Bolshetagninskoe Deposit Microcline–Pyrochlore Ore Process Mineralogy

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Abstract Bolshetagninskoe deposit is one of the most valuable potential Russian niobium resource. It contains challenging pyrochlore ore that in the pre-feasibility study stage has been divided into a few geological–metallurgical units by metallurgical–geological mapping (in general, it is adequate to geometallurgy field). The microcline–pyrochlore ore is the predominant and most challenging metallurgical unit at the deposit. To optimize this unit ore processing flowsheet, broad-view process mineralogy approach was applied. It was shown that preliminary processing of the microcline–pyrochlore ore by radiometric separation stabilizes floatation feed ore grade by decreasing gangue mineral content and content of pyrochlore grain of size less than 10 μm. Comparing pyrochlore grain size and liberation of it in the ore, comminuted by both conventional ball mill and innovative impact centrifuge mill, some grounds of dramatically increased floatation concentrate grade and recovery have been discovered. The fine-grained ore-forming pyrochlore (the mineral average weighted grain size is 61 μm in the radiometric separated ore) has a relatively low liberation degree in the grinding ore (63 %) that, in addition to close association of the mineral with microcline, causes reduced content of Nb_2O_5 (29.9 %) and high content of SiO_2 (22.8 %) in the floatation final product. SiO_2 is concentrated by microcline that is definitely needed for an intensive hydrometallurgy processing flowsheet to produce ferroniobium from the product.

Keywords Bolshetagninskoe • Microcline–pyrochlore ore • Challenging rare-metal ore • Liberation degree • Niobium • Geological–metallurgical mapping • Geometallurgy

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1 Introduction

Rare-metal (RM) ore process mineralogy has been developed in Russia since 1950–1960. The main results were covered by A. I. Ginzburg, I. T. Aleksandrova, and L. B. Chistov' publications and summarized in 1991 monograph [1]. The approach was widely integrated in complex geological and mining projects that helped metallurgists to develop robust processing flowsheets of challenging domestic RM ores.

VIMS has grown to become the leader of RM ore mineralogy, geology, and metallurgy by planning and coordinating Soviet RM ore exploration programs, and Giredmet (State Research Institute of RM industry) has been one of the leaders of RM ore processing flowsheet development. 2008–2012 pre-feasibility study of the Bolshetagninskoe niobium deposit is an example of a current approach, taken by VIMS in cooperation with Giredmet to metallurgical assessment of challenging RM ore in early exploration stage.

Bolshetagninskoe deposit is one of the most important Russian niobium resource. It is confined to carbonatite complex of the same name that is situated in the Sayan Mountains, Eastern Siberia. Ores contain 1.0 % Nb_2O_5 and are unique in that the economic pyrochlore mineralization is concentrated in alkaline metasomatic rocks but not in carbonatites [2–4]. In 1988 pre-feasibility study of the deposit was commenced. The result was that preliminary orebody reserve assessment and processing flowsheet was developed in general. In 2008 the pre-feasibility study has been continued and successfully completed in 2012. As economic viability of the deposit ore was confirmed, the niobium ore reserves were applied by Russian State Committee on Mineral Reserves.

To get orebody knowledge and assess its variability, the method of so-called geological–metallurgical mapping (GMM) was used. The base of this approach, developed since 1940–1950 in Russia, is an integration of complex mineralogical, chemical, and metallurgical investigation of a large number of small-scale samples and traditional bulk sample testwork [5]. It is vital that a few domestic standards and instructions formalize GMM methodology depending on exploration stage and ore deposit type. Generally, GMM conforms to reinvented field of "geometallurgy." The latter involves geometallurgical mapping and modeling, based on orebody mineralogy study, and integrates ore characteristics with the mine plan and processing [6].

The current pre-feasibility study of the Bolshetagninskoe deposit ore involves drilling nine holes. A total of 1,998 m of core was extracted for the purpose of sampling and GMM for the project. To perform GMM, 47 small-scale samples were selected based on core logging and analytical data. The samples were analyzed with process mineralogy techniques and partly (26 samples) were roughly floated. Mineralogical, analytical, and metallurgical data were interpreted with mathematical statistic methods [7].

