

Research Article

Heat-Resistant Ceramic Pigments on the Base of Waste Vanadium Catalyst and Alumina

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Ceramic pigments on the base of technogenic silica-containing material—waste vanadium catalyst were obtained in this work. Corundum is identified along with the predominant mullite phase in the composition of pigments. The ions of nickel, chromium, and iron are embedded in the structure if the concentration of the corresponding oxide in the initial mixture does not exceed 10 wt.%. In this case, the oxide is not identified in a free form according to the results of X-ray diffraction analysis. Spinel CoAl_2O_4 is formed in cobalt pigments. The developed pigments keep the firing temperature up to 1200°C. The obtained pigments may be recommended for ceramic paints and colored glazes for building materials.

1. Introduction

At the present, the construction industry needs decorative building materials, which are produced with the applying of ceramic pigments, dyes, and decorative glaze. There has been a great interest within the ceramic industry in the development of high-stability pigments, which show intense tonality and satisfy both technological and environmental requirements [1]. While the first step in pigment production involves the judicious choice of raw materials, current trends are towards alternative and less expensive raw materials [2–4]. Normally, the materials of a high chemical purity are used for pigment production. Selected industrial wastes have been investigated for this purpose and, in particular, metal-rich sludges [5–8]. Indeed, industrial processes such as galvanizing or surface coating consume large amounts of water, yielding high volumes of sludge, which requires both environmental and economic treatments [7]. Black ceramic pigments were prepared from Cr/Ni-rich sludge generated from Cr/Ni plating and Fe-rich galvanizing sludge generated during steel wire drawing [9]. In another work, chroma-tin red malayaite $\text{Ca}(\text{Cr}, \text{Sn})\text{SiO}_5$ pigment was synthesized using Cr/Ni plating sludge [10]. The ceramic pigments with wollastonite and diopside structures were produced using nepheline sludge [11].

The requirements to raw materials for ceramic pigment production are constant chemical composition, purity (no coloring impurities), and the ability to form stable crystalline structure. Ceramic pigments with the structure of the potassium feldspar were obtained in [12] with the use of a waste vanadium catalyst. The drawback of these pigments is low synthesis temperature 800–950°C and limited application: in overglaze ceramic dyes and for coloring of easily fusible glazes. Ceramic pigments with the mullite structure are characterized by high fire resistance and can be used for both overglaze and underglaze dyes.

The crystal structure of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is similar to the sillimanite one, despite some differences in their compositions. A characteristic feature of the mullite structure is the presence of two types of the Al^{3+} ions; a half of them enter into the crystal lattice with the coordination number 6, the other half with the coordination number 4 [13]. The pigments with the mullite structure are widespread and well known. They are synthesized from pure chemical agents at 1200–1300°C [14].

The purpose of this work was the production and investigation of heat-resistant ceramic pigments with mullite structure by using industrial waste vanadium catalyst.

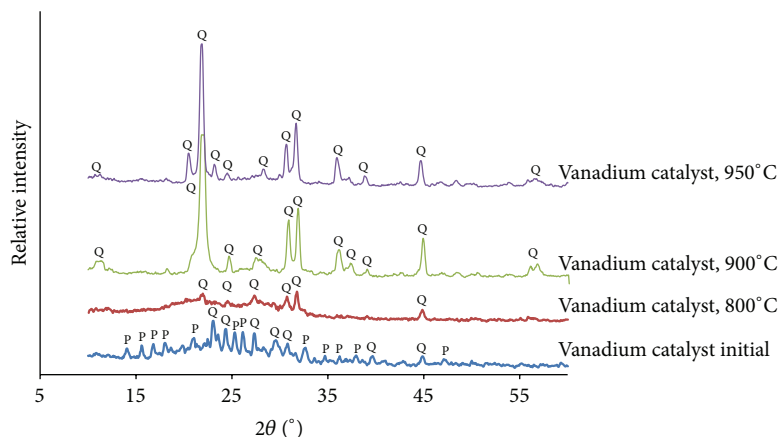


FIGURE 1: The XRD data of vanadium catalysts initial and calcinated at the temperatures 800, 900, and 950°C. Q quartz; P and potassium vanadium sulfate.

TABLE 1: Chemical composition of the waste vanadium catalyst.

