Evaluation and development of integrated technology of rare metal concentrate production in high-level ore processing at Zashikhinsk deposit

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Abstract. The authors discuss material constitution of columbite ore sample and recommend optimized pretreatment modes to obtain ball milling products at the maximum dissociation of ore minerals in aggregates. A concentration technology is proposed, with division of material into two flows –0.315 mm and –0.2 mm in sizes, generated in the milling and screening cycles and subjected to gravity–magnetic and magnetic–gravity treatment, respectively. It is shown that the technology ensures production of both tantalum–niobium and zircon concentrates. It has become possible to additionally recover rare metal components Nb₂O₅ and ZrO₂ from tailings through flotation.

In the recent decades, an increasing number of international industries use rare metals and rare earths, ore their alloys and compounds. These are, primarily, tantalum, niobium and zirconium, as well as many rare earth elements extracted from mineral concentrates of various tantalum–niobium ore processing. In particular, there are more than 50 known minerals of niobium and minerals, mostly represented by complex oxides [1].

As a rule, such ores contain a number of components concentrations of which justify feasibility and economic efficiency of industrial utilization [2]. Thus, development of a technology for integrated and deep concentration is in this case a critical task from the viewpoints of economic efficiency and environmental safety.

Russia takes one of the world’s top leadership positions in terms of proven reserves of most rare metals and rare earths though stands down in terms of quality of these ores characterized by complex texture and structure, low or variable content of useful elements as well as regarding geographical location of such ore deposits.

Russia’s reserves of rare earths in terms of oxides make round 28 Mt [3], which ranks Russia second to China in this respect. More than two thirds of Russia’s resources of rare earths occur and are under development in the Murmansk Region: unique Khibiny apatite–nepheline field, which holds 42.2% of registered economic resource base of Russia, and the largest Lovozero Ti–TR–Nb–Ta deposit holding 25.4% of reserves [4].

Processing of tantalum–niobium and zirconium ores currently uses conventional pre-treatment followed by sufficiently developed stage-wise flow charts of combinations of gravity, magnetic and electrical separation conditioned by high density and paramagnetic and diamagnetic properties of
valuable elements [5, 6]. At the same time, the use of these process results in high metal loss in tailings due to fineness of mineral grains.

Production of niobium and tantalum in Russia is based on loparite ore of Lovozero deposit. The bulk concentrate contains round 95% of loparite including 9% of niobium and tantalum oxides, more than 38% of titanium dioxide and over 32% of rare earths.

As a rare metal supply, Russia plans to use columbite ore of Zashikhinsk deposit to be developed in the East Siberia and source tantalum–niobium and zirconium production. A sample of this ore was taken for technological study to substantiate and develop an integrated processing scheme for this kind of ore. The data on mineral composition and chemistry of columbite ore are given in Table 1.

Table 1. Mineral and chemical composition of columbite ore.

| Minerals      | Content, % | Elements     | Content, % |
|---------------|------------|--------------|------------|
| Columbite     | 0.30       | Nb₂O₅        | 0.30       |
| Zirconium     | 0.92       | Ta₂O₅        | 0.026      |
| Xenotime      | 0.02       | ZrO₂         | 0.59       |
| Thorite       | 0.01       | SiO₂         | 0.01       |
| Cryolite      | 0.32       | Al₂O₃        | 0.32       |
| Siderite      | 0.34       | Na₂O         | 0.34       |
| Amphiboles    | 0.14       | K₂O          | 0.14       |
| Feldspar      | 75.52      | Fe₂O₃        | 1.53       |
| Quartz        | 17.57      | CaO          | 1.16       |
| Mica          | 4.41       | MgO          | 0.12       |
| Fluorite      | 0.20       | MnO          | 0.11       |
| Iron oxides   | 0.18       | TiO₂         | 0.065      |
| Other         | 0.07       | V₂O₅         | 0.012      |
| Total         | 100.0      | Cr₂O₃        | 0.0012     |

