Beneficiation of oil-saturated leucoxene ore by physical methods with preliminary thermal oil removing

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The paper presents the results of studies on the beneficiation of leucoxene ore from the Yaregskoe deposit (Komi Republic) with preliminary thermal petroleum removing by water vapor. It was shown that heat treatment of oil-bearing leucoxene ore allows to achieve complete extraction of oil into a separate fraction (8–9% by weight of the original ore) at heat treatment temperatures of 550–600 °C.
The beneficiation possibility of the mineral part of the ore by electrostatic and magnetic separation methods was studied. It has been established that the use of electrostatic separation does not allow complete selective removal of free quartz grains due to the fact that during the thermal distillation, oil pyrolysis occurs, resulting in the formation of coke residue, which is located on the surface of ore grains in the form of thin films. In this regard, the possibility of electrostatic separation with preliminary washing of ore from oil with an organic solvent was investigated. At the same time, the through yield of the conductive fraction was 16% with a TiO_2 content of 40–50%. An increase in the number of purifications leads to a decrease in titanium extraction (up to 65–70%). Significant heterogeneity of the distribution of components by fractions occurs due to the presence of leucoxene and quartz intergrowths in the concentrate, which distribute the charge non-uniformly.
Due to the fact that the resulting coke residue during pyrolysis can be used as a reducing agent, a combined process of heat treatment of ore was carried out, which combine the operations of oil distillation (550–600 °C) and magnetizing roasting (1100–1200 °C). As a result of magnetic separation of the reduced ore, a rich leucoxene concentrate (65% TiO_2) was obtained with TiO_2 extraction of about 90%. This combined process of heat treatment of oil-saturated leucoxene ore with subsequent magnetic separation will increase the efficiency of its beneficiation in comparison with the flotation method.

Key words: Yaregskoe deposit, leucoxene ore, titanium concentrate, magnetizing roasting, electrostatic separation, magnetic separation, pyrolysis.

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Introduction

More than 90% of titanium raw materials in the world are used to produce pigment titanium dioxide, which is used in the production of titanium white, paper, plastics, ceramics, perfumes, etc. Metallic titanium is widely used in the aerospace industry and in the military-industrial complex. Russia is one of the leaders in the reserves of titanium raw materials in the world [1]. In categories A + B + C1, the balance reserves amount to more than 260 million tons in terms of TiO_2. However, none of the country's existing deposits are developed in corpore. This is primarily due to the fact that the mineral resources of titanium in Russia are complex and difficult to beneficiation. The lack of cost-effective technologies for the complex processing of our own titanium deposits leads to dependence on foreign supplies of titanium raw materials (ilmenite). Therefore, the creation of new technological solutions for the development of our own titanium deposits is an extremely urgent task.

One of the largest titanium deposits in Russia is Yaregskoe (Komi Republic). 46.4% of Russia's titanium reserves are concentrated in the oil-bearing leucoxene sandstones of this deposit [2]. Leucoxene, the main titanium-containing mineral of this deposit, is a fine structure of the intergrowth of rutile and quartz (Fig. 1).

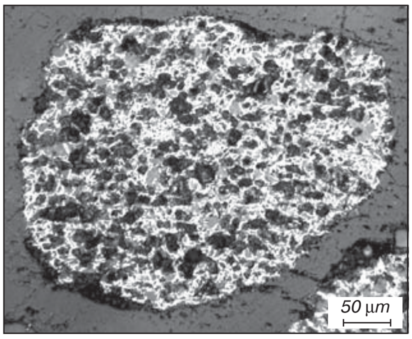

Fig. 1. Micrograph of leucoxene grain:
white – rutile; gray – quartz; black – pores

Ores of the Yaregskoe deposit contain 10–12% TiO_2 and up to 80% SiO_2; they are saturated with oil, represented by heavy fractions. Therefore, in the processing of oil-bearing leucoxene ore from the Yaregskoe deposit, the primary task is to separate the oil and mineral part of the ore. The extraction of heavy oil into a separate product will reduce the cost of the resulting leucoxene concentrate, because Yarega oil has a number of specific properties (heavy — 0.945 g/cm^3, highly viscous — 10000–12000 mPa·s (at an initial reservoir temperature of 8 ^oC), low-sulfur — up to 1.1% by weight, low-paraffin — up to 0.5% by weight) therefore, it is a valuable raw material for the oil refining industry [3–4].

