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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Pigments Based on Thermally Treated Iron-Containing Slimes

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Abstract—The effect exerted by chemical and phase composition on the color characteristics of the products of a heat treatment of slime obtained at purification of model wastewaters containing prescribed amount of zinc(II), nickel(II), copper(II), and chromium(III) compounds using ferroferrihydrosol was studied. The dependence of pigment properties of the products of the heat treatment of slimes on the concentration of metal compounds in them was determined.

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The treatment of wastewaters with ferroferrihydrosol (FFH) [aqueous suspension of iron(II) and iron(III) oxohydrates] to remove heavy metal ions yields slime containing high concentration of iron compounds. This makes it possible to obtain iron oxide pigments on its basis [1–3]. The slime contains metal compounds, main of them are zinc(II), nickel(II), copper(II), and chromium(III) compounds. Their concentration may reach 10 wt % and higher.

As known, a majority of 3*d*-metal ions are chromophores. The presence of even minor amounts of them can affect color shadow of pigments. This property is used in a so-called structural modification of pigment materials [4, 5].

The previous studies showed that cations present in slime not only affect the color characteristics of the heat-treatment products, but also change their phase composition, dispersion, and properties [6]. According to [6], other than hepatite crystalline phases in the thermally treated slime are associated with the formation of interstitial and substitutional solutions with participation of metal ions present in them. The formation of the above phases at the thermal treatment of slime affects the properties of the obtained products, in particular, their color characteristics. Data on the color and paint technical characteristics of the thermally treated slime containing a number of metal chromophores are virtually lacking, which essentially impedes their estimate as pigments.

Therefore, the study is concerned with the composition, color, and paint technical characteristics of the products of the thermal treatment of slimes obtained at treatment with FFH of model wastewaters containing prescribed amount of zinc(II), nickel(II), copper(II), and chromium(III) compounds.

EXPERIMENTAL

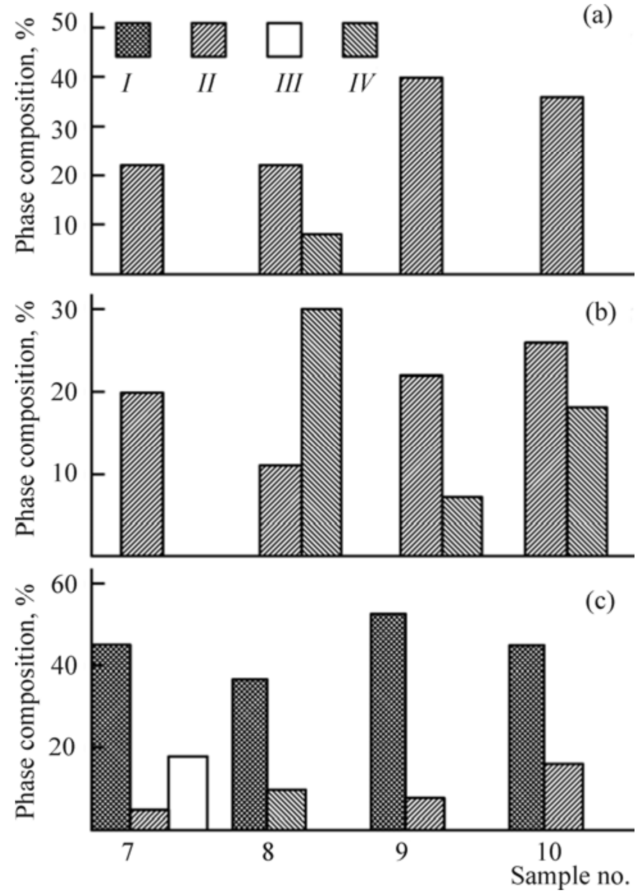
Model wastewaters with prescribed concentration of zinc(II), nickel(II), copper(II), and chromium(III) compounds and their treatment FFH were performed, according to the method described in [6]. The slimes thus obtained were dried at 200°C to constant mass and then heat-treated within 200–900°C. The concentration of main components in slime and thermal treatment products was determined by the known procedures of chemical analysis [7]. The phase composition of thermal treatment products was studied on a “Bruker” AXS 08 Advance diffratometer (Germany). The color characteristics of pigments were determined on a SF-18 spectrophotometer (“B” radiation source). The paint technical characteristics of pigments (covering power, oil number) were determined by the standard procedures [4].

The chemical composition of slimes obtained at treatment of model wastewaters with FFH and heat-treated at 200°C to constant mass is given in Table 1. In slime, as in FFH, the iron(II) compounds are major. The total concentration in slime of zinc, chromium, copper, and nickel compounds in terms of oxides lies within 10.0–20.0%. The concentration of each above-cited metal oxides in the samples varies from 0.9–1.0 to 14.1–14.3 wt %. The composition of a commercial slime sample is close to that of slime obtained from model solutions containing predominant amount of zinc compounds (sample no. 7).