The sample contains more than 93% of quartz and feldspar. Mica is represented by muscovite and biotite in total amount of more than 4%. Overall content of rock-forming minerals is above 99%. Fraction of rare metal minerals makes no more that 1.2%. The rare metals are columbite and zircon. TR are represented by xenotime and thorite. Basic components of the ore are silicon oxide and alumina. There overall content exceeds 86%. The ore sample features low content of CaO, MgO, MnO and TiO₂ (0.065%) and insignificant content of Fe₂O₃ (1.53%). Total content of alkalis is 8% with the domination of sodium over potassium. The useful components are Nb₂O₅—0.30%, Ta₂O₅—0.026% and ZrO₂—0.59%.

The optical studies show that columbite occurs in free condition only in fine particles 0.2–0.16 mm in size. This fact is to be taken into account in development of the targeted processing technology for the bulk of tantalum–niobium minerals in larger particles are closely intergrown with the rock-forming minerals. Full dissociation of columbite and aggregates takes place in particles smaller than 0.1 mm.

Extraction of free columbite grains from large size grades of finely milled ore was achieved with the selected optimized mode of ball milling in a closed loop with a screen, which allowed production of screen undersize of -0.315 mm for gravity separation.

The figure below depicts a basic flow chart of gravity-and-magnetic separation of milled ore. Spiral separation of screen undersize with the subsequent table concentration of the rough concentrate produced a concentrate containing 12% of Nb₂O₅, 1.13% of Ta₂O₅ and 23.4% of ZrO₂ to be sent to magnetic separation in a weak field with the magnetic induction not higher than 0.1 T to separate scrap material.

For re-extraction of useful components, spiral separation and table concentration tailings containing aggregates of columbite and rock-forming minerals were mixed and forwarded to ball re-milling down to the size of -0.2 mm.
The magnetic separation of the screen undersize in the low induction field produced scrap material and nonmagnetic fraction composed of minerals with low paramagnetic properties (columbite, tantalite, siderite) and diamagnetic properties (zircon, pyrochlore, quartz, feldspar). It was found that the nonmagnetic fraction subjected to high-intensive magnetic separation with the field induction of 1.5 T was separated into nonmagnetic, intermediate and magnetic fractions.

The subsequent two-cycle centrifugal separation of the nonmagnetic fraction with the rougher and recleaner stages allows a crude product sent to the table concentration. The centrifugal separation and table concentration tailings are discharged (see the figure).

With the aim to improve concentrations of niobium and tantalum oxides and zirconium dioxide, the middlings of the high-intensity magnetic separation are sent to the table concentration to obtain a concentrate containing 12% of Nb₂O₅, 1.13% of Ta₂O₅ and 23.4% of ZrO₂. The middlings are subjected to recleaning and the resultant middlings are mixed with the rougher table concentration middlings. The recleaning concentrate is mixed with the bulk table concentrate to be then subjected to the high-intensity magnetic separation.

The magnetic fraction of the high-intensity magnetic separation goes to table concentration to reach the wanted content of Nb₂O₅ and Ta₂O₅. The table concentration middlings of this stage are fed to recleaning in the next-stage table concentration tailings of which are discharged. The gross concentrate of all table concentrations is a finished product with the overall yield of 0.088%, containing 35.81% of niobium oxide, 2.41% of tantalum oxide and 7.08% of zirconium oxide with the respective recoveries of 10.23%, 9.2% and 1.06%.

The aftertreatment of the combined products represented by rougher table concentrates of nonmagnetic fraction and high-intensity magnetic separation middlings as well as of nonmagnetic fraction of low-intensity magnetic separation after separation of the bulk rougher table concentrate from the spiral separator feed, involves high-intensity magnetic separation under magnetic field induction of 1.5 T. The first stage of this magnetic separation produces nonmagnetic and magnetic
fractions. The nonmagnetic fraction is zircon concentrate, and the magnetic fraction is subjected to the second stage separation under the magnetic field induction of 1.0 T, the product of which is columbite concentrate.

In this manner, the developed flow chart of integrated gravity and magnetic separation produces both columbite and zircon concentrates.

