

UDC 553.493+553.465+661.865

Technological Aspects of Processing the Rare Metal Ore from the Chuktukon Deposit

V. I. KUZMIN¹, G. L. PASHKOV¹, V. N. KUZMINA¹, S. N. KALYAKIN¹, L. I. DOROKHOVA¹, V. F. PAVLOV² and V. G. LOMAEV³¹*Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marksa 42, Krasnoyarsk 660049 (Russia)**E-mail: kuzmin_vi@mail.ru*²*Special Designing and Technological Bureau "Nauka", KSC of Siberian Branch of the Russian Academy of Sciences, Pr. Mira 53, Krasnoyarsk 660040 (Russia)*³*Geokomp Ltd., Ul. K. Marksa 56, Krasnoyarsk 660049 (Russia)*

Abstract

Technological problems of processing rare metal ore species from the Chuktukon deposit (Krasnoyarsk Territory) are considered. The ore species represent ferromanganese oxide ones, they contain 3–7 % of rare earth oxide species in the form of phosphates (monazite, florencite) and 0.5–1 % of niobium oxide (pyrochlore); these ore species are almost unconcentratable. Potentialities of their direct chemical processing were studied. A scheme is suggested that involves autoclave nitrate leaching and extractive isolation of rare earth elements, regenerative processing of leaching tails and the isolation of niobium concentrate to result in a non-magnetic fraction. According to this scheme, nitrate solutions are exposed to thermal decomposition with the purpose of nitric acid regeneration. A pyrometallurgical process is analyzed concerning the reduction of ore with obtaining pig-iron and rare metal production. The realization of the process demands for solving complicated technological problems on obtaining high-quality products.

Key words: rare metal ore species, rare earth elements, niobium, leaching, extraction, reduction

INTRODUCTION

The Chuktukon rare metal deposit represents one of the major objects of the lower Priangaria of Krasnoyarsk Territory [1–3]. This ore object is comparable with well-known Tomtor deposit. However, when the Tomtor deposit is located in the north Yakutia almost on coast of the Arctic Ocean, the Chuktukon deposit is located 110 km from the town of Codinsk, where the well-known Boguchany Heat and Electric Power Plant is nowadays constructed. These two deposits concentrate about 80 % of rich Russian ore resources concerning rare earth elements (REE) and niobium. To all appearance, only after their development Russia could seriously compete with world monopolists such as Brazil (with respect to niobium) and China (with respect to REE).

The REE and niobium market intensely develops, which is connected with the use of these metals in manufacturing marketable hi-tech

products. The world production of REE and niobium has exceeds USD 2 billion, whereas annual gain rates (in volume and price) are amounting up to 10 %.

The cost of elements extracted from 1 t of ore for the Tomtor ore species is equal to 60 thousand roubles, for the Chuktukon ore that is of about 20 thousand roubles.

At the same time, the processing of ore species from these Russian rare metal deposits demands for novel approaches and technologies, since the ore species almost unconcentratable due to a high dispersity level of mineral components and their mutual splicing [3]. A complex research work was carried out at the Institute of Chemistry and Chemical Technology (ICCT) of the SB RAS (Krasnoyarsk) concerning the estimation of the Chuktukon ore technological properties, the development of different methods for their processing.

Some results of this research work are presented in this work.

CHARACTERISTICS OF THE CHUKTUKON DEPOSIT AND RARE METAL ORE SPECIES

The ore body of the Chuktukon of a deposit is located on the surface in the form of a dome divided into two bodies – Southern one and Central one. The area of the ore zone is rather small; the zone is characterized by the high thickness increasing to the dome part of the structure up to 300 m. The base of deposit resources with a cutoff grade of rare metals equal to 1 % amounts to almost 1 billion t.

The ore species of the Chuktukon deposit are complex; they exhibit mainly oxide ferromanganese composition (40–70 % Fe_2O_3 and 1–20 % MnO). For the technology of processing the fact is important that ore contains about 1–2 % of phosphorus in the form of REE phosphates and apatite. Conditionally, the Chuktukon ore species could be divided into two technological types such as rare earth one and niobium one. The composition of the representative samples of these two ore types of (TP-6 and TP-7) is presented in Table 1. For the central part of the deposit, an abrupt (10–15-fold) REE prevalence comparing to niobium is ob-

served, the same ratio is inherent in ore species in the southern part of the deposit. For another part of the area the REE/Nb ratio amounts to 1.5–2.0. Rare earth ore species contain up to 8–10 % $\Sigma\text{R}_2\text{O}_3$ (REE oxides) and 0.6 % Nb_2O_5 , niobium ore species contain 1.0–1.5 % Nb_2O_5 and 3 % $\Sigma\text{R}_2\text{O}_3$ [2, 3].

