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OBTAINING OF BROWN PIGMENTS FROM CONCENTRATED WASTE WATER CONTAINING NICKEL

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Abstract. The possibility of obtaining brown pigments with the use of blast furnace slag from waste water containing nickel is justified. The scheme of the main reactions is proposed. The kinetics of the reactions is studied. The contribution of the chemical interaction into the overall degree of treatment is established by potentiometric titration. The influence of the main factors on the degree of nickel extraction is determined. The phase composition of the formed pigment is established with the help of X-ray analysis. Rheological properties of the pigment particles are set. The main color characteristics of the obtained products are identified by visual and spectrophotometric way. X-ray microanalysis indicated the presence of the two phases in the obtained precipitate. Dispersed and phase compositions of the original slag determine the rheological properties of the pigment. By varying the synthesis parameters, the obtained patterns provide us with possibility of receiving pigments of the color from light brown to deep brown.

Keywords: pigment, chromophores, slag, nickel.

1. Introduction

The limitation of negative human impact on the environment and the rational use of natural resources is the major environmental and economic problem.

Billions of cubic meters of waste water containing heavy metals salts, large-tonnage solid waste including steel and blast furnace slag, waste of wet magnetic separation of ferruginous quartzite, *etc*. are formed and accumulated annually.

In many cases wastewaters treatment is not complete and large-tonnage solid waste is not used or slightly involved in the recycling process, which is caused by multi-component and variability of their composition, the lack of reliable recycling technologies, as well as by the versatility of physico-chemical processes and the influence of various factors on these systems.

Moreover, the wastewater treatment uses expensive chemicals. The most important techniques are membrane filtration: ultrafiltration, nanofiltration and reverse osmosis chemical precipitation, coagulation–flocculation, flotation; electrochemical treatment techniques: electrodialysis, membrane electrolysis and electrochemical precipitation, electroextraction; and sorption treatment techniques: ion exchange, adsorption, and biosorption [1-10]. Similar to other heavy metals the presence of nickel in the environment is a major concern due to their non-biodegradability, bioaccumulation tendency, persistence in nature and toxicity to many life forms. Therefore, treatment of wastewaters containing heavy metal ions before discharge is an important component of water pollution control and becomes more important with the increasing of industrial activities

The approach is alternative and optimal when physico-chemical properties of the substances that make up the industrial waste are used for treatment and waste products themselves serve as raw materials [11-18].

In connection with this, the researches directed at solving the problems of complex processing and disposal of solid and liquid waste are opportune and topical.

The aim of this work is to study the possibility of obtaining pigments with the use of blast furnace slag, to develop the technology of recycling nickel-containing waste water with obtaining the pigments of brown color gamma that are capable of replacing toxic pigments which are used in serial primers at present.

2. Experimental

We used model solutions based on nickel(II) sulfate (purchased from Aldrich) of different concentrations (mol/l):0.77; 0.37 and 0.17.

The experiments were performed in a thermostatically controlled cell at the temperatures of 293, 313 and 333 K. The temperature was kept constant ±0.5 K by the thermostat UT-5.

The concentration of nickel in the solution was determined by trilonometry.

The phase composition of the dried powders was determined by X-ray diffraction (DRON-2.0, Cu- K_α-radiation), the color characteristics of the pigments were studied by colorimetric method.

Scanning electron microscopy with X-ray microanalysis was implemented on the device Remmy-102 (SELMI, Ukraine).

Energy dispersive spectrometer EDX (Edar) was used for the microanalysis of the elemental composition of nanoparticles.

The studies on obtaining pigments on the base of metallurgical industry waste were carried out by using blast furnace slag.

In this work the effect of temperature, slag mass and duration of the process on the residual concentration of nickel in the solution and the color characteristics of the pigment were studied. At the first stage of the research it was necessary to estimate the adsorption capacity of the slag which determines the ability to bind nickel cations. Various combinations of Slag: Ni^{2+} were used for the more detailed study of the conditions of obtaining the precipitate.

