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Use of Chromium-Containing Sewage Water Slime in the Technology of a New Abrasive Material

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Abstract

A technology for recycling of chromic waste to obtain abrasive material for polishing has been proposed whose introduction will efficiently solve the ecological problem of the region. The abrasive material obtained has a polishing ability which exceeds by 5–7 times that of currently produced abrasive chromium oxide and ensures a high purity of treating the surface of steel ShKh-15 (R_z = 0.08–0.10 μm), which is due to formation of solid solutions and, as a consequence, a change of abrasive activity and of dispersed composition of the material.

INTRODUCTION

The problem of protection of environment is associated, as a rule, with its three main components – atmosphere, lithosphere and hydrosphere. As long ago as the 1960ies, the great radiobiologist and geneticist N. V. Timofeev-Resovskiy pointed out that only 3 % of the Ural waters are fit for drinking and 20 % are so for industrial use. At present, out of 18 414 rivers, 1200 ponds and 2500 lakes of the Sverdlovsk Region none may be considered as clean, and only 10 % of surface waters are purified to standard criteria [1].

Production of chromium compounds belongs to the category of dangerous to man and environment, especially dangerous being chromium (VI) which possesses carcinogenic and mutagenic properties. In Russia, there are two plants that produce chromium compounds, and both of them are situated in the Urals: one is in Pervoural'sk, the other one in Novotroitsk. According to the currently existing technology for production of chromium compounds, obtaining 1 t of ready product is accompanied by release of 2 t of solid wastes containing up to 5 % of chromium (VI). Particularly, at the Pervoural'sk Plant (Russian Chromium-1915 Co.), the mass of these wastes amounts to 7 mln t. Therefore, their possibly rapid processing or neutralization is urgent.

Besides, there is an acute problem of processing the slime of chromium-containing sewage waters. So, *e. g.*, since the production began in Pervoural'sk, as a result of neutralization of chromium-containing sewage waters using the reagent method in slime pond, about 100 000 t of solid wastes containing chromium, iron, calcium, magnesium hydroxides and calcium sulphate have been accumulated. Although the proportion of these wastes in the slime obtained from chromium ore processing amounts only to 1.5 %, nevertheless this problem must be solved as soon as possible, because the water, and partially the slime, are discharged into the Chusovaya river. According to the data of the Sverdlovsk Sanitary and Epidemiological Station, the chromium (VI) concentration in the waters of the Chusovaya river exceeds by 14 times the maximal permissible concentration .

When choosing the sewage purification technique, one proceeds from the volume, concentration of harmful compounds and qualitative composition of the water, and from the concentration of these compounds that is permissible for discharge. For example, the maximal permissible concentration of Cr(VI) for fishery water bodies is 0.001 mg/l, for potable water bodies 0.05 mg/l, while its concentration in chromium production sewage waters may be as high as 500–1500 mg/l at the expenditure rate of 150–200 m^3/h; therefore, efficient purification methods are necessary.

The currently used methods of sewage detoxication in the production of chromium compounds, such as reagent [2–5], sorption [6–16], coagulation and electrochemical [17–20], flotation [21, 22] and biological [23, 24], cannot ensure a complete utilization of solid wastes formed as a result of neutralization of sewage waters. On the basis of ion-exchange [25–27] and membrane [28–30] methods, the task of purification of sewage waters from chromium without formation of solid wastes can be solved, however there arise difficulties of regeneration of exchangers and membranes with attainment of a degree of purification corresponding to the maximal permissible concentration of chromium.

When using methods based on sorption or adsorption of Cr(III) and Cr(VI) by peat [6], $Cr_2O_7^{2-}$ ions by active carbon [7–10], Cr(III) by iron hydroxide [11, 12], ions by magnetite [14], ferrite [15] and natural materials [13, 16], solid wastes requiring utilization are formed. The use of reagent methods for neutralization of sewage waters in the production of chromium compounds with reduction of chromium (VI) and its sedimentation according to reaction

$$Na_2Cr_2O_7 + 6FeSO_4 + 7H_2O + 5Ca(OH)_2 = Na_2SO_4 + 6Fe(OH)_3\downarrow + 2Cr(OH)_3\downarrow + 5CaSO_4\downarrow \quad (1)$$

results in a 10-fold increase in the sediment mass which it is necessary to separate from the liquid part and to utilize or to store in storage ponds. As the reductant, sodium sulphite or pyrosulphite, powdered iron, or iron sulphide are also used [2–5]. The composition of the solid part of the suspension obtained in neutralization of the sewage waters is close to that of chromate slime, therefore it may be used as a raw material in the same production as that of the main slime; however, there arise difficulties in separating the solid part from the liquid one.

