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Combined approaches for comprehensive processing of rare earth metal ores

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ABSTRACT

Technologies for processing rare earth ores (Chuktukon deposits, East Siberia, Russia) have been developed. The ores are composed of iron-manganese oxides and contain 3–7% of rare-earth oxides in the phosphate form (turnerite, florencite) and 0.5–1% of niobium oxide (chalcolamprite). These ores are refractory and do not lend themselves to concentration, therefore various processes for their direct chemical processing have been considered. A number of investigations to estimate the technological behavior of the Tomtor and Chuktukon ores, and to develop various processes for their treatment, have been carried out. Two approaches for processing the Chuktukon ores have been suggested. The first one comprises extraction of the rare earth metals and production of a niobium concentrate; the second one provides a method for processing the complex ores resulting in the production of rare earth metals, iron and manganese alloys.

1. Background

The market for rare earth elements (REE) is highly developed. The annual rate of increase (by volume and cost) in rare earth production is around 10%. The main supplier of rare earth elements to the world market is currently China.

The rare earth metals reserves in Russia consist of 14 deposits which differ significantly in the size and quality of the ores. Of these deposits, the 3 most promising are Kii, Tomtor and Chuktukon (Table 1). All these are situated in the Central and East Siberia regions.

The Kii deposit is located in the Krasnoyarsk region (the central part of Siberia). Rare earth metals are present in the three main ore mineral species – bastnaesite, parisite and monazite. The average content of the rare earth metals is about 2%. The ore is poorly enriched but readily broken down for subsequent leaching. The high radioactivity of the ore is the main drawback of the deposit.

Over 80% of the resources of REE and niobium-rich ores in Russia are concentrated in the two other deposits – Tomtor and Chuktukon. It is likely that only these deposits may seriously compete with the world class deposits in Brazil and China for niobium and REE, respectively. The weathered carbonatite crusts are the basis of the REE ores of the Tomtor and Chuktukon deposits. Such types of ores are very similar and characterized by the high dissemination and intergrowth of the mineral species, which makes ore dressing very difficult and therefore inefficient.

The value of the metals (rare-earth elements, niobium, vanadium, manganese, and iron) recovered from 1 ton of the ore is \$2000 and \$700 for the Tomtor and Chuktukon ores, respectively. With regard to this factor, the Tomtor deposit is undoubtedly preferred. However this deposit is situated in an outlying and undeveloped area of Siberia, 200 km from the Arctic Ocean coast, while the Chuktukon deposit is located 110 km from Kodinsk city where a large water-power plant is currently being constructed. Therefore, in our view, by content, reserves and location, the Chuktukon rare metals deposit is more attractive for development (Kuzmin et al., 2006; Lomayev and Kuzmin, 2004; Lomayev and Lomayeva, 2006).

The aim of the paper is to develop methods of unlocking the REE in the refractory Chuktukon ores and to develop methods for their further chemical processing.

2. Experimental

The inorganic salts, acids and bases used were of chemically pure or analytical grades. Commercial tributyl phosphate (TBP) was used as the extractant. Octane of chemically pure grade was used as the diluent.

The ore was first ground in a ball mill down to a particle