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Complex Processing of Rare Metal Concentrate

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Abstract

Complex processing of the oil-containing flotation leucoxene concentrate accompanied by recoating the organic fraction was investigated. In order to obtain the pigment titanium dioxide concentrate from the leucoxene concentrate, reducing roasting with petroleum coke was used, at the temperature of 1100–1150 °C.

Key words: oil-containing leucoxene flotation concentrate, reducing roasting, oleum, titanium dioxide pigment

INTRODUCTION

High demand in the domestic and foreign markets for high-quality mineral titanium concentrates for the production of titanium pigments, titanium metal, titanium alloys and welding electrodes determine the relevance of studying the complex processing of oil-containing flotation leucoxene concentrate. In particular, of a great practical value is the leucoxene concentrate with the following composition, %: TiO_2 39.6–43.6, SiO_2 31.5–41.1, Fe_2O_3 1.1–1.8, FeO 2.8–3.9, Al_2O_3 2.4–4.5, CaO 0.2–0.3, MgO 0.8–1.0, MnO 0.05–0.15.

Leucoxene concentrates are characterized by thin (2–3 μm) mutual germination of rutile and quartz: the dominant mass of leucoxene grains of greenish-gray colour is covered on the outside with “shirts” or “fringes” consisting of a fine-grained peach quartz aggregate, sometimes containing siderite. Inside the leucoxene grains there are quartz or pyrite inclusions of a few micrometers in size, thus well-known pyrometallurgical methods [1, 2] for the processing of leucoxene concentrates are inapplicable.

The alkaline autoclave leaching of the leucoxene flotation concentrate, preliminary calcined at 900–1000 °C, with the following treatment of an enriched product by hydrochloric acid and fine-tuning at the concentration table, resulted in obtaining a product containing 80–85 % of titanium dioxide [3]. This processing method has the following disadvantages: 1) need for an additional operation such as acidic leaching, 2) a significant consumption of alkaline reagent and large amounts of alkaline solutions (5–6 m^3 per 1 t of TiO_2) with a high content of SiO_2 (~110 g/dm^3), which does not allow one to utilize these solutions (*e. g.*, $CaSiO_3$ precipitation) with the regeneration of the alkaline reagent, and 3) irreversible oil loss in the course of roasting the flotation concentrate.

It is interesting to investigate the complex processing of petroleum- and titanium-containing flotation concentrate with utilizing the organic phase and obtaining artificial rutile.

EXPERIMENTAL

The object of studies was presented by leucoxene flotation concentrate, the product of enriching petroliferous siliceous titanium ore from the Yareg deposit with the following composition, %: TiO_2 9.1–9.3, SiO_2 67.1–69.3, Fe_2O_3 0.3–0.4, FeO 6.9–7.1, Al_2O_3 3.5–3.8, CaO 0.6–0.7, MgO 0.7–0.8, MnO 0.1–0.12, oil 7–9. The leucoxene flotation concentrate is supplied from the processing plant as a slurry wherein the fraction of the mineral phase (leucoxene concentrate) amounts to 34.3 %, the fraction of the organic phase (oil) is equal to 34 %, the fraction of water being of 31.7 %.

In the course of the initial flotation of siliceous titanium ore the concentrate obtained is enriched with the oil fraction, whose content increases from 9.7 to 34 % due to oil preferential adsorption onto the surface of the leucoxene concentrate grains, comparing to silica. Due to the high adhesion of organic and mineral phases one cannot quantitatively extract oil from the flotation concentrate, using mechanical methods, such as rubbing-off (the process based on the friction of high-density particles in the pulp. As the result of this process the surface of particles is cleaned and polished whereas aggregates bound together are disintegrated.

The recovery of the organic fraction could be performed *via* washing the flotation concentrate by a solvent or the distillation of oil. In order to study these processes, derivatogfaphy was used, the method of thermal analysis concerning physical transformations, accompanied by changing in the internal heat of the system (enthalpy, ΔH) [4, 5].

The samples of the source and washed in benzene flotation concentrate were analyzed using a Paulik-Paulik-Erdey Q-1500 derivatograph (MOM, Hungary) and a Rigaku Thermoflex thermal analyzer (Japan) in the dynamic and quasi-isothermal (Q-mode) modes, in air and helium atmosphere.

RESULTS AND DISCUSSION

The data of the thermogravimetry (TG), derivative thermogravimetry (TGP) and the differential thermal analysis (DTA) were obtained under the following conditions: the weighed sample portion amounting to 0.3 g, the potential magnitude equal to 500 mV, the heating rate of 5 °C/min, helium flow rate equal to 5.5 dm^3/min, the heating temperature of 700 °C (Fig. 1).

Upon heating the samples of the source flotation concentrate in air, the DTA curves exhibited four peaks at the temperature values of 82–88, 218–224, 346–352 and 625–630 °C corresponding to the maximum mass loss rate of the samples ($d^2m/d\tau^2 = 0$).