The chemical composition of slime essentially affects the phase composition of heat treatment products [6]. The figure shows the phase composition of slimes under study heat-treated within 400–800°C. The main crystalline phase formed at 400°C was magnetite (Fe_3O_4). The diffraction pattern of sample no. 8 containing the maximal amount of nickel compounds also has reflections with the interplanar spacings typical of maghemite (γ-Fe_2O_3). Raising the heat treatment temperature of the samples to 600°C led to the formation of maghemite in other samples too. Exception was sample no. 7 containing 14.3% ZnO. The maximum concentration of γ-Fe_2O_3 had sample no. 8 containing predominant amount of nickel compounds in comparison with zinc, chromium, and copper compounds (Table 1). At thermal treatment of sample no. 10 containing maximal amount of chromium compounds, a γ-Fe_2O_3 phase was formed to lesser extent and in sample no. 9 containing maximal amount of copper it was formed to even lesser extent.

The samples thermally treated at 800°C also markedly differed by the phase compositions. Though the main crystalline phase was hematite, zincite (ZnO) and magnetite (sample no. 7), maghemite (sample no. 8), and magnetite (samples nos. 9 and 10) were also present in the thermal treatment products. Thus, the presence of the Zn^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+} cations in slime markedly affected the phase transformations proceeding in the course of thermal treatment and these phase transformations were responsible for the phase composition of the products being formed. The quantitative content of the phases formed jointly with hematite at thermal treatment of slime depends on the nature and mass fraction of the cations present in them [6, 8]. The given phases incorporated into the thermal treatment products had fairly intense color. Hematite is red, ferrites of many metals, Ni, Cu, and Cr in particular, black, and γ-Fe_2O_3, brown [4]. As noted, the thermal treatment products containing jointly hematite and magnetite (or maghemite) are dark brown or reddish-brown.

Table 2 presents the color characteristics determined spectroscopically and visually for samples nos. 1, 7–10 obtained at thermal treatment of slime using FFC, in which the concentration of zinc, nickel, copper, and chromium compounds was maximal (about 14 wt % in terms of metal oxides). The products obtained at thermal treatment using FFC at 700°C had dark reddish color and in the color characteristics were similar to red iron oxide pigments. For the product of FFC treatment (sample no. 1) obtained at 700°C, a color purity P was 34%, brightness was ρ = 10.6%, and a dominant wavelength, λ = 630 nm. For red iron oxide pigments the given characteristics are: λ = 598–605 nm, P = 17.5–420%, and ρ = 9.4–13.2% [6].



Phase composition (%) of slimes thermally treated at (a) 400, (b) 600, and (c) 800°C. Samples nos. 7–10 (see Table 1). (*I*) Hematite, (*II*) magnetite, (*III*) zincite, and (*IV*) maghemite.

The color of the products of thermal treatment of slimes within 400–900°C was changed markedly. The analysis of the data showed that the phase composition of the above products correlated to a certain extent with their color characteristics. For example, the initial slime dried at 200°C was black, greenish black or dark

Table 1. Chemical composition of slimes thermally treated at 200°C

Sample no.	Concentration of main components in terms of metal oxides, wt %						
	Fe_2O_3	FeO	ZnO	NiO	Cr_2O_3	CuO	Mass loss by calcination (900°C)
1[a]	85.6	9.2	–	–	–	–	5.2
2	76.5	7.2	2.8	2.9	2.8	2.7	5.1
3	72.1	6.9	10.1	1.9	1.8	1.8	5.4
4	68.9	8.3	2.6	9.9	2.5	2.4	5.4
5	74.2	7.2	2.3	2.2	2.4	9.8	1.9
6	74.5	6.1	2.0	1.9	10.1	1.8	3.6
7	70.3	7.4	14.3	1.4	1.2	1.4	4.0
8	73.4	6.8	1.0	14.1	0.9	0.9	2.9
9	72.5	6.1	1.4	1.1	1.3	14.2	3.4
10	72.3	7.1	0.9	1.0	14.2	0.9	3.6
11[b]	69.8	6.5	11.8	2.4	2.4	2.3	4.8

[a] FFH. [b] Sample of commercial slime.

brown, depending on the concentration of zinc, nickel, copper, and chromium compounds. The thermal treatment of slime with high concentration of zinc compounds yielded red or reddish brown product whose color intensified with temperature (sample no. 7). This may be due to splitting of metal-coordinated OH groups and formation of a new phase, zincite. The samples containing about 14.3 wt % of zinc oxide had higher brightness and better color purity than other samples of thermally treated slime.