Raw material	Oxide content, wt. %				Δm^1
	SiO ₂	Al ₂ O ₃	V ₂ O ₅	K ₂ O	
Waste vanadium catalyst	64.90	5.20	6.20	9.10	14.60

¹Ignition loss, wt. %.

2. Materials and Methods

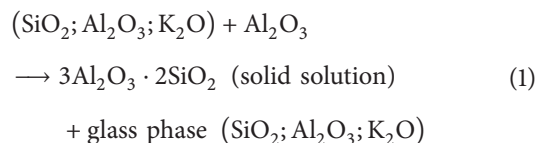
2.1. Raw Materials and Formulations. The raw material used in the study was a waste vanadium catalyst (WVC), which is used for the manufacture of sulfuric acid in the plant “Nitrogen” (Kemerovo, Russia) in the work.

Raw materials for WVC are natural diatomite, vanadium oxide (V₂O₅), potassium oxide (K₂O), and sulfur oxide (SO₃) in the form of potassium vanadium sulfate (K₂S₂O₇·V₂O₅). Diatomite contains 90% of the shells of diatomite seaweed; 2–7% of quartz; the rest are feldspar, glauconite, and mica.

The chemical composition of WVC was determined by X-ray fluorescence analysis (XRF, Philips X’UNIQUE II) (Table 1). Initial WVC contains significant amount of highly volatile components in the form of sulfur oxide SO₃. Thus, previously WVC was treated by heating at the temperatures 900–950°C for one hour to apply it for ceramic pigment production. Calcination at this temperature is necessary to remove the volatile impurities of sulfur oxide; at the same time, vanadium oxide is removed too. The main product of calcination is SiO₂ according the XRD data (Figure 1). The other oxides (Al₂O₃, K₂O) are contained in small quantities (see Table 1); so their reflexes are weak on radiographs. The major part of V₂O₃ was captured and removed along with volatile compounds during the heat treatment. The final color of pigments and dyes was not affected by V₂O₃, which has its own coloring ability.

The WVC comprised the structure-forming oxides—SiO₂, and Al₂O₃. Aluminum oxide (Al₂O₃) was added to the catalyst to provide mullite structure formation. Al₂O₃ was 99.9% of purity and particle size of 20–30 μm.

2.2. Preparation and Characterisation of Pigments. Waste vanadium catalyst was milled up to particle size less than 20–30 microns. Aluminum oxide is included in the catalyst composition but in a small concentration (up to 5 wt.%), which is not enough to form mullite. So additional alumina was added to WVC to obtain stoichiometric mullite by the following reaction:



Firstly, WVC of 42 wt.% and alumina of 58 wt.% were mixed without any chromophore by dry method in a ball mill for 3 h. This mixture was named as “check sample” (CS) and used to determine structure formation. The prepared composition mixture was sintered in corundum pots at $T_{\text{sint.}} = 1100\text{--}1200^\circ\text{C}$. The XRD analysis showed that mullite-corundum structure was formed instead of expected mullite one. This indicates that Al₂O₃ has not completely reacted and remained in the reaction products. But this fact does not affect the properties of the obtained pigments, in particular, on heat resistance. The mixtures on the base of WVC/Al₂O₃ in proportions, considering the content additive, were made to obtain pigments (Table 2). Water-soluble salts (nitrate or sulfate) of the d-elements: Ni²⁺, Co²⁺, Fe³⁺, and Cr³⁺ were injected in the mixture as chromophores. When heated, the decomposition of salts up to oxides and the removal of volatile residues take place. The chromophores have a high diffusion capacity in this state and, as a result, provide a stable bright color of pigments. The prepared mixture was subjected to wet grinding in a ball mill for 1 h, dried at $T = 120^\circ\text{C}$ for 2 h, and sintered in corundum pots at $T_{\text{sint.}} = 1100\text{--}1200^\circ\text{C}$. Prepared materials were being grinded in a ball mill for 24 h. The obtained samples were ground to a residue on the sieve no. 0063 (the size of the cell is 63 μm or 10.000 hole/sm²) no more than 0.2 wt.% to provide a uniform coating during further pigments application.

TABLE 2: The initial compositions to obtain mullite pigments.