Table 1 Selected average chemical (XRF) and mineral (OMA) composition of geological–metallurgical units of Bolshetagninskoe deposit (including all of the Nb-minerals), wt%

Geological–metallurgical units	Nb_2O_5	P_2O_5	Pcl	Clb	Mi	Bi	Crb	Py + Po	Pcl locked Mi (rl%)
Microcline–pyrochlore	1.0	3.6	1.4	0.1	62	6	12	4.6	52
Carbonate–pyrochlore	0.7	4.5	1.5	0.1	11	31	30	4.8	13
Biotite–columbite–pyrochlore	1.2	3.8	1.4	0.7	10	56	10	6.2	6

Analyzed in volumetric samples materials, grounded by wet-ball milling to 125 μm
Pcl pyrochlore, *Clb* columbite, *Mi* microcline, *Bi* biotite, *Crb* carbonates, *Py* + *Po* pyrite + pyrrhotite

Three geological–mineralogical and metallurgical ore types were determined by GMM at the Bolshetagninskoe deposit: microcline–pyrochlore (MP), biotite–columbite–pyrochlore (BCP), and carbonate–pyrochlore (CP) (Table 1).

Three represented ore-type volumetric samples have been tested by commissioned flowsheet (radiometric separation → milling → selective floatation → pyrochlore leaching → ferroniobium) to verify different processability of the ore types and deliver viable processing flowsheets. To develop the robust flowsheets, process mineralogy methods were integrated into laboratory testworks.

The most important Bolshetagninskoe deposit ore type is the MP one, as it will be mined and processed at first 10 years of the mining project life cycle. BCP and CP ore types are deep mined and their processing is more straightforward; therefore results from them are not discussed in this chapter.

MP ore consists of microcline (59–70 wt%) with minor carbonates, apatite, sulfides, and goethite. Pyrochlore, the essential ore niobium mineral (94 % of a total ore Nb content), occurs as fine grains. It is indicated by GMM; a few geometallurgical variables of the feed MP ore impact pyrochlore' rougher floatation grade and recovery: content of Nb_2O_5, P_2O_5, share of liberated pyrochlore and the locked one in apatite particles.

Since the MP ore pyrochlore grains are fine and friable, viable grinding ore coarseness and device were assigned by metallurgists as a key instrument to optimize pyrochlore concentrate grade and recovery. While primary ore processing by radiometric separation is effective to remove about 30 % waste material, it was also important to evaluate its impact of it on floatation feed grade. And an additional challenge was final float pyrochlore concentrate that contained 22.8 % SiO_2. The necessary information has been provided by process mineralogy approach that was the main objective of this research.

2 Materials and Methods

In order to characterize the mineral composition and liberation of the MP ore processing products, seven samples were collected: two samples represented radiometric separation products (tails, RT1, and concentrate, RC1), another two samples were collected from grinding by ball and impact mill ore, and three samples were selected from final floatation concentrate and its scavenging floatation products. To analyze pyrochlore grain size, thin sections were made of the 37 MP ore fragments, which were selected from 150 fragments of the ore fraction size $-30+50$ mm. The latter were preliminarily studied by X-ray radiometric method involving Nb concentration characterization and divided into a few groups by the metal content.

Mineral composition and liberation, as well as pyrochlore grain size, were analyzed by traditional expert-mineralogist-driven optical microscopy. As control methods X-ray powder diffraction and X-ray fluorescence spectroscopy were used.

Traditional expert-mineralogist-driven optical microscopy analyses (OMA) were performed by optical microscope Olympus BX 51 in accordance with national branch instructions that formalize semiquantitative optical mineralogical and geometrical analysis.

X-ray powder diffraction (XRD) analyses were obtained in X'pert Pro PANalytical equipment, with CuKα radiation using inclusive standard method and X'pert High Score software with a PDF2 database.

X-ray fluorescence spectroscopy analyses were performed by PANalytical MagiX PRO instrument. The domestic branch standard was entered in the analytical procedure.