Iron and manganese compose main rock-forming minerals being mainly are presented by oxides and hydroxides. Iron is presented mainly in the form of goethite and hematite. Manganese oxides and hydroxides occur both in close contact with iron, and as separate phases, presumably in the form of psilomelan.

Rare earth elements in the Chuktukon ore are mainly presented by florencite, monazite and cerianite. The prevailing mineral form of niobium occurring in the ore species is presented by secondary strontium, barium and cerium pyrochlores. Phosphorus is rather homogeneously distributed throughout different size classes being a part of monazite, florencite, and occurring in the form of iron and aluminium phosphates.

Studies performed at the IMGRE, GIRED-MET, ICCT of the SB RAS and other scientific research organizations demonstrated that the granulometric composition of ore species is characterized by the predominance of fine particles with the size <0.074 mm those compose more than 50 % of the material. The ore is presented by agglomerates, whose structure includes particles with the sizes less than 1 μm . Just the exclusive dispersity level of the minerals and their splicing between each other, to all appearance, cause the problems of concentrating for these ore species [3].

TABLE 1

Chemical composition of the Chuktukon deposit ore species

Oxides	Mass fraction, %	
	Rare earth type (sample TP-6)	Niobium type (sample TP-7)
ΣREO (including Y_2O_3)	7.1	3.0
Nb_2O_5	0.5	1.2
TiO_2	0.9	0.3
Al_2O_3	4.9	1.2
P_2O_5	4.8	4.5
Fe_2O_3	51.4	40.0
MnO_2	12.4	7.0
CaO	0.9	0.9
SrO	0.4	0.4
BaO	2.5	3.7
SiO_2	4.8	1.0
SO_3	–	0.1
CO_2	–	1.0

ANALYSIS OF HYDROPYROMETALLURGICAL SCHEMES FOR PROCESSING THE CHUKTUKON ORE SPECIES WITH OBTAINING RARE EARTH AND NIOBIUM PRODUCTS

Besides large-scale resources of ore species, compact ore body bedding and geographical position, the Chuktukon deposit is unique also with respect to a high content of REE and niobium. In this connection, the possibility of obtaining rare-earth and niobium products was estimated first of all. Of significant interest is a scheme including the opening of REE minerals in ore with the use of traditional alkali-acid processing at the first stage, and the fur-

ther removal of the main part of iron from niobium-containing magnetic separation residue after preliminary regenerative cake processing at the second stage. The first stage should provide not only REE extraction, but also the liberation of pyrochlore (niobium-containing mineral). The niobium concentrate obtained could be further processed using the method of chlorination.

Rare earth elements occur in the Chuktukon ore species in the form of phosphates (monazite, florencite). The most efficient known process for opening these minerals consists in alkali-acid processing. At the first stage, lanthanide phosphates decompose with the formation of lanthanum hydroxide and trisodium phosphate:

$$\text{LaPO}_4(\text{s}) + 3\text{NaOH}(\text{soln}) \leftrightarrow \text{La}(\text{OH})_3(\text{s}) + \text{Na}_3\text{PO}_4(\text{soln}) \quad (1)$$

where (s) is solid, (soln) is solution.

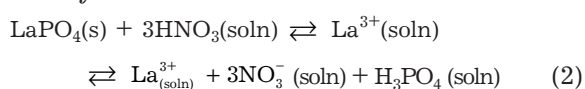
Further the hydroxides are dissolved, as a rule, in nitric acid. Then REE are purified of impurities using extraction from mother solutions by tributylphosphate.