Sample number	The content of main components, wt.%					
	WVC	Al ₂ O ₃	CoO	NiO	Cr ₂ O ₃	Fe ₂ O ₃
CS ²	42	58	—	—	—	—
M1	38	57	5	—	—	—
M3	34	51	15	—	—	—
M4	38	57	—	5	—	—
M6	34	51	—	15	—	—
M7	38	57	—	—	5	—
M8	36	54	—	—	10	—
M9	38	54	—	—	—	5
M10	36	57	—	—	—	10

²CS: check sample (without chromophores).

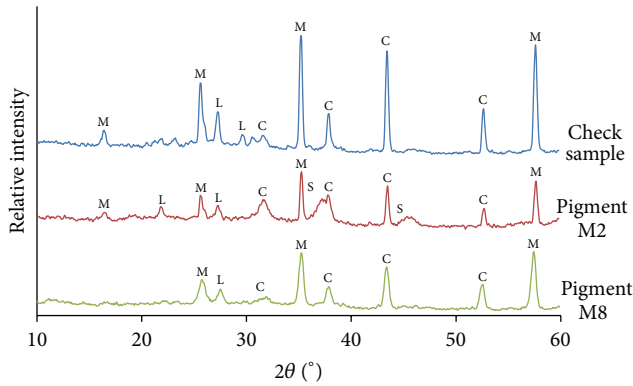


FIGURE 2: Radiograms of the check sample and the pigments of mullite composition, ($T_{\text{sint.}} = 1200^{\circ}\text{C}$): M: mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$); C: corundum (Al_2O_3); L: leucite ($\text{K}(\text{AlSi}_2\text{O}_6)$); S: spinel (CoAl_2O_4).

A preliminary characterisation of pigments involved the identification by X-ray diffraction (XRD-7000S Shimadzu) of the main crystalline phases formed, upon firing, and measurements of the CIE Lab colour parameters. The reflectance data in the visible region were used to obtain the three relevant parameters, L^* , a^* , and b^* , measuring the lightness, red/green and yellow/blue hue intensities, respectively [15]. The spectral reflection curves were measured on the spectrophotometer Cary 100 Scan to determine the color characteristics using MgO as a reference. The microstructure of the powders was revealed by scanning electron microscope (Philips SEM 515).

3. Result and Discussion

Polyphase structure was obtained at the firing of the samples without chromophores at the $T = 1100^{\circ}\text{C}$. It consisted of mullite ($d = 0,540; 0,348; 0,255\text{ nm}$), corundum ($d = 0,282; 0,208; 0,173\text{ nm}$), and leucite in a small quantity ($d = 0,326, 0,2827\text{ nm}$) (Figure 2). SEM data confirmed the formation of mullite and corundum (Figure 3). The needle crystals were characteristic for mullite, and the plate ones for corundum.

TABLE 3: The color of the pigments and some overglaze dyes.

Sample number	The color of overglaze dyes		
	1100°C^3	1200°C^3	850°C^3
M1 (Co^{2+})	Sky blue	Greenish blue	Sky blue
M3 (Co^{2+})	Blue	Blue	Blue
M4 (Ni^{2+})	Light green	Light olive	Light green
M6 (Ni^{2+})	Turquoise	Turquoise (darker)	Turquoise
M8 (Cr^{3+})	Dark olive	Dark olive	Brownish pink
M9 (Fe^{3+})	Light brown	Reddish brown	Brown
M10 (Fe^{3+})	Brown	Reddish brown	Brown

³Sintering temperature ($T_{\text{sint.}}$), $^{\circ}\text{C}$.

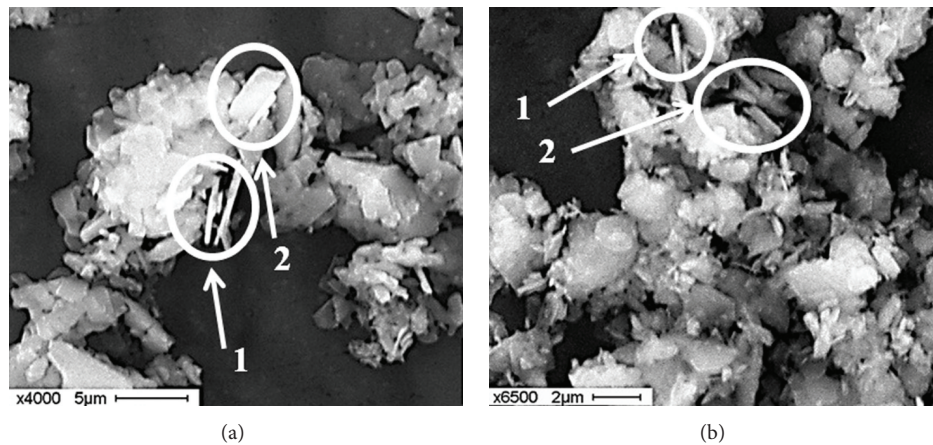
Some amorphization of the pigment structure was observed with the increase in the firing temperature up to 1200°C . It was associated with the presence of fusible potassium oxide K_2O in the WVC (9.1 wt.%) (see Table 1).