The thermal treatment of slime containing high content of other metals yielded brown products differing in the shadows. In the case of thermal treatment of slime containing 14.4% NiO (sample no. 8), the products were dark brown, owing to nickel maghemite and nickel ferrites. At the same time, the thermal treatment products containing predominant amount of copper or chromium compounds (samples nos. 9, 10) had dirty brown color, which turned into dark brown at higher temperatures. This is because within 600–900°C maghemite and magnetite may exist. The diversity of colors of thermally treated slimes is accounted for by presence of Zn, Ni, Cu, and Cr metals, which are responsible for the direction of the phase and chemical transformation, composition of thermal treatment products, and for the formation of crystalline products of certain composition jointly with hematite.

The color characteristics for samples nos. 8–10 were comparable with those for brown iron oxide pigments with a dominant wavelength of 585–590 nm, color purity 10–30%, and brightness 10–15% [4].

To establish, if products of thermal treatment of slime may be used as inorganic pigments, we studied the pigment characteristics (covering power and oil number). As known, the covering power is expressed as the mass of the pigment per unit surface area (g m^{-2}) required for the formation of a homogeneous covering layer. The covering power of inorganic pigments varies within wide range. For example, for natural iron oxide pigments it varies from 10 to 90 g m^{-2} and for red synthetic pigment, within 4–7 g m^{-2}. It was shown that the covering power of the products of thermal treatment of slimes under study varied within wide range. Note, samples with the minimal covering power (6–10 g m^{-2}) were obtained at treatment of slime within 600–800°C. The products obtained at higher temperatures had the covering power 18–50 g m^{-2}. The decrease in the covering power at higher treatment temperatures may be caused not only by an increase in the average size of particles being sintered but also by the change in the phase composition of the thermal treatment products. In the temperature range from 800°C and above the processes of ferrite formation proceeded more intensely. For example, the main crystalline

Table 2. Phase composition and color characteristics of the products of thermal treatment of slimes

Sample no.[a]	Phase composition of thermal-treatment products	Thermal treatment temperature, °C	Color characteristics			Color characterization by visual observation
			P, %	ρ, %	λ, nm	
1	Hematite	700	34	10.6	630	Dark red
7	Magnetite	400	37	14.3	603	Reddish brown
		700	37	15.3	602	Reddish brown
	Hematite, zincite, magnetite	800	41	17.1	603	Red
	Hematite, franklinite,	900	40	17.6	603	Red
8		400	25	11.4	605	Brown
	Magnetite, maghemite	600	23	13.0	603	Brown
		700	20	13.4	605	Dark brown
	Hematite, maghemite	800	20	11.7	608	Dark brown
9	Maghemite, magnetite	600	7.5	10.4	500	Cherry-brown
		700	30	12.9	604	Dirty brown
	Hematite, magnetite	800	25	11.5	603	Brown
		900	15	10.2	605	Dark brown
10	Magnetite, maghemite	600	25	12.3	598	Brown
		700	24	11.3	602	Brown
	Hematite, magnetite	800	27	12.3	598	Dark brown
Red iron oxide pigment	Hematite	–	17.5–42.0	9.4–13.2	598–605	Red or reddish brown, depending on brand

[a] Sample nos. are the same as in Table 1.

phase in sample no. 7 with high zinc content obtained at thermal treatment at 900°C was franklinite ($ZnFe_2O_4$), whereas at 600–800°C, hepatite.

The oil number is one of main characteristics of the pigment quality associated with their wetting ability by hydrophobic fluids. For the products of thermal treatment of slime the given characteristics was 45–75 g/100 g. This was somewhat higher than for red and brown natural and synthetic iron oxide pigments (20–50 g/100 g). As noted, the oil number of the products decreased with increasing temperature (55–75 g/100 g at 500–600°C and 45–60 g/100 g at 700–900°C).

CONCLUSIONS

(1) It was shown that thermal treatment of iron-containing slime obtained at treatment of wastewaters with ferroferrihydrosol within 600–900°C yields products, which in paint technical characteristics are comparable with natural and synthetic iron oxide pigments.

(2) It was found that the thermal treatment of slime containing 10.0–14.0 wt % of zinc compounds in terms of ZnO at 800°C yields products containing reddish brown hematite as major component, which have higher brightness and better color purity. The crystalline products obtained at thermal treatment of slime containing 10.0–14.0 wt % of copper or chromium are brown hematite, magnetite, and maghemite.

(3) The formation of maghemite and nickel ferrites, along with hematite, at thermal treatment of slimes containing predominant amount of nickel compounds leads to dark brown products.

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