At present, the mine operates an oil-bearing bed by the thermal mine method, the main principle of which is to reduce the viscosity and increase the mobility of oil by heating the bed by injecting heat-transfer agent (steam) [5]. The mining of bitumen sands at the world's largest viscous oil field in Athabasca (Alberta, Canada), where it is carried out using steam gravity drainage, is based on a similar principle [6]. After mining, bitumen sand is diluted with hot water and subjected to pulsed mechanical action to separate the organic, aqueous and mineral phases [7]. When processing Yaregsky sandstones, the previously developed scheme is applied, which includes direct thickening of the mineral fraction in oil for its subsequent flotation with preliminary grinding to a fineness of 0.3 mm [8]. In this case, the required grinding significantly reduces the degree of extraction of titanium in leucoxene concentrate, and is also an expensive operation.

To concentrate the mineral part of the ore, a flotation method was developed at VNIIPG, the essence of which is the reagent-free flotation of the mineral part, since the oil itself is used as a collector [9]. After flotation, the concentrate undergoes oxidative roasting (800–1000 ^oC) to remove residual organic phase. The resulting flotation leucoxene concentrate contains 50% TiO_2 and up to 40% SiO_2. At the same time, about half of the quartz is represented by free grains, and the rest of the quartz is in the leucoxene grains in fine intergrowth with rutile and is not removed during flotation. Due to the high content of quartz, flotation leucoxene concentrate is a substandard raw material and cannot be directly processed by known methods to produce titanium metal or its pigment dioxide.

In this regard, a process of magnetizing roasting of leucoxene concentrate was developed at IMET RAS, which increases the contrast of the magnetic properties of leucoxene and free quartz, which allows them to be separated using magnetic separation [10]. At the same time, the TiO_2 content in the concentrate rises to 65%. The remaining quartz is associated with leucoxene grains and its content does not exceed 25%. Removal of bound quartz is possible by chemical beneficiation [11–12], which allows one to obtain synthetic rutile (≥90% TiO_2), a high-quality product for the production of pigment titanium dioxide by the chlorine method. In addition, research is underway at IMET RAS on the processing of leucoxene concentrate to produce porous anosovite, a raw material for producing pigment titanium dioxide by the sulfuric acid method [13–14].

Obtaining a rich leucoxene concentrate by the methods described above has the following disadvantages: the flotation process is characterized by a low extraction of TiO_2 in the concentrate and the need for its calcination to remove oil residues; beneficiation by magnetic separation also requires execution of magnetizing roasting, which is necessary for the appearance of magnetic properties in leucoxene grains. All this leads to an increase in energy consumption. In this regard, to concentrate leucoxene ores, it is of interest to use the method of electrostatic separation, which does not require preliminary high-temperature firing of the material.

Electrostatic separation of minerals is based on their different electrical conductivity. Considering that free leucoxene grains (containing rutile) have a higher electrical conductivity than quartz grains (rutile — $1–10^4$, quartz — $10^{-16}–10^{-13}$ $Ohm^{-1}·cm^{-1}$ [15]), then with electrostatic Separation should be achieved selectivity of their distribution with the concentration of leucoxene in the conductive fraction, and quartz in the non-conductive.

Initial materials and experimental procedure

In the work, a sample of the oil-bearing leucoxene ore of the Yaregskoe deposit was used, containing 7–9% of oil. For distillation of oil in the presence of water vapor, we performed heat treatment of ore in an atmosphere of inert gas (argon). The process was carried out in the temperature range 200–600 ^oC in a vertical laboratory tube furnace in a quartz reactor. Water vapor from the boiling water tank was captured by a stream of inert gas (flow rate 50 l/h) and sent to the reaction zone (absolute humidity of the gas-vapor mixture 440 g/m^3). Electrostatic separation was carried out on an ES-3 device (voltage on the corona-forming electrode 22 kV, voltage on the deflecting electrode 7.5 kV, drum rotation speed — 120 rpm). Magnetic separation was carried out on a laboratory electromagnetic separator EVS-10/5 in the range of magnetic field strengths of 1–5 kOe. The distribution of leucoxene and quartz grains by fractions was studied by optical microscopy (optical microscope of the CarlZeissAxioScopeA1 brand). The total carbon content was determined by oxidative melting on a CS-400 gas analyzer.