To obtain analyses by XRD and XRF, sample material was comminuted in laboratory disk-mill to particle grain size less than 40 μm.

3 Results and Discussion

3.1 Radiometric Separation Impact on Floatation Feed Ore Grade

The first stage of the MP ore treatment is radiometric separation. At this stage, the preliminary crushed ore is separated by threshold content of 0.2 wt% Nb_2O_5 into waste product (about 30 % of a total ore, radiometric tails, RT1) and concentrate. The latter one is integrated with the ore non-separated fraction (less than 30 mm) and this product («radiometric concentrate», RC1, later) is a feed of the floatation circuit.

Data of the Table 2 characterized mineral composition and liberation degree in radiometric separation feed ore and products.

The MP ore separated by radiometric separator (RT1) contains not only more pyrochlore (1.87 wt%, +44 rl%), but also apatite (11 and 9 wt% accordingly) and

Table 2 Mineralogical composition (wt%) and pyrochlore liberation degree (rl%) of microcline–pyrochlore ore[a] and products of the ore radiometric separation (mineralogical analysis were performed with optical microscopy methods)

Mineral	RT1	RC1	MP ore[b]
Liberated microcline	34	60	50
Microcline with Fe hydroxides, hematite	15	3	8
Carbonates	8	1	4
Biotite	25	10	16
Apatite	6	11	9
Fe hydroxides >> hematite	10	12	11
Liberated pyrochlore	0.22	1.19	0.81
Pyrochlore with microcline	0.19	0.68	0.49
SUM pyrochlore	0.41	1.87	1.30
Pyrochlore liberation degree, −0.125 + 0.07 mm	11	26	20
Pyrochlore liberation degree, −0.125 + 0.01 mm	46	57	53

[a]Volumetric sample material of oxidized microcline–pyrochlore ore products was analyzed (grounding by laboratory ball mill to 125 μm)

[b]The MP ore characterization was calculated using data of it radiometric separation products analysis (RT1 and RC1)

microcline (63 and 58 wt% accordingly) have been grown; then the separation waste material is characterized by higher contents of biotite (25 and 16 wt% accordingly) and carbonates (8 and 4 wt% accordingly) (Table 2). It can be explained by pyrochlore's close association with microcline (the mineral forms disseminated fine grains and thin veins) and apatite (apatite–pyrochlore veins in microcline matrix), whereas carbonate and biotite aggregates usually don't contain the mineral. Another important radiometric separation result, as seen in Table 2, is that the content of liberated pyrochlore has been increased in RC1 to 1.19 wt% (+38 rl% in comparison with the feed ore); then in the RT1 content of it is only 0.22 wt%.

The data of pyrochlore grain size analysis in the MP ore can clarify this result (Table 3).

To interpret pyrochlore grain size composition data right, it firstly should be mentioned that to study the MP ore floatation and grinding variables the ore was grounded by different devices to 125 μm or 200 μm (basing on pyrochlore grain friable and average size of it 54 μm, Table 3). Thus this grinding coarseness prevents the significant pyrochlore losses with slim fraction, which determines that pyrochlore grain of size less than 16 μm will be mostly locked in the comminuted ore (so-called "hard-liberated" pyrochlore) and lost at rough floatation tails.

As seen in Table 3, more than a half pyrochlore grain of the MP ore is a size less than 32 μm, and 37.8 rl% of it is distributed in the floatation hard-liberated size fraction −16 μm. If ore fragments' content is less than 0.2 wt% Nb_2O_5 to delete (as operated by radiometric separation), then pyrochlore grain size composition smoothly changes: content of pyrochlore of well-liberated size fraction +32 μm increases from 38.2 to 44.8 rl% and it declined from 37.8 to 31.8 rl% in the fraction

Table 3 Pyrochlore grain size composition (optic geometrical analysis results) of the microcline–pyrochlore ore and some radiometric concentrates of it, predicatively calculating by different Nb_2O_5 content threshold