In the present work, it is proposed to use flotation as the separation technique, whereupon the solid part of the slime may be used for production of modified abrasive chromium oxide which possesses a high polishing ability ensuring the 13th class of purity of treatment of metallic surfaces in finishing polishing operations. The use of such a method makes it possible to solve two tasks – ecological one and that of heightening the quality of abrasive material for polishing.

In this way, the goal of the present work is development of a technology for processing of the slime formed in neutralization of sewage waters discharged in the production of chromium compounds with obtaining a modified chromium oxide possessing a high polishing ability.

EXPERIMENTAL

Specimens of modified chromium oxide were obtained by the method of isothermic stand of a mixture of CrO_3 and slime formed in neutralization of chromium production sewage waters for 1.0–1.5 h at the 1st stage temperature of 350–500 °C, and for 1.5–2.0 h at the 2nd stage temperature of 900–1150 °C. The slime formed as a result of neutralization of sewage waters by reaction (1) represents a suspension containing hydroxides of Fe^{2+}, Cr^{3+}, Ca^{2+}, $CaSO_4$ and $CaCO_3$. After a partial separation of the liquid phase by filtration and washing with water, the composition can be as follows, % mass: Fe_2O_3 8.1, Cr_2O_3 2.1, CaO 1.07, H_2O 84.2.

RFA analysis of specimens was carried out using diffractometers DRON-3M (CuK_α radiation, Ni filter) and DRON-2 with a high-temperature attachment UVD-2000. The dispersion composition was assayed by means of sedimentation technique on a sedimentograph Analyzer SA-CP2 (Shimadzu) (ethylene glycol as the dispersion medium, with the density of 1.5 g/cm^3, the speed of rotor rotation 1500 r.p.m.), and by electron-microscopic photographs made with the help of an electron microscope D-2 Zeiss and a scanning electron microscope JSM-35 CF at the accelerating voltage of 15 kV.

According to standard techniques, the abrasive properties of the specimens were estimated by the change of efficiency (or polishing ability) and the surface roughness after abrasive treatment (R_z) as measured by the average profile unevenness over 10 points on the reference stretch of 0.08 mm. The surface roughness after polishing was controlled using a microinterferometer MII-4 according to [31].

RESULTS AND DISCUSSION

The pattern of synthesis of modified chrome oxide has been considered in [32–34]. According to RFA data, annealing a mixture of CrO_3 and slime paste within the temperature range of 350–450 to 900–1100 °C results in formation of a substitution solid solution based on α-$(Cr_{1-x}, Fe_x)_2O_3$. The process of obtaining modified Cr_2O_3 may be represented as follows:

$$CrO_3 + Fe(OH)_3 \xrightarrow{200-250\ °C} Fe_2(OH)_2(Cr_2O_7)_2$$

$$^{350\ °C}\quad Fe_2(OH)_2(CrO_4)_2 \quad ^{500\ °C}\quad Fe_2O_3$$

$$+ Cr_2O_3 \xrightarrow{950-1150\ °C} \alpha\text{-}(Cr_{1-x},Fe_x)_2O_3 \qquad (2))$$

The dependence of parameters a, c and volume V lattices on the concentration of Fe_2O_3 in solid α-$(Cr_{1-x}, Fe_x)_2O_3$ solutions obeys the Vegard's law, and the homogeneity region corresponding to the maximal polishing ability is $0.025 < x < 0.18$.