The ratio was determined by the formula:

$$n = \frac{m_{slag}}{V \cdot C_{Ni2+}} \quad (1)$$

where C_{Ni2+} is the concentration of the initial solution, g/l; m_{slag} is mass of slag, g; V is the volume of solution, l.

3. Results and Discussion

The justification of the conditions of conducting the experiments, the basic properties and characteristics of the slag are given in Table 1.

It is the high basicity of the slag that maintains pH in the solution which is necessary for the formation of poorly soluble hydroxide $Ni(OH)_2$. Besides, the presence of polysilicon acids increases the process efficiency.

Having a high surface, polysilicon acids form colloidal particles which are capable to interact with nickel ions with the formation of hydroxysilicates according to the scheme:

$$SiO_3^{2-} + 6H_2O + Ni^{2+} \rightarrow NiSiO_3 \cdot 6H_2O \quad (2)$$

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \quad (3)$$

At the first stage of the research the ability of the slag to bind nickel cations was determined. The results of the research are presented in Figs. 1 and 2.

Based on the obtained data from Fig 1, it can be stated that the optimum ratio depends on the initial concentration of nickel in the solution. The higher the content of nickel in the solution, the greater the value of n which provides the high degree of treatment. The degree of nickel extraction increases with the increase of the temperature during the process. The initial concentration of nickel has no appreciable effect on the degree of conversion – residual concentrations of nickel are low in all model solutions. The ratio equal to $n = 4$ is limiting and further increase has no effect on the residual concentration of nickel sulfate in the solution, therefore a fixed amount of slag was chosen when studying the kinetics of the process.

When studying the kinetics of the reaction (3) at the constant temperatures of 293, 313 and 333 K, different initial concentrations and the optimal ratio n were selected.

By analyzing Fig. 2, we can say that the reaction rate increases sharply with the temperature increase. All plots are similar in character: the reaction rate in the first region is relatively low and is apparently determined by the chemical interaction of nickel cations with amorphous alkaline-earth oxides and is almost independent of the temperature.

The differences in the reaction rate are found in the second stage of the process defined by the chemisorption of the hydroxide formed.

To confirm the assumption of the possibility of chemical interaction slag with nickel cations the process of the precipitation of poorly soluble compounds was studied by potentiometric titration of the model solution of nickel sulfate with the products of slag hydrolysis.

The curve of potentiometric titration is characterized by a decrease in pH at the initial stage that is defined by the hydrolysis of salts being formed and the presence of numerous plateaus due to the complex composition of the precipitate formed. The degree of extraction in this case is not more than 42 %.

Thus, we can assume that there is an overlapping of the chemical interaction at the first stage with further chemisorption of the precipitate on the slag surface with the degree of nickel extraction of 98–99 %.

Table 1

The chemical composition of slag samples in terms of oxides

Oxides	SiO_2	$A1_2O_3$	CaO	MgO	FeO	Fe_20_3	TiO_2	K_2O	Na_20	SO_3
Content, wt %	38.46	7.16	46.04	4.91	0.49	0.28	0.22	0.51	0.32	1.61

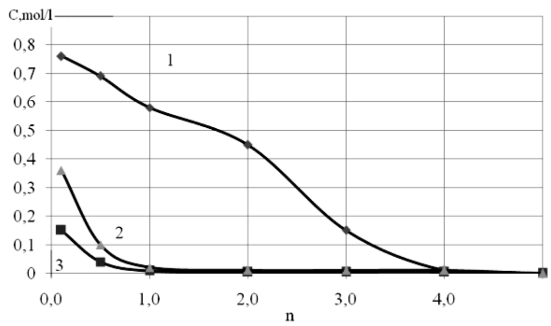


Fig. 1. Dependence of the concentration of Ni^{2+} (mol/l) on the value of *n* (*t* = 30 min, *T* = 293 K)