The investigation of this scheme demonstrated [3] that the direct use of the Chuktukon ore species is unacceptable for processing, since cerium is oxidized by manganese (V) to give a tetravalent state at the stage of the alkali processing of the ore with the formation of cerium dioxide resistant against the action of acids. Soluble manganese (V) salts are formed resulting from the reaction of manganese (III) and (IV) oxides disproportionation in a strongly alkaline medium. It was established that alkali opening in an oxidative environment results in a decrease of the extraction into solution not only for cerium, but also for all the groups of REE. The total level of extraction into solution for the sum of REE according to this scheme does not exceed 30–40 %.

In order to eliminate this problem, we carried out a preliminary magnetizing roasting of ore with the transformation of iron oxides and hydroxides iron into magnetite. The magnetizing roasting procedure does not cause any considerable difficulties and the process readily enough proceeds at the temperature of 500–600 °C within 1–1.5 h under ore interaction with 5–10 % of coal in the presence water vapour. Such a processing prevents completely cerium from oxidation and provides good parameters of REE extraction into solution.

Nevertheless, the mentioned process does not allow one to liberate completely pyrochlore as well as to obtain rich concentrates after removing iron oxides by magnetic separation. Moreover, one of considerable disadvantages of the scheme under consideration consists in the problem of forming various difficultly filtered alkaline pulps at the first stage of processing the ore.

In this connection, another procedure of ore species processing was analysed. It is based on a direct decomposition of monazite and florencite by nitric acid:



In this case, the technological scheme becomes to a considerable extent simpler due to the elimination of operations concerning ore alkali decomposition and the filtration of alkaline pulps. However, the realization of such process is complicated by the problem of REE extraction from phosphoric acid solutions and by a significant dissolution of iron oxides and hydroxides.

The studies on this system demonstrated the potentiality of carrying out the process in such a mode, when iron and phosphorus almost completely remain in the solid phase due to the formation of complex hydroxyferrophosphates low-soluble in nitric acid. The process of opening lanthanides occurs according to the scheme

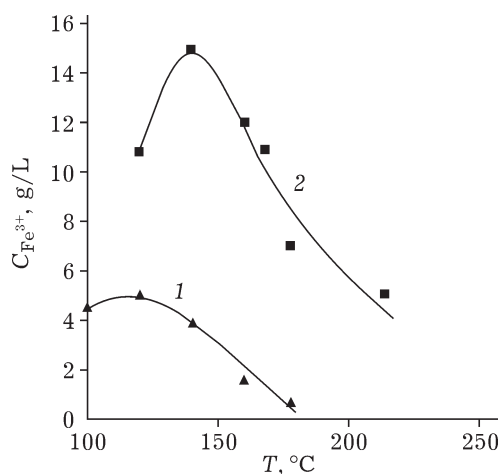


Fig. 1. Effect of temperature on the concentration of iron in the solution at leaching the Chuktukon ore species: 1 – 1.5 M HNO₃ solution; 2 – 3 M HNO₃ solution; S : L = 1 : 10, t = 2 h.

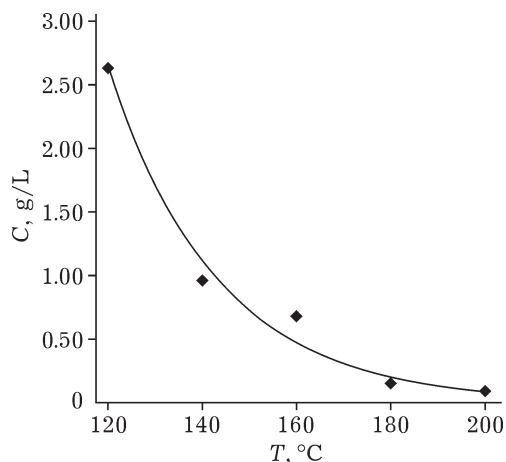
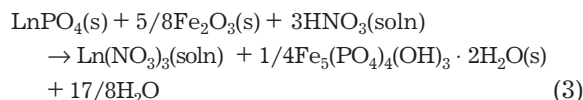


Fig. 2. Phosphorus concentration in the solution depending on temperature at leaching the Chuktukon ore species by 3 M HNO_3 solution ($S : L = 1 : 10$).