Total yield of columbite concentrate made 0.68% with the content of 33.91% of Nb₂O₅, 2.18% of Ta₂O₅ and 10.8% of ZrO₂ at the respective recoveries of 74.83%, 63.56% and 12.48%. The yield of zircon concentrate was 0.835% with the content of 46.41% of zirconium dioxide and admixtures of niobium and tantalum oxides in amount of 2.18% and 0.274%, respectively. The end-to-end recovery of the listed useful components made 65.87%, 5.92% and 9.83%, respectively.

With the aim to additionally extract fine dissociated grains of tantalum–niobium minerals from discharged tailings where loss of Nb₂O₅ and ZrO₂ reached 20% and Ta₂O₅—more than 26%, feasibility of flotation of these elements was studied.

The grain-size analysis of the tailings showed relatively high content of size grade under 0.071 mm (40%), with the concentrations of Nb₂O₅ and ZrO₂ round 67% and more than 60%, respectively. Niobium oxide content of the tailings was 0.065% and zirconium dioxide—0.098%.

The mineralogical analysis showed the need for additional milling which increased the content of the size grade -0.071 mm up to 64.3%, with the higher content of free grains with renewed and activated surfaces.

Prior to flotation, the tailings were deslimed to remove size grade 20 μm in an open cycle with fresh water; then subsequent cycle contained stages of the rougher flotation (RF) and recleaner flotation (ReF) and 2–3 stages of scavenging of froth product of RF (S-1, S-2 and S-3).

The tests used the known reagent regimes in alkaline medium (pH approx. 10) [7–9] with the collecting agent represented by hydroxamic acid (HA) in combination with fatty acids and mines, or xanthate with the frother T-80 and liquid glass as a depressor. Another reagent regime tested was a collecting agent from the class of esters of phosphorus-berating compound in combination with sulphonyl reagent and finishing of RF froth product in strong acid medium (pH = 2) [10]. However, with the use of these reagent modes, the concentration of useful components in RF froth product was low—6–14 at the recovery no more than 60%. Scavenging stages, either without reagents or with ethane diaacid, were inefficient. The bulk concentrates contained 2.71% of ZrO₂ and 1.65% of Nb₂O₅ at the recovery of 52.8% and 48.2%, respectively, at the rate of concentration not higher than 27 and 25.

For the metals of Zr, Nb and Ta are highly prone to complexing, the selected collecting agent was alkyl hydroxamic acids with a high constant of complexing, including zirconium ions [11]. The selected agent HA was analogous to the reagent IM-50—a mix of 75% of alkyl (C₇–C₈) hydroxamic and 25% of carboxylic acids at a ratio of 3:1.

The use of HA in combination with different depressing agents for rock-forming minerals, such as sodium hexametaphosphate (SXP), liquid glass and sodium lignosulfonate, which were at the same time dispensers for slime particles, exhibited the highest efficiency of SGP.

Table 2 reports the results of flotation with HA (pH = 9.7) after pulp slurry treatment with SGP.

The froth product contains 65.7% of Nb₂O₅ and 73.5% of ZrO₂ with the sufficiently lean tailings (0.019% of Nb₂O₅ and 0.016% of ZrO₂) with weak concentration rate (4); the effect of selective separation shows in the scavenging operations that yield concentrates S-1 and S-3 with the contents of 4.67 and 7.42% of Nb₂O₅ and 7.98 and 13.02% of ZrO₂ at the recovery of 61.8 and 50.2 and 70.0 and 548.5% and the rates of concentration of 130 and 115, respectively.

The reagent regime with SXP and HA agents was tested in flotation of milled tailings without desliming. The results (Table 2) show that at the optimal consumption of the reagents, it is possible to obtain the bulk rare metal concentrate with the content of 6.78 % of Nb₂O₅ at the recovery of 58.4% and 12.28% of ZrO₂ with the recovery of 70.2%. The optimal pH ranges as 9.7–10.0 with SPX and HA. When pH is under 9.7, floatability of the collecting agent drops; when pH exceeds 10 floatability grows, which leads to the need for additional scavenging stages for RF froth product.
Conclusion

The analyses of the material constitution of a columbite ore sample containing 0.3% Nb₂O₅, 0.027% Ta₂O₅ and 0.526% ZrO₂ have shown that the basic mineral of the ore are columbite, zircon, quartz and feldspar.