	MP ore fragment group (by content of Nb_2O_5 from–to, %)									Predictive radiometric concentrate by different Nb_2O_5 content threshold		
Size fraction (mm)	4.2–6.7	2.1–3.8	1.7–1.8	1.1–1.5	0.7–1.0	0.4–0.7	0.2–0.4	<0.2	A total ore	0.2	0.4	0.7
Amount of ore fragments and analyzed thin sections	5	19	8	8	14	31	38	27	150	123	85	54
	7	4	2	4	5	5	4	6	37	31	27	22
−0.25 + 0.125	26.9	44.6	0.0	62.5	24.5	0.0	0.0	0.0	12.2	14.8	21.5	33.8
−0.125 + 0.064	25.3	24.0	9.8	19.2	31.3	0.0	18.7	0.0	13.1	16.0	14.7	23.2
−0.064 + 0.032	28.2	16.2	14.7	8.9	12.5	9.5	16.3	8.0	12.9	14.0	13.0	15.0
−0.032 + 0.016	7.1	10.8	32.7	4.6	21.9	27.9	30.6	26.7	24.0	23.4	20.1	15.7
−0.016 + 0.008	11.1	3.3	33.1	4.1	8.0	53.8	24.0	51.1	29.9	25.2	25.9	9.8
−0.008	1.4	1.1	9.7	0.7	1.8	8.8	10.4	14.2	7.9	6.6	4.8	2.5
SUM	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Pyrochlore grain average size (μm)	91	135	28	141	87	18	36	19	54	61	72	104

size −16 μm. The pyrochlore grain average weighted size increases from 54 to 61 μm in the example.

To dramatically change pyrochlore grain size distribution, as shown in Table 3, ore fragments containing less than 0.7 wt% Nb_2O_5 should be deleted from the MP ore by radiometric separation that is unviable. A product which contains only 12.3 rl% of pyrochlore of hard-liberated fraction size will be obtained by the operation and pyrochlore grain average weighted size will be increased to 104 μm in the floatation feed ore (Table 3).

3.2 Preferential Ore Comminution Method

As early mentioned, a comminution circuit development is vital to the MP ore processing. To grind the ore, two comminution devices have been tested: conventional wet ball mill and dry impact centrifuge mill [8]. To test the first one, the ore has been grounded to particle size less than 125 μm. Dry impact milling performance has been studied by grinding the ore to particle size less than 200 μm, while preliminary optical mineralogical analysis was identified earlier pyrochlore liberation by this comminution device in comparison with the ball mill.

Both pyrochlore and microcline liberation degrees are essential to floatation selectivity and its final product grade and recovery, while non-liberated pyrochlore is locked in microcline and the latter is the main MP ore gangue mineral. Therefore increasing microcline liberation degree from another gangue minerals and pyrochlore has positive impact on the ore floatation selectivity.

Although the impact mill product has coarser content than the ball mill one (51 % less than 74 μm and 66 % less than 74 μm, respectively), the products pyrochlore (63 and 70 rl% accordingly) and microcline (90 and 82 rl% accordingly) liberation degrees are similar (Table 4).

Liberated pyrochlore average weighted grain size is larger in impact mill product (32 μm and 25 μm in ball mill product accordingly) that improves floatation characteristics of the ore. Another impact grinding device advantage is declined content of fine-liberated pyrochlore particle of size less than 10 μm (17 rl% and 35 rl% of the liberated ore in the ore grinding by impact and ball mill accordingly), which is hard extracted by conventional floatation technique.

MP ores grounded by both devices have been tested by commissioned floatation circuit. The best floatation results have been obtained from the impact mill product in comparison with ball mill one due to preferential pyrochlore liberation and fresh surfaces of mineral particles: the concentrate grade and recovery increased to 11 and 25 % of Nb_2O_5 relatively [8].