As temperature increases, iron behaves in a complicated manner (Fig. 1): when the temperature increases up to 120–140 °C its content in the solution grows, further this value is decreases to a considerable extent. So, for 1.5 M HNO_3 solution at the temperature values 180 and 250 °C the content of iron amounts to 0.6 and 0.23 g/L, respectively. The content of phosphoric acid formed according to reaction (2) is simultaneously sharply reduced which acid is co-precipitated with iron oxides or adsorbed on the surface of iron oxides and hydroxides (Fig. 2). In this case the extraction of REE into solution increases up to 87–90 %.

The binding of phosphoric acid in nitrate solutions is confirmed by the studies on model systems: I ($\text{H}_2\text{O}-\text{H}_3\text{PO}_4-\text{HNO}_3-\text{Fe}_2\text{O}_3$) и II ($\text{H}_2\text{O}-\text{HNO}_3-\text{LnPO}_4-\text{Fe}_2\text{O}_3$). It was demonstrated that phosphoric acid is adsorbed on iron (III) oxide from nitrate solutions at the temperature higher than 120 °C with the formation of hydroxyferrophosphate solid phase. For the temperature values ranging within 180–220 °C, for the system II the conditions are realized corresponding to a primary formation of hydroxyferrophosphate solid phase and the solution of lanthanide nitrates.

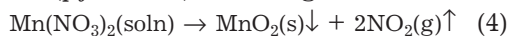
Obtaining the nitrate dephosphorized solutions under the autoclave nitrate leaching of the Chuktukon ore species allows one to use efficient extraction and purifying REE from

mother solutions via the extraction by tributylphosphate at the following stage.

The extreme behaviour of iron is used also for the increase in the opening level for the minerals of niobium. With this purpose, the process was carried out in the two modes. Firstly, the ore was processed with nitric acid at the temperature of 120–140 °C corresponding to the maximal solubility of iron, which provides the dissolution of iron oxides on the surface of rare metal minerals. Further, the temperature was increased up to 180–220 °C for iron nitrate decomposition, REE leaching and purifying the solutions of phosphoric acid.

Under the autoclave opening of the solution is entered by as much as 50 % of manganese. It was established that the introduction of reducers into solution causes the extraction of manganese to increase. The most efficient reagent for these purposes is presented by nitrogenous acid, whose additives result in increasing the extraction level of manganese into solution up to 80–85 %.