Earlier, it was established that the optimal CrO_3 to slime mass ratio was 1/0.75–2.25. Therein, a necessary amount of iron oxide was added to the solid solution (content of Fe_2O_3 is 0.038–0.11 % mol.). It was also established that the heat treatment regime in the process of synthesis of modified chromium oxide influenced the polishing ability of the specimens. At an iron oxide mole fraction of 0.038–0.11 % in the specimens, the optimal temperature of the 1st stage was 350–400 °C, that of the 2nd stage was 1000–1100 °C; therein, the surface roughness varied within the range of 0.08–0.10 μm, and the polishing ability was 0.50–0.76 mg/(min cm^2). The pattern of dependence of the polishing ability on the iron oxide concentration and on the regime of heat treatment of the mixture of chromium anhydride and slime gives reasons to suppose that the synthesis of solid solution based on chromium and iron oxides with the high polishing ability (0.5–0.76 mg/(min cm^2) and therefore with a high abrasive activity is determined by the formation, at the 1st stage of heat treatment (350–450 °C), of iron chromates and bichromates (see scheme (2)).

By the data of sedimentation (Fig. 1) and electron-microscopic (Fig. 2) analyses, addition of Fe_2O_3 (0.038–0.11 % mol.) to chromium oxide in the form of slime increases the size of particles of the basic fraction (as compared to Cr_2O_3 specimens) to 2–3 μm. The particles are characterized by a pronounced crystalline edging and have an equiaxial hexagonal form. The fraction with a size of less than 0.5 μm is absent. As the mole fraction of Fe_2O_3 increases to more than 0.138 %, the size of particles of the basic fraction shifts to the fine-grained region of ≤0.5 μm. The minimal surface roughness after polishing (0.08–0.09 μm) is observed within the Fe_2O_3 mole fraction of 0.01–0.038 % in the mixture, and heightens to 0.1 μm as the latter increases.

As a result of physicochemical study of the synthesis pattern and of tests on a model device, an enlarged lot of modified chromium oxide has been obtained, and a technological diagram has been proposed which includes the following stages:

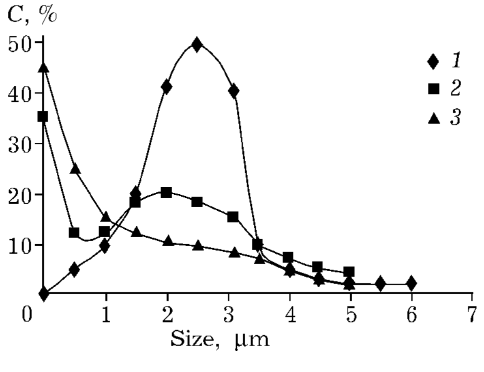

Fig. 1. Curves of distribution of specimens obtained at the 2nd stage heat treatment temperature of 1000–1100 °C with respect to particle size. The Fe_2O_3, % mol.: 0.038–0.11 (*1*), 0.006–0.012 and 0.125–0.138 (*2*), 0.138–0.15 (*3*).

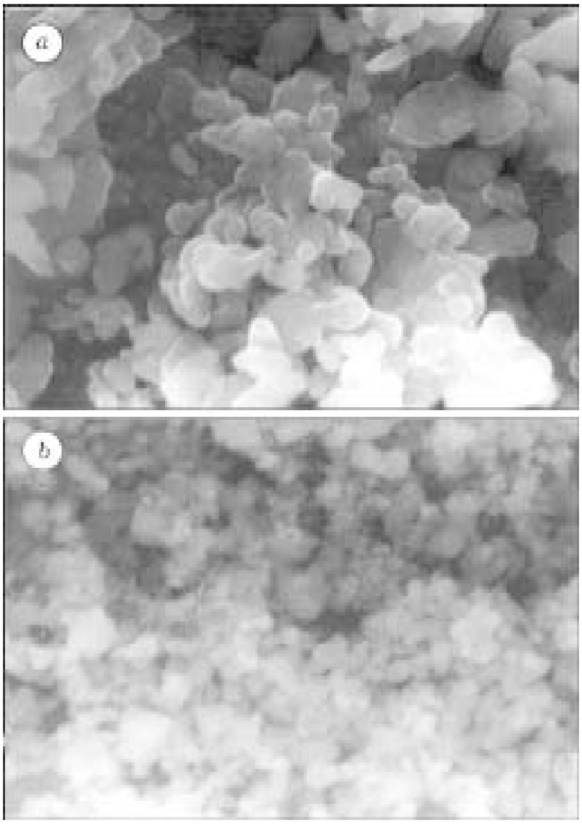

Fig. 2. Electron micrographs of specimens made on a scanning electron microscope (×30 000). Fe_2O_3 content, % mol.: 0.06 (*a*) and 0.15 (*b*).