Results and discussion

First, the influence of the temperature of the distillation process on the oil yield in a separate fraction was studied, which was indirectly estimated by the loss of mass of the sample. The results are presented in Fig. 2, from which it can be seen that complete removal of oil is achieved at temperatures of 550–600 ^oC with a processing time of at least 30 minutes. The maximum weight loss of the sample associated with the removal of oil was 8.7%. The result is a material in which oil is almost completely absent.

Table 1.
The chemical composition of leucoxen ore

Component	TiO_2	SiO_2	$Fe_2O_{3(total)}$	Al_2O_3	Na_2O	MgO	K_2O	CaO	P_2O_5	$SO_{3(total)}$	i.l.
Content, %	7.68	85.05	1.31	3.49	0.17	0.45	0.61	0.12	0.03	0.36	0.47

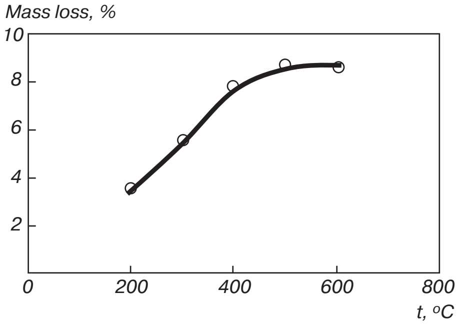

Fig. 2. Dependence of oil-bearing ore mass loss from temperature (duration of heat treatment 30 min.)

Table 2.
Granulometric composition of the mineral part of the ore

Fraction size, mm	Mass, %
+1.00	44
−1.00 + 0.63	14
−0.63 + 0.315	20
−0.315 + 0.05	19
−0.05	3

Reducing the duration of heat treatment leads to incomplete oil output. For example, the weight loss during the process at 600 °C with a duration of 15 minutes is 8%.

A study of the material composition of titanium ore refined from oil showed that it contains 7–8% TiO_2 and up to 85–90% SiO_2. The chemical composition of the mineral part of the ore after oil removal is presented in Table 1.

Granulometric analysis (Table 2) showed that 44% of the mineral part of the ore is in particle size classes >1.00 mm and is represented by free quartz grains. The TiO_2 content in them does not exceed 0.7%. In this regard, the use of classification methods of beneficiation with the removal of coarse size classes will increase the titanium content in the crude concentrate up to 18–20%.

Exploratory studies on the electrostatic beneficiation of the mineral part of the ore after distillation of the oil fraction showed a poor separation of leucoxene and quartz. A study of the composition of the conductive fraction showed that it contains about 0.5–1.0% carbon (in the form of a coke residue). Obviously, it is formed during thermal distillation of oil during the pyrolysis of the hydrocarbon fraction. According to the data of electron microscopy and microprobe analysis, the coke residue forms a thin electrically conductive film on the surface of the particles, and therefore some of the free quartz grains are not removed from the conductive fraction (Fig. 3).

To determine the possibility of selective removal of free quartz grains by electrostatic methods, the separation of leucoxene ore was carried out on a sample washed from oil with an organic solvent. At the same time, the electrostatic separation indicators can be significantly improved when using a material classified by particle size class. This is due to the fact that with increasing particle size, not only the charge received in the corona discharge field or on the charged drum grows, but also the centrifugal force detaching the grains from the drum surface, which makes it difficult to clearly separate the grains during material separation with a wide range of sizes. Therefore, the possibility of beneficiation of leucoxene ore purified from oil was studied using electrostatic separation at a fineness class of −0.315 + 0.05 mm. The electrostatic separation scheme with the distribution of the outputs of the fractions is shown in Fig. 4. The conducting fraction was subjected to three purifications with the isolation of non-

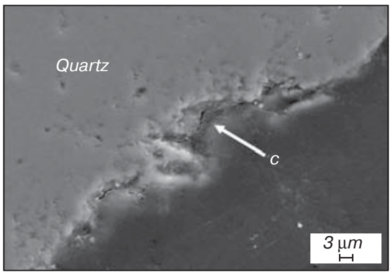

Fig. 3. Micrograph of a cross section of a quartz grain. The black shell is carbon (C) on the surface of quartz