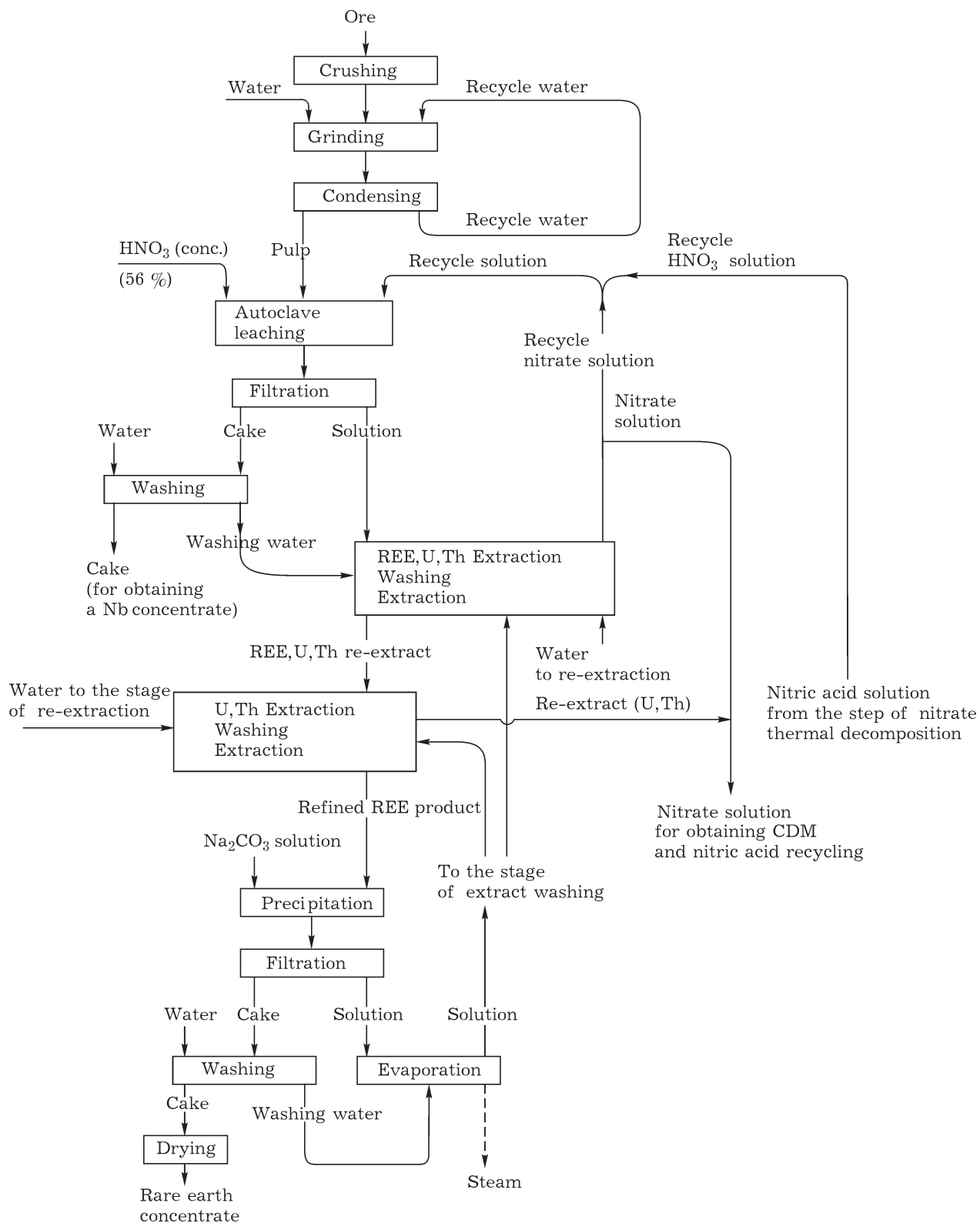
In order to reduce the consumption of nitric acid it was suggested to expose the mother leaching solution to thermal decomposition with obtaining nitric acid (*via* the condensation vapour-gas mixture) and the oxides of impurity metals. The process is realized in two stages. At the first stage at temperature 220–230 °C, a hydrothermal decomposition of deironized nitrate solution with a high content of manganese is performed to obtain coarse-crystalline manganese β -dioxide (pyrolusite) according to the reaction



At the second stage the evaporation concentrating and calcination of the solid precipitate results in a profound decomposition of other nitrates and an almost complete regeneration of nitric acid. The acid loss in the course of this operation does not exceed 2 %.

The process of nitric acid regeneration is efficient; it could be used in other processes when the consumption of nitric acid is excessively high [4].

For niobium isolation from the tails of leaching, a process for iron reduction to form the metal state at the temperature of 1000–1200 °C with its removal *via* magnetic separation was proposed and investigated. At this stage considerable ore enrichment with niobium and obtaining the concentrate with the content of nio-