Table 2. Flotation of tailings of gravity and magnetic concentration of columbite ore.

| Dressing product | Results, % | Test conditions and reagent consumption, g/t | γ | β | ε | β | ε |
|------------------|------------|---------------------------------------------|----|----|---|----|---|
| Pulp slurry      | 11.1       | With desliming:                             | 0.066 | 11.3 | 0.092 | 10.4 |
| RF froth product | 18.4       | RF: SXP—900                                 | 0.232 | 65.7 | 0.392 | 73.5 |
| ReF froth product| 7.9        | HA—1350                                     | 0.042 | 5.1  | 0.075 | 6.0  |
| Tailings         | 61.6       | ReF: HA—225                                 | 0.019 | 17.9 | 0.016 | 10.1 |
| Initial feed     | 100.0      |                                             | 0.065 | 100.0| 0.098 | 100.0|
| S-2 concentrate  | 0.86       |                                             | 4.67 | 61.8 | 7.98  | 70.0 |
| S-3 concentrate  | 0.44       |                                             | 7.42 | 50.2 | 13.02 | 58.5 |
| RF froth product | 29.5       | Without desliming:                          | 0.172 | 78.0 | 0.288 | 86.4 |
| ReF froth product| 15.4       | RF: SXP—1000                                | 0.032 | 7.6  | 0.036 | 5.7  |
| Tailings         | 55.1       | HA—1670                                     | 0.017 | 14.4 | 0.014 | 7.9  |
| Initial feed     | 100.0      | ReF: HA—300                                 | 0.065 | 100.0| 0.098 | 100.0|
| S-2 concentrate  | 1.10       |                                             | 4.14 | 70.1 | 6.88  | 77.3 |
| S-3 concentrate  | 0.59       |                                             | 6.58 | 59.8 | 11.48 | 69.1 |
| RF froth product | 5.6        | Without desliming:                          | 0.889 | 76.0 | 1.559 | 88.4 |
| Tailings         | 94.4       | RF: SXP—2000                                | 0.017 | 24.0 | 0.012 | 11.6 |
| Initial feed     | 100.0      | HA—2670                                     | 0.065 | 100.0| 0.098 | 100.0|
| S-1 concentrate  | 1.0        |                                             | 4.43 | 67.6 | 7.939 | 81.0 |
| S-d concentrate  | 0.56       |                                             | 6.78 | 58.4 | 12.28 | 70.2 |

The authors have selected optimal modes for ball milling of ore and dressing products to ensure high dissociation of columbite grains, which enables preparing screen undersize for subsequent processing cycles.

The developed technology of combination gravity–magnetic concentration of columbite ore ensures production of tantalum–niobium and zircon concentrates:

—Columbite concentrate: yield: 0.68%;
  content: 33.91% Nb₂O₅, 2.18% Ta₂O₅ and 10.8% ZrO₂;
  recovery: 74.8%, 63.6% and 12.5%, respectively.

—Zircon concentrate: yield: 0.835%;
  content: 46.41% ZrO₂; 21.8% Nb₂O₅ and 0.274% Ta₂O₅;
  recovery: 65.9%, 5.9% and 9.8%, respectively.

The studies have demonstrated feasibility of improving completeness of extraction of valuable components by means of concentration of tailings based on flotation and an optimal reagent regime in an alkaline medium using a complexing collecting agent represented by hydroxamic acids and sodium hexametaphosphate as dispergator of slime particles and depressor of barren rocks. The resultant open-cycle bulk rare metal concentrates contain 6.78% of Nb₂O₅ and 12.28% of ZrO₂ at the recovery of 58.4% and 70.2%, respectively.

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