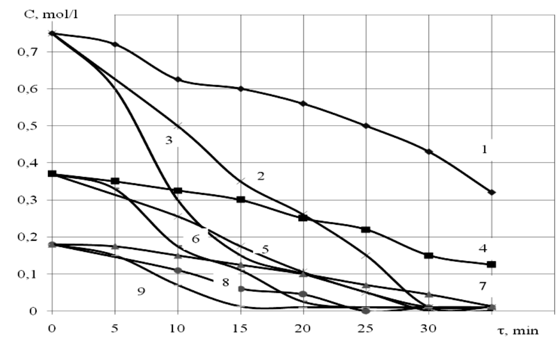


Fig. 2. Dependence of the concentration of Ni^{2+} (mol/l) on time at different temperatures (K): 293 (1, 4, 7); 313 (2, 5, 8) and 323 (3, 6, 9). $C^0_{Ni^{2+}}$ (mol/l): 0.77 (1-3); 0.47 (4-6) and 0.17 (7-9)

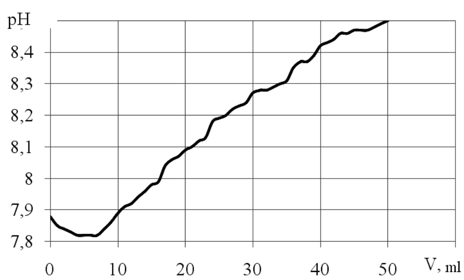


Fig. 3. The dependence of the solution pH on the amount of the slag extract (slag mass ratio to the weight of water 1:40)

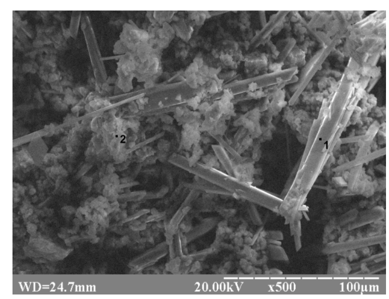
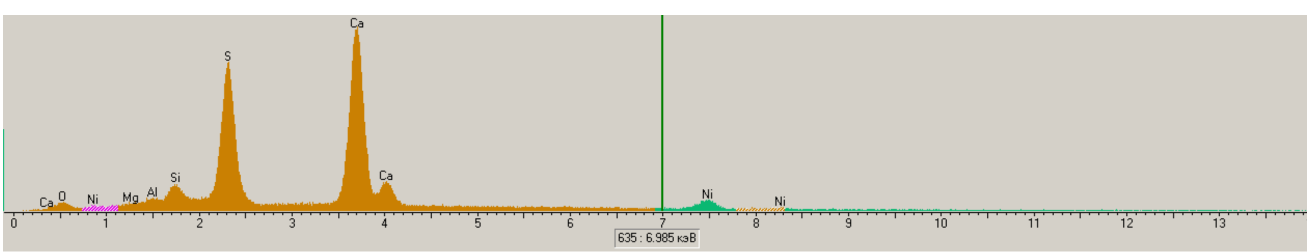
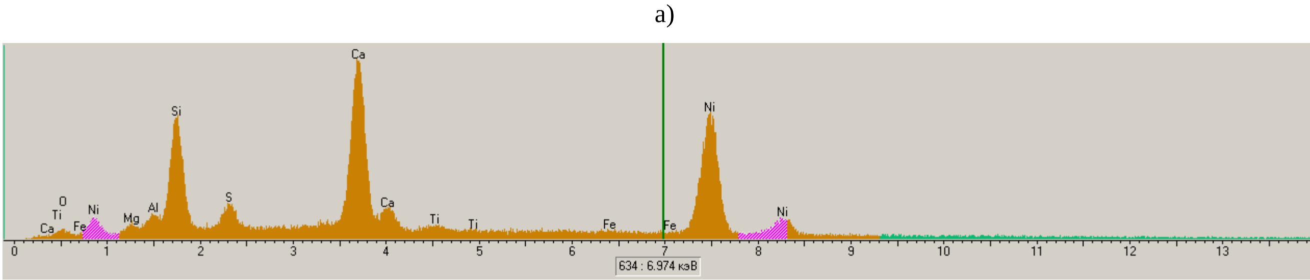


Fig. 4. The microphotograph of the particles of the obtained pigment on the basis of blast-furnace slag



a)



b)

Fig. 5. Elementwise composition of the powders: phase 1 (a) and phase 2 (b) (*vide* Fig. 4)