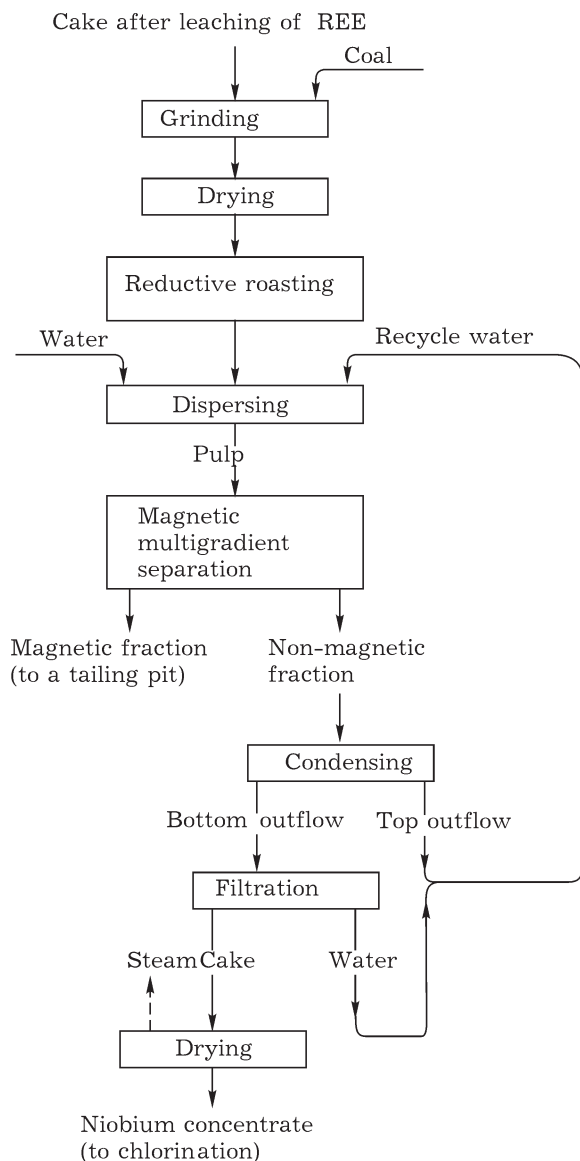


Fig. 4. Process flowsheet for obtaining the niobium concentrate from nitric acid leaching tails.

niobium (V) oxide about 5.5 % is reached. The process of iron oxide reduction at these temperature values proceeds within 15–30 min. An increase in temperature up to 1200 °C promotes melting the metal and results in improving the parameters of niobium extraction into a non-magnetic product.

The technological scheme taken as a basis includes three main repartitions: 1) opening ore and obtaining rare earth concentrate (Fig. 3); 2) regeneration of nitric acid with a side obtaining of chemical manganese dioxide; 3) obtaining niobium concentrate (Fig. 4).

The mentioned scheme was taken in 2007 as a basis for calculating the resources and State

registering of the surveyed ore species area of the Chuktukon deposit by the State Commission on Mineral Resources “Rosnedra”.

ESTIMATING THE POSSIBILITY OF COMPLEX PYROHYDROMETALLURGICAL PROCESSING THE CHUKTUKON ORE SPECIES

As it was mentioned above, the REE and niobium market is monopolized by Brazil and China: about 90 % rare earth products supplies China and about 95 % of niobium products are supplied by Brazil. At the same time, China holds the leading positions in the world due to a low price of rare earth products and a large-scale of manufacture, whereas Brazil does so due to the uniqueness of the niobium ore deposit, while the prices for the same ferroniobium remain very high. The uniqueness of Brazilian niobium ore consists not only and even not so much in their resources, but many in the quality ore species and the ease of their enrichment. In this connection, when creation rare metal manufacture for processing the Chuktukon deposit ore species, entering the market with the production of a new enterprise is considered as problematic enough, taking into account climatic problems besides the complexity of a technology.

Taking into account these circumstances, another approach to the development of the Chuktukon deposit was considered. According to the composition of ore species and scales this deposit is not only rare metal one, but also iron-ore deposit. The content of valuable elements in ore (due to iron and manganese) amounts up to 80–90 %: 0.6–1 % Nb_2O_5 , 5–7 % REO, 12–15 % MnO_2 , 50 % Fe_2O_3 , about 10 % oxides of other elements. For the listed series of elements, as the commodity output on their basis depreciates the content of elements in ore and their resources increase approximately in proportion. Correspondingly, the cost of these elements in 1 t of ore species is comparable to each other amounting to about USD 270 as calculated for ferroniobium, USD 200 as calculated for REE carbonates, USD 150 as calculated for ferromanganese and pig-iron.

The two latter products were stably marketable in the Russian and the world markets.

To all appearance, after withdrawal from crisis the market of this ferrous metallurgy production would be restored. Owing to this fact, ferromanganese and pig-iron could be considered as base products, whereas the niobium and rare earth products could be considered as passing products. With such an approach, it is necessary to develop profitable manufacture of basic elements such as iron and manganese, which is determined by the scales of manufacture, ore quality and obtained production. With a positive solution of the problem of obtaining pig-iron and ferromanganese as independent products and with passing extraction of niobium and REE, entering the rare earth market becomes only a matter of time.

The scale of ore processing in ferrous metallurgy should amount to 1–5 million t a year with obtaining of pig-iron, alloys and rare earth elements with a total cost ranging from 500 million up to 2.5 billion USD/year.