The intensity of the all reflections decreased when the chromophore was added (see Figure 2). This was due to the symmetry breaking and the crystal lattice distortion when the ionic chromophores incorporated into the structure and solid solutions formed [16]. It was assumed that the process of isomorphous entry of ionic-chromophores in mullite structure occurred in the position of aluminum Al^{3+} ($r_{\text{Al}^{3+}} = 0.053\text{ nm}$). Based on the similarity of the ionic radii and the equality of the charges, the process was more active with the participation of Cr^{3+} ($r_{\text{Cr}^{3+}} = 0.063\text{ nm}$) and Fe^{3+} ($r_{\text{Fe}^{3+}} = 0.064\text{ nm}$) ions, than at the presence of the Co^{2+} ($r_{\text{Co}^{2+}} = 0.072\text{ nm}$) and Ni^{2+} ($r_{\text{Ni}^{2+}} = 0.069\text{ nm}$) ones. Nickel, chromium, and iron ions were embedded in the structure up to the concentration of the corresponding oxide 10 wt.% at $T_{\text{sint.}} = 1200^{\circ}\text{C}$. The oxides were not identified in a free form according to the result of XRD analysis (see Figure 2). It is known that the maximum solubility of Fe_2O_3 in mullite at $T_{\text{sint.}} = 1600^{\circ}\text{C}$ is 12 wt.%, Cr_2O_3 —10 wt.% [13].

The spinel CoAl_2O_4 ($d = 0,242; 0,200\text{ nm}$) formed in the cobalt pigments. As a result, the pigments were colored in bright blue tones due to the tetrahedral coordination of the ion Co^{2+} in the spinel structure. The tone of the cobalt-containing pigments might be changed from sky blue to

TABLE 4: Color characteristics of the obtained ceramic pigments and dyes ($T_{\text{sint.}} = 1200^{\circ}\text{C}$).

Sample number	Pigment colour parameters			Dye colour parameters		
	L^*	a^*	b^*	L^*	a^*	b^*
M1 (Co^{2+})	48.0	0.0	-16.0	58.0	0.0	-15.0
M3 (Co^{2+})	38.0	0.0	-19.0	44.0	0.0	-10.0
M4 (Ni^{2+})	53.0	-6.0	6.1	66.0	-1.0	11.0
M6 (Ni^{2+})	46.0	-6.0	4.7	56.0	-4.0	9.4
M8 (Cr^{3+})	44.0	2.4	2.8	54.0	10.0	19.0
M9 (Fe^{3+})	47.0	4.3	9.9	57.0	11.0	15.0
M10 (Fe^{3+})	38.0	7.6	7.1	54.0	5.2	18.0

FIGURE 3: SEM images of the pigments of mullite composition: (a) check sample; (b) chromium-containing pigment. The areas on the images are 1—mullite, and 2—corundum ($T_{\text{sint.}} = 1200^{\circ}\text{C}$).

blue, depending on the concentration of oxide CoO (Table 3, Figure 4). Nickel oxide NiO gave pigments turquoise color, iron oxide Fe_2O_3 —reddish brown one. The coloration of the chromium-containing pigments varied from brownish pink (5 wt.% Cr_2O_3) to dark olive (10 wt.% Cr_2O_3). It depends on the polarization value and the distance between the chromium ion and its surrounding ions. The greater the distance between the Cr^{3+} and O^{2-} the weaker the connection and the less polarization of chromium ion. The absorption maximum was shifted to the red spectrum; thus, the pigments were painted in green tones.