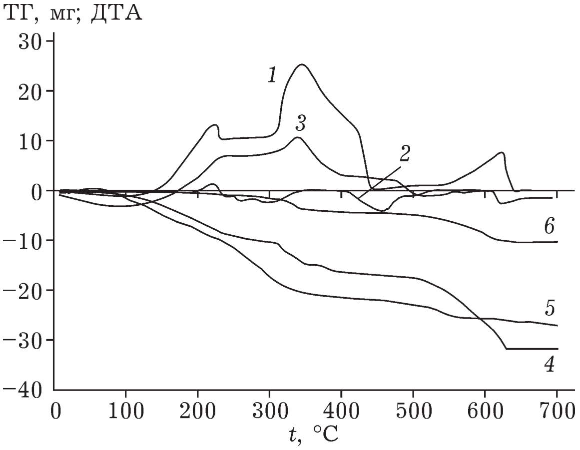

Fig. 1. Thermal analysis curves DTA (*1–3*) and TG (*4–6*) for the samples of flotation concentrate: *1*, *2*, *4*, *5* – initial; 1, 3, *4*, *6* – heated in air; *2*, *5* – heated in a helium; *3*, *6* – washed in benzene.

The small endothermic effect (+*Q*) at 85 °C is associated with the removal of adsorbed moisture ($\Delta m = 2.4$ %). The further three exothermic effects (−*Q*) at temperature values, °C: 220 ($\Delta m = 7.6$ %), 350 ($\Delta m = 6.8$ %), 628 ($\Delta m = 14.8$ %) is caused by the oxidation of the hydrocarbons of the methane naphthene and aromatic series, respectively ($\Sigma\Delta m = 29.2$ %).The values of the exothermic effect for the series of hydrocarbons decreases according the following sequence: naphthene > methane > aromatic.

As the temperature increases from 700 to 1000 °C, the petroleum coke ($\Delta m = 4.8$ %) remaining in the flotation concentrate after oxidation of hydrocarbons is burning out.

In the course of in-air heating the samples of flotation concentrate washed in benzene the curves of DTA-3 also exhibited four peaks at the characteristic temperature values, °C: 62–68 ($\Delta m = 0.4$ %), 238–242 ($\Delta m = 1.5$ %), 338–342 ($\Delta m = 3.7$ %), 603–607 ($\Delta m = 4.9$ %). These peaks correspond to the dehydration of the samples, as well as the oxidation of methane naphthene and aromatic series hydrocarbons ($\Sigma\Delta m = 10.1$ %).

Thus, washing in an organic solvent provides removing 65.4 % of oil (from its original content in the flotation concentrate).

Upon heating the samples of the source flotation concentrate in an atmosphere of helium volatile components of the organic phase are sublimated, being condensed then in a water cooler. The DTA-2 curves demonstrate five peaks at the characteristic temperature values of 60–64, 268–272, 308–312, 358–362 and 538–542 °C.

The only exothermic effect at 270 °C is due to the thermal decomposition of the most part of methane and naphthene series higher homologues to the lower homologues. The first endothermic effect at the temperature of 62 °C is associated with the removal of moisture (Δm = 1.4 %); the following three effects at the temperature of 310 (Δm = 15.7 %), 360 (Δm = 1 %) and 540 °C (Δm = 3.3 %) are due to the sublimation of lower and higher hydrocarbon homologues from methane, naphthene and aromatic series, respectively ($\Sigma\Delta m$ = 20 %).

Thus, after first removing the water from the source flotation concentrate via the sublimation of the organic phase at the temperature of 700 °C in the helium atmosphere with the subsequent condensation of the gas phase one could perform recycling 59 % of oil, mostly of light fractions from the flotation concentrate, whose final composition is represented by a mineral phase (leucoxene concentrate) and the organic phase (oil cake) with the content of 71 and 29 %, respectively.

The further processing of the flotation concentrate consists in performing the reducing roasting in an inclined rotary kiln, which allows destroying the higher oxide such as rutile (TiO_2) to yield a more soluble lower oxide such as anosovite (Ti_3O_5). The lattice of the latter being more defective is more reactive, too. The total reactions are as it follows:

$$6TiO_2 + C = 2Ti_3O_5 + CO_2 \quad (1)$$

$$CO_2 + C = 2CO \quad (2)$$

$$3TiO_2 + CO = Ti_3O_5 + CO_2 \quad (3)$$

In the course of roasting the flotation concentrate at the temperature values above 700 °C the oil cake is converted into petroleum coke (4.1–4.7 %) in the composition of titanium-containing mineral residue (leucoxene concentrate 95.9 %, TiO_2 38–41.8 %), whose amount is sufficient for the reactions (1)–(3) to proceed.