In the research work performed at the IM-GRE and GIREDMET institutes, there was a pyrometallurgical scheme approved for processing the ore. At the first stage, a direct reduction of iron oxides by coke was performed, at the second stage the reduction of niobium and manganese-containing slag by means of metal aluminium was carried out. It was demonstrated that the mentioned process does not provide obtaining the required quality products with

acceptable reagent consumption due to their pollution by phosphorus and silicon.

The process of reduction could be carried out more profoundly with the transition of manganese and niobium into the metal phase. Table 2 demonstrates data we obtained concerning the regenerative melting of ore with coke at 1500–1600 °C. Under these conditions, niobium, alongside with manganese, titanium and phosphorus almost completely passes into the phase of metal iron. It is quite important that uranium and thorium from low-radioactive ore species remain in slag liquid melt, and the level of their concentration in pig-iron does not exceed allowable values.

Rare earth elements are concentrated in slag liquid melt. After regenerative melting, the content of REE exhibits a five-fold increase. Slag liquid melt was further transformed into a metastable foamed material (foamed silicate) through quenching a liquid melt by thermal shock [5, 6]. This provided a high reactivity of the material in the subsequent hydrometallurgical processing and a complete leaching of REE by nitric acid even at a room temperature.

Different variants of purifying pig-iron and obtaining niobium products were considered. Now a pyrohydrometallurgical scheme for obtaining pig-iron, manganese-niobium alloy and rare earth concentrate were studied. It is based on the reduction of iron and phosphorus by coke, smelting of manganese-niobium alloy,

TABLE 2

Results for profound reductive melting of the Chuktukon ore

Composition	Content, %		Level of extraction into metal phase, %
	Initial ore	Slag, %	
Al ₂ O ₃	7.7	–	10
SiO ₂	6.5	34	30
Nb ₂ O ₅	0.88	0.012	>99
ZrO ₂	0.095	0.048	9
TiO ₂	0.87	0.23	95
MnO	7.5	0.14	>99
Fe ₂ O ₃	47	–	>99
CaO	0.95	4	7
P ₂ O ₅	4.02	0.035	99
ΣREO	6.8	33	95
ThO ₂	0.104	0.57	35
U ₃ O ₈	0.007	0.024	34

purifying pig-iron from phosphorus by the oxidative processing and the hydrometallurgical processing of slag (foamed silicate) with obtaining a rare earth concentrate.

CONCLUSION

The market of REE and niobium for today is almost monopolized by China and Brazil.

The Chuktukon rare metal deposit located in the Bottom Priangaria of the Krasnoyarsk Territory is as a matter of fact is the only ore object in territory of the Russian Federation. Owing to enormous resources and unique composition of the ore species, the development of the Chuktukon deposit could increase to a considerable extent the competitiveness of Russia in the REE and niobium market. At the same time, the Chuktukon ore species are almost unconcentratable, and the development of the deposit directly depends on the efficiency of chemical technology for their processing.

Two approaches were considered concerning the processing of the ore species. The first one is focused on the extraction of REE and obtaining niobium concentrate, the second one is aimed at the complex processing of ore species with obtaining, alongside with rare met-

als, iron and manganese products. The second variant exhibits advantages provided the creation of a profitable enterprise with respect to iron and manganese, since in this case the rare metal products represent by-products, which facilitate the market entry of the enterprise.

As the first variant is concerned, the most part of problems is already solved. For processing the Chuktukon ore species, we suggested to use an autoclave technique of REE opening with the subsequent pyrometallurgical obtaining of niobium concentrate. According the second variant, one could organize obtaining phosphorus pig-iron or the alloys containing phosphorus, manganese and niobium with no complications.

REFERENCES

- 1 Lomaev V. G., Lomaeva N. V., *Geologiya i Poleznye Iskopayemye Krasnoyarskogo Kraya* (A Collection of Papers), Krasnoyarsk, 2006, issue 7, pp. 20–24.
- 2 Lomaev V. G., Kuzmin V. I., *Razvedka i Okhrana Nedr*, 6 (2004) 23.
- 3 Kuzmin V. I., Lomaev V. G., Pashkov G. L., Ovchinnikov S. V., Kuzmina V. N., Dorokhova L. I., *Tsv. Metally*, 12 (2006) 62.
- 4 RU Pat. No. 2293134, 2007.
- 5 RU Pat. No.1742250, 1992.
- 6 RU Pat. No. 2132306, 1999.