The pigments of mullite composition were tested as overglaze colors (see Table 3). They were mixed with the flux. The chemical composition of concentrated flux was as follows (wt.%): SiO_2 (16.8), B_2O_3 (15.8), PbO (7.4). The contents of the pigment and flux were in the ratio 1:3. Such dyes were deposited on glazed ceramic articles and fired at a temperature of 850°C . Blue, turquoise, red, and brown paints were gotten. The color of the pigments did not change in overglaze dyes. Besides, the obtained pigments were added to the compositions of porcelain glazes in the amount of 5 wt.%. The glazes were calcinated at the temperature 1200°C . As a result, bright colored coverings were obtained. The color of all pigments in a glaze did not change too, which indicated the stability of the pigments under high temperatures in contrast to the pigments presented in [12].

The color coordinates L^* , a^* , and b^* (Table 4), which characterize the color properties of the pigments, were calculated using the spectral reflectance curves (Figure 5). For example, cobalt pigments had a higher color saturation, which was confirmed by high values of b^* in the blue spectral region of the system CIE L^* , a^* , and b^* [15].

4. Conclusion

The ceramic pigments were produced using technogenic silica-containing raw material—waste vanadium catalyst in the work. Corundum phase along with the predominant mullite is identified in the composition of the obtained pigments and dyes. The ions of nickel, chromium, and iron are embedded in the structure up to the concentration of the corresponding oxide 10 wt.%; in this case, the oxide is not identified in a free form on XRD pattern. The spinel CoAl_2O_4 forms in the cobalt-containing pigments. Cobalt pigments are characterized by the highest color saturation. The developed pigments keep a firing temperature up to 1200°C .

The research results show that the usage of vanadium catalyst is promising and economically expedient because the pigments synthesized on its basis are not inferior industrial pigments by color properties and heat resistance, and they exceed the pigments described in [9–12]. The pigments obtained in this work can be recommended for underglaze

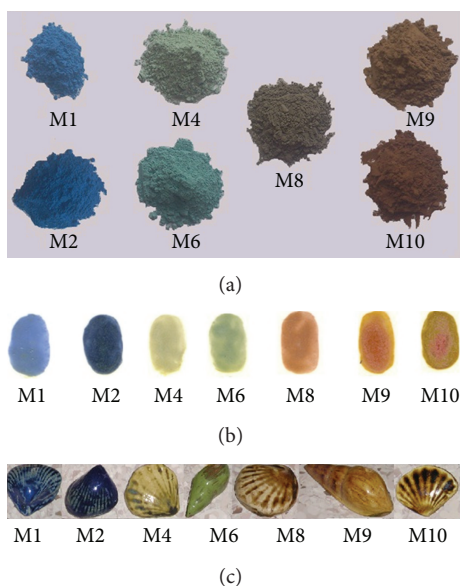


FIGURE 4: The color of the obtained pigments (a), overglaze dyes (b) and glazes (c).

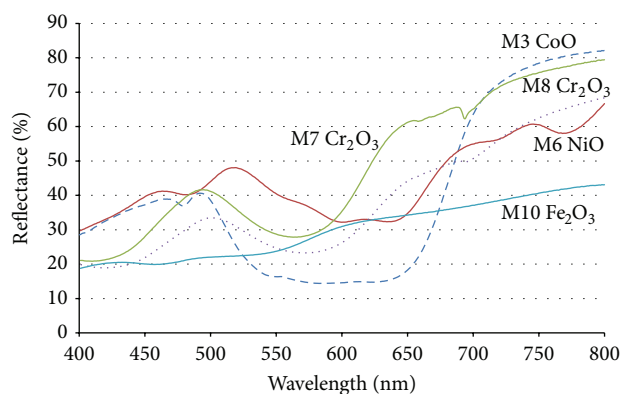


FIGURE 5: Spectral reflectance curves of the obtained pigments ($T_{\text{sint.}} = 1200^{\circ}\text{C}$).

and overglaze ceramic dyes, colored glazes, and for coloring of building materials.

Abbreviations

XRF:	X-ray fluorescence
XRD:	X-ray diffraction
SEM:	Scanning electron microscopy
WVC:	Waste vanadium catalyst
$T_{\text{sint.}}$:	Sintering temperature, $^{\circ}\text{C}$
CIE Lab:	Commission Internationale l'Eclairage—international commission on illumination of the standard colorimetric coordinates L^* , a^* , and b^* .

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