Table 2

The color characteristics of the obtained pigments

Experimental conditions	*X*	*Y*	*Z*	*x*	*y*	*λ*, nm	*P*, %
n = 5; *T* = 313 K; $C^0_{Ni^{2+}}$ = 0.77 mol/l	22.47	17.92	5.258	0.4921	0.3926	615	15
n = 5; *T* = 773 K; $C^0_{Ni^{2+}}$ = 0.77 mol/l	17.63	14.03	4.463	0.4880	0.3883	618	5

The main technological properties of the pigment are its color characteristics. Nickel cations are traditionally used for producing the pigments of black and brown color gamma. Therefore we investigated the effect of synthesis conditions on the color gamma and color intensity.

To obtain a pigment of specified color gamma the precipitate was calcined at the temperature of 773 K.

To determine the chemical composition of the formed compounds we performed microscopic analysis, which showed that the system is two-phase one (Figs. 4 and 5).

The first phase is depleted by nickel and contains silicates and sulfates of calcium, the second phase is enriched in nickel and is apparently presented by hydroxides and silicates. Under the interaction with concomitant sulfate ions, calcium hydroxide forms a thermally stable and neutral (relative to the pigment) compound.

Thus, the overlapping of the chemical interaction at the first stage with further precipitate chemisorption on the slag surface is confirmed.

Under the investigation of the formed precipitate it was ascertained that the granulometric composition of the obtained pigment is defined by the size of blast furnace slag particles and is 2–4 microns.

The characteristics of the powders are shown in Fig. 6 and Table 2.

The phase composition of the initial slag, as well as uncalcined and calcined precipitates have the fundamental differences: the initial slag is amorphous, while the slag treated in the solution has a peak corresponding to nickel and aluminum compounds, the final product has the peaks corresponding to the complex color-forming compounds being formed during sintering.

It has been determined that the intensity of pigment coloring depends in a large measure on the ratio of *n* and less on the process duration and temperature.

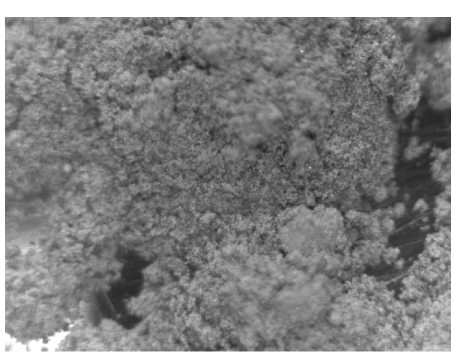


Fig. 6. The powder of nickel containing precipitate after calcinations

4. Conclusions

As the result of the investigations performed, the possibility of obtaining pigments of brown color gamma based on blast furnace slag with the conversion of 97–98 % is established. Dispersed and phase compositions of the initial slag determine the rheological properties of the pigment. By varying the synthesis parameters, the obtained patterns provide us with possibility of receiving pigments of the color from light brown to deep brown.

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ОДЕРЖАННЯ КОРИЧНЕВИХ ПІГМЕНТІВ З НІКЕЛЬВМІСНИХ КОНЦЕНТРОВАНИХ СТІЧНИХ ВОД

Анотація. *Обґрунтовано можливість одержання коричневих пігментів з нікельвмісних стічних вод, використовуючи доменний шлак. Запропоновано схему основних реакцій. Вивчено кінетику реакцій. Методом потенціометричного титрування встановлено внесок хімічної взаємодії в сумарний ступінь перетворення. Визначено вплив основних чинників на ступінь вилучення нікелю. За допомогою рентгенофазового аналізу встановлений фазовий склад пігменту, що утворюється. Встановлені технологічні властивості частинок пігменту. Візуально і спектрофометрично визначені основні колірні характеристики одержаних продуктів. За допомогою рентгенівського мікроаналізу показано наявність двох фаз в отриманому осаді. Дисперсний і фазовий склади вихідних шлаків визначають технологічні властивості пігменту. Отримані закономірності дають можливість, варіюючи параметрами синтезу, одержувати пігменти від блідо-коричневого до насиченого коричневого кольору.*

Ключові слова: *пігмент, хромофори, шлаки, нікель.*