Table 1 demonstrates the results of the reductive roasting of rutile for 1–2.5 h in the samples of flotation concentrate (40.3 % TiO_2, 4.5 % C) and the mixture containing 40 % TiO_2 and 4.6 % C.

The solid-phase transition of higher titanium oxides into lower oxides at the decomposition level of rutile (γ) equal to 99 % in the flotation concentrate occurs at lower temperature values (t = 1100–1150 °C) and during less time interval (τ = 50–60 min) as compared to samples of working mixture, where the titanium dioxide decomposition level is equal to 96.5 % at the temperature of 1200–1300 °C during 2–2.5 h.

TABLE 1

Parameters of rutile reduction

Roasting temperature, °C	TiO_2 content/Decomposition level, %	
	Flotation concentrate (τ = 0.85–1 h)	Mixture (τ = 2–2.5 h)
20	40.3/0	40.0/0
900	4.7/88.3	8.8/78.0
1000	2.5/93.8	5.4/86.5
1100	0.4/99.0	2.7/93.3
1200	0.5/98.8	1.4/96.5
1300	0.6/98.5	1.45/96.4

The best parameters of the rutile reduction process are achieved due to the presence adsorbed oil cake on the surface of the leucoxene flotation concentrate grains which cake is converted into petroleum coke in the course of calcination.

After preliminary grinding the cinder in a rod mill to obtain the particle size of –0.1 mm, the sulphatization of obtained anosovite $[Ti_3O_5]_m \cdot [SO_3]_n$ was carried out by oleum (SO_3 > 19 %) and concentrated sulphuric acid in a sealed heat-insulated unit with the ratio S/L = 1 : 1, temperature τ_s = 150–200 °C during τ_s = 12 h. A cooled slurry of titanium sulphate was leached with water at S/L = 1 : (1–5), temperature t_l = 90–95 °C for during τ_l = 0.85–1 h (Table 2).

TABLE 2

Exponents for the sulphatization of anosovite (α) by oleum and sulphuric acid and for leaching titanium sulphate (β) by water

S/L	α/β, %	
	Oleum (t_s = 150 °C, τ_s = 1 h)	Sulphuric acid (t_s = 200 °C, τ_s = 2 h)
1 : 1	99/54.5	97.5/53.7
1 : 2	99/69.3	97.5/68.3
1 : 3	99/81.2	97.5/80.0
1 : 4	99/91.1	97.5/89.7
1 : 5	99/97.8	97.5/96.3
1 : 10	99/98.0	97.5/96.5

The chemical processing titanium-containing cinder results in further destroying the structure of silicates to form a fine-disperse fraction, which contributes to cleaning the grains of anosovite from splices. The best parameters of titanium sulphatization by oleum ($\alpha = 99$ %, $t_s = 150$ °C, $\tau_s = 1$ h) and leaching it with water ($\beta = 98$ %) comparing to concentrated sulphuric acid ($\alpha = 97.5$ %, $t_s = 200$ °C, $\tau_s = 2$ h, $\beta = 96.5$ %) are caused by the presence of 19–24 % free sulphur trioxide SO_3 in oleum, contributing to the completion of sulphatization reaction.

If the ratio S/L = 1 : 5, the process of leaching the titanium sulphate solutions results in forming the following composition g/dm^3: TiO_2 80 (in the form of $TiOSO_4$), Fe 6.7, H_2SO_4 50. Filtered $TiOSO_4$ solution was hydrolyzed at the boiling point temperature. After calcination the precipitate at 800 °C a product was obtained with the following composition, %: TiO_2 98.5, Fe_2O_3 0.5, SiO_2 0.05, Al_2O_3, CaO, MgO 0.03.

SUMMARY

1. Owing to the utilization of a part of oil from the leucoxene flotation concentrate *via* the sublimation of light fractions in an inert gas (59 % of the initial oil content), a profitability was increased for the process of obtaining titanium dioxide pigment.

2. Increasing the reactivity of titanium was performed *via* obtaining anosovite (Ti_3O_5) in the course of the reductive roasting of rutile (TiO_2) with heavy oil fractions (oil cake) from the leucoxene flotation concentrate with no additional consumption of metallurgical coke (a reducing agent).

3. In the course of the sulphatization lower oxides of titanium and the destruction of silicate structure, an additional purification level of anosovite grains from splices was achieved.

4. The presence of 19–24 % free sulphur trioxide (SO_3) in oleum provides a more completion of the sulphatization reaction at lower temperature values and duration time of the process, in comparison with concentrated sulphuric acid.

5. As the result of the leucoxene flotation concentrate complex processing, a concentrate was obtained with the following composition, %: TiO_2 98.5, Fe_2O_3 0.5, SiO_2 0.05, Al_2O_3, CaO, MgO 0.03.

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