciju; teški metali