Table 4 Pyrochlore and microcline liberation in microcline–pyrochlore ore grounding by different methods (optic mineralogical analysis results)

Grinding method and size	Liberated pyrochlore weighted average grain size (μm)	Share of liberated pyrochlore in size fraction (%)		Liberation degree (rl%)	
		−40 + 10 μm	−10 μm	Pcl	Mi
Wet ball milling, 66 % less than 74 μm	25	59	35	70	82
Dry impact milling, 51 % less than 74 μm	32	71	17	63	90

Table 5 Pyrochlore and microcline liberation characterization of floatation final product and its scavenging products (optic mineralogical analysis results, content of Nb_2O_5 is obtained by XRF)

Floatation product	Content of (wt%)			Pyrochlore liberation (rl%)			Microcline liberation from pyrochlore grain degree (rl%)
	Nb_2O_5	Pcl	Mi	Liberated	Middling	Locked	
Final product	29.9	53	26	75	18	7	24
Final product scavenging "concentrate"	39.5[a]	67	20	92	5	3	30
Final product scavenging waste material	20.7[a]	35	38	51	35	14	17

[a]It is calculated by pyrochlore average content of 59 wt% Nb_2O_5

3.3 *Floatation Final Product Grade Assessment*

Floatation final product grade is low (29.9 wt% Nb_2O_5, 22.8 wt% SiO_2), as pyrochlore liberation degree from microcline in the comminuted MP ore is not high enough (63 rl%, Table 4) to float the niobium mineral more selectively.

To investigate the feasibility of increasing floatation selectivity, the final product was scavenged. As shown in Table 5, the scavenging final product has higher pyrochlore liberation degree than the feed product (75 and 92 rl% accordingly) that positive impacts niobium content (39.5 wt% of Nb_2O_5), but a lot of microcline particles still have contained pyrochlore impurities (microcline liberation degree from pyrochlore is smoothly increased from 24 rl% in the final product to 30 rl% in the scavenging final product).

As seen in Table 5, the final product scavenging waste material is characterized by reduced values of pyrochlore and microcline liberation degree (51 and 17 rl% accordingly), but it still contains too much pyrochlore (35 wt%), the tails to consider.

The obtained data have shown that the final product scavenging could not be recommended, while the middling product contains a lot of pyrochlore and scavenging concentrate still has been too low grade to process it viably by pyrometallurgy in order to produce ferroniobium. It is much more preferable to achieve higher pyrochlore recovery in this nonconventional product and process it by modern hydrometallurgy techniques with further ferroniobium production.

4 Conclusions

The Bolshetagninskoe deposit microcline–pyrochlore ore is the new Russian challenging niobium resource. It can be viably processed by complex flowsheet that involves preliminary radiometric separation, grounding to 200 μm by impact centrifuge mill, selective floatation, pyrochlore concentrate leaching, and finally ferroniobium production. To deliver the robust processing flowsheet, the domestic RM process mineralogy approach was integrated into laboratory testwork.

By the process of mineralogy study, some essential problems of the MP ore processing were covered.

1. The positive radiometric separation impacts on the floatation feed ore characteristics have been shown. Due to radiometric preliminary processing, the content of gangue minerals in the floatation feed ore is declined and pyrochlore grain size distribution is smoothly corrected to increase the mineral average grain size from 54 to 61 μm. The result is increasing floatation sustainability and selectivity, declining losses of hard-treated and hard-liberated pyrochlore.
2. Compared with wet ball mill, using dry impact mill to ground the MP ore helps to prepare it to flotation processing better due to earlier pyrochlore liberation and coarser size of liberated pyrochlore particle. In addition to fresh surfaces of mineral particles, dramatically increased floatation recovery (+25 % of a total ore Nb_2O_5) and grade (+11 wt% Nb_2O_5) are determined.
3. Pyrochlore liberation is 75 rl% and microcline liberation (from pyrochlore) is 24 rl% in the analyzed final float pyrochlore concentrate. There is 18 rl% of middling pyrochlore and 7 rl% of the locked one (in microcline) in the concentrate that determines its inadequate quality (29.9 wt% Nb_2O_5, 22.8 wt% SiO_2). By pyrochlore and microcline liberation analyses, it has been shown that the further concentrate scavenging could not be viable: thus pyrochlore losses are increased significantly by the operation, and the content of microcline (mineral-concentrator of SiO_2) too smoothly declined, to process this product by pyrometallurgy in order to produce ferroniobium. It is much more preferable to achieve higher pyrochlore recovery in this nonconventional pyrochlore product and process it by modern hydrometallurgy techniques with further ferroniobium production.

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