1) separation of sediment from the liquid phase after neutralization of sewage waters;

2) obtaining a suspension of chromium anhydride and a sediment;

3) heat treatment of the suspension at 350–370 °C for 0.75–1 h and at 980–1100 °C for 1.5–2 h;

4) extinction and liming the chromium oxide cake;

5) grinding, classification and washing from water-soluble compounds.

For a complete transition of chromium (VI) to Cr_2O_3, as it is shown in [35], heat treatment of the cake of modified chromium oxide in the presence of a reductant of urea type at the temperature of 220–280 °C, *i. e.*, another supplementary stage is necessary.

For a reducing sedimentation of chromium (VI) in sewage waters and separation of slime from the aqueous part taking into account the known data [21, 22] and our laboratory tests, we propose the following. In order to decrease the amount of slime sediment, reducing sedimentation of chromium hydroxide is carried out at pH 7–8, without addition of calcium hydroxide, according to reaction

$$Na_2Cr_2O_7 + 6FeSO_4 + 7H_2O = 2Cr(OH)_3\downarrow + 6FeOHSO_4\downarrow + 2NaOH \quad (3)$$

which creates conditions for a complete sedimentation and at the same time rules out the use of $Ca(OH)_2$. The sediment of chromium hydroxide and Fe(III) hydroxy sulphate obtained is separated from the liquid part by means of foam flotation according to [22].

Since the most efficient is the pressure flotation with the 25–30 % water recirculation, in this technology it is recommended to use just it. In this case, the circuit of devices for flotation purification of water consists of a chamber for preliminary coagulation and flocculation, a radial flotation plant with devices for distribution and collection of water and for collection and removal of floating foam, as well as a system for air saturation of the clarified part of water (25–30 %) under an excessive pressure. In the flocculation chamber, treatment with a flocculant, *e.g.*, sodium lauryl sulphate with the concentration of 100 mg/l, is carried out as it is proposed in [22]. Thereupon, the colloidal mixture is sent to the central part of the flotation plant, and the air-supersaturated clarified water is also fed there at the rate of 1–2 m/s, which creates favourable conditions for the formation of air bubbles and adsorption of colloidal particles of hydroxide sediments on them. Further on, the suspension separated from the water is collected on the surface as a thin layer of foam whose volume is by 2–4 times smaller than that of the sediment in the settling tanks. In order to obtain an air-supersaturated water, a saturation system is used which consists of a pump that creates an excessive pressure, a device for introduction and dispersion of air in water, and a pressure capacitance – a saturater where saturation of water under the pressure of 0.15–0.7 MPa for 1–5 min is carried out. The most efficient is an atomizing or jet saturater, as well as checker saturater with charging from Raschig rings.

As it is known [36], the size and number of air bubbles released from water exert a considerable influence on the flotation purification effect. In order to obtain bubbles of optimal size (≤ 80 μm), a 70 % degree of saturation is necessary, which is possible under an excessive pressure. The water is clarified within 15–40 min at the rate that exceeds by 4–5 times the rate of sedimentation, with the energy expenditure of 0.1–0.2 kW h/m^3. Therein, constructions by 6 to 8 times smaller than those for settling are used.

The sediment collected after the flotation plant with the humidity of 80–90 % is directed to production of modified chromium oxide. Clarified water contains 0.03 % mass NaCl and 0.01 % mass Na_2SO_4, which corresponds to standards of sewage discharge into water bodies. The solution with a 0.1 % mass CrO_3 after the filtration stage is partially used at the liming stage. The abrasive material obtained has the polishing ability of 0.5–0.76 mg/(min cm^2) and ensures, in polishing high-precision ShKh-15 steel articles, the surface roughness R_z = 0.1 μm, which corresponds to the 13th class surface purity.

CONCLUSION

As a result of the physicochemical studies and tests on a model device, a technology of processing the slime of chromium-containing industrial sewage waters for obtaining abrasive materials based on modified chromium oxide with a lishing ability exceeding by 5–7 times that of the currently produced abrasive chromium oxide for finishing operations of polishing metallic articles. Introduction of the proposed technology will make it possible to solve efficiently the problem of utilization of chromic waste.

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