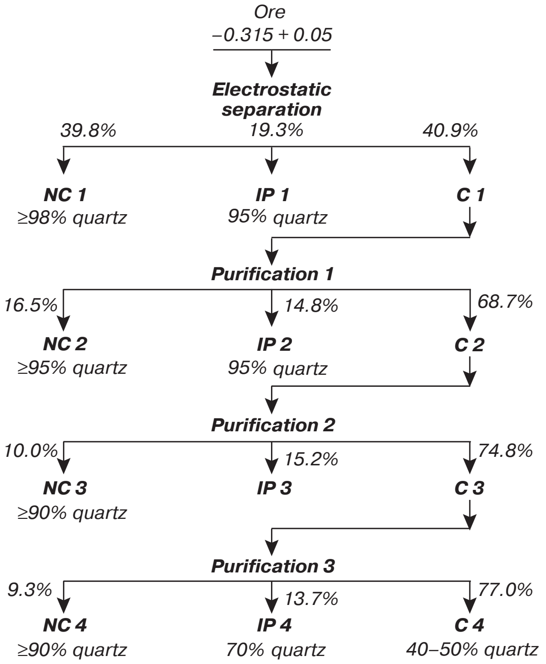

Fig. 4. Scheme of electrostatic separation of ore with a fineness of −0.315 + 0.05 mm:
C — conductive fraction; IP — intermediate product; NC — nonconductive fraction

conducting fractions and intermediate products into separate products.

According to the data obtained, the through yield of the conductive fraction was 16%. The content of free quartz in it is 40–50% (Fig. 5, *a*). The non-conductive fraction after the main separation is represented by free quartz grains (Fig. 5, *b*). At the same time, an increase in the number of purifications leads to a decrease in titanium extraction (up to 65–70%) in the conductive fraction due to the transfer of part of leucoxene grains (mainly splices) into the intermediate product and to a lesser extent into non-conductive fractions. Significant heterogeneity of the distribution of components by fractions oc curs due to the presence of leucoxene and quartz intergrowths in the concentrate, which unevenly distribute the charge and, as a result, get into different fractions. Therefore, already at the third purification, the non-conducting fraction contains 10–15% of leucoxene grains, and the intermediate product is 30%. Thus, electrostatic separation, even with an increase in the number of purifications, does not completely remove free quartz grains. At the same time, the conducting fraction (P 4) is not inferior in terms of TiO_2 content to the leucoxene concentrate obtained by flotation beneficiation.

Earlier in work [10], we showed that during magnetic separation in the range of a magnetic field of 3–5 kOe of a leucoxene concentrate subjected to magnetizing roasting, free quartz is almost completely removed. The result is a rich titanium concentrate with TiO_2 recovery of more than 90%. This is due to the appearance of magnetic properties in leucoxene grains during the recovery process, which is caused by the presence of a small amount of iron oxide ($\leq 3\%$ Fe_2O_3) in them, which is in direct contact with leucoxene grains.

At reducing by solid carbon, the optimum temperature range for the process is the range 1100–1200 °C. In this case, the necessary degree of reduction of iron oxides is achieved when 0.6–1.0% carbon is added to the charge. Considering that when oil is removed from the ore during the pyrolysis process, the same amount of carbon is formed, oil distillation can be combined with magnetizing roasting as part of a single process with sequential heating to 1100–1200 °C. At the first stage, when heated to 550 °C, the liquefaction of oil is achieved, and under the influence of an inert gas and water vapor stream, it separates from the mineral part of the ore. In the second stage, when the temperature rises to 1100–1200 °C, the reduction of iron oxides to metal in the leucoxene grains proceeds, which gives them magnetic properties that allow the use of magnetic separation to secession them.

Under these conditions, a combined roasting of oil-saturated leucoxene ore was carried out with successive heating to a temperature of 1150 °C. The obtained sample of the ore mineral part was subjected to magnetic separation at 3 kOe in order to extract a strongly magnetic fraction. As a purification, the non-magnetic fraction was subjected to separation at 5 kOe to obtain an intermediate product. Microscopic analysis of magnetic fractions showed that they consist mainly of leucoxene grains (Fig. 6, *a*). The non-magnetic fraction (84% yield) is almost completely represented by free quartz grains (Fig. 6, *b*). Separation tails contain more than 95% quartz (Table 3).

Thus, obtaining a reduced concentrate will allow complete removal of free quartz grains by magnetic separation and obtain a rich titanium concentrate (up to 65% TiO_2). In this case, TiO_2 extraction into the concentrate is about 90%, which is significantly higher than when ore is flotated (about 70%).

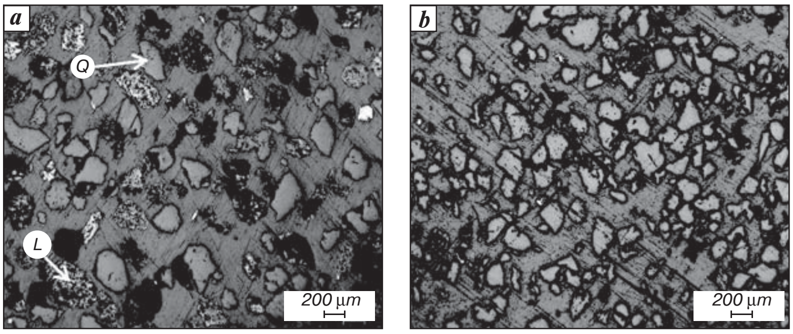

Fig. 5. Micrographs of fractions of electrostatic separation of particle size class –0.315 + + 0.05 mm:
a — conductive (C 4); *b* — non-conductive (NC 1); *L* — leucoxene; *Q* — quartz

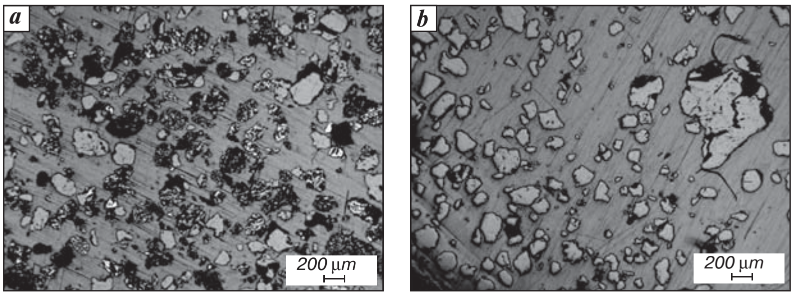

Fig. 6. Micrographs of fractions of magnetic separation of magnetizing roasting products:
a — magnetic at 5 kOe; *b* — non-magnetic at 5 kOe

Table 3.
The chemical composition of the magnetic separation tails

Component	TiO_2	SiO_2	$Fe_2O_{3\,(total)}$	Al_2O_3	Na_2O	MgO	K_2O	CaO	P_2O_5	$SO_{3\,(total)}$	i.l.
Content, %	1.06	95.26	0.48	1.72	0.18	0.13	0.29	0.10	0.03	0.07	0.53

Conclusion

The process of heat treatment of oil-bearing leucoxene ore with the participation of water vapor is investigated. The main parameters that allow the separation of the organic and mineral phases are determined. It is shown that complete oil extraction is achieved at heat treatment temperatures of 550–600 °C and a duration of at least 30 minutes.

The possibility of separation of leucoxene and quartz grains using electrostatic separation was studied. It was shown that the separation of the fineness classes –0.315 + 0.05 allows one to remove about 40% of free quartz grains during the main separation and to obtain a titanium concentrate with a content of up to 40–50% TiO_2. An increase in the TiO_2 content in the conductive fraction due to an increase in the number of purifications leads to a significant decrease in the extraction of titanium into the conductive fraction.

It was found that at oil distillation during pyrolysis process, 0.5–1.0% carbon is formed in the mineral part of the ore in the form of a coke residue, which, located on the surface of free quartz grains and increases their electrical conductivity, but reduces the selectivity of the leucoxene and quartz distribution during electrostatic separation. The coke residue formed during the pyrolysis of the organic phase at oil distillation can be used as a reducing agent in the magnetizing roasting of leucoxene ore, which is used for the separation of leucoxene and quartz by magnetic separation.

Combined roasting at a temperature of 550 °C for the distillation of oil, followed by heating to 1200 °C for the reduction of iron oxides, allowed to completely separate the oil from the mineral part of the ore. Subsequent magnetic separation of the reduced ore made it possible to obtain a rich leucoxene concentrate with a TiO_2 content of 65% with its extraction of about 90%, which significantly exceeds the indicators of leucoxene ores flotation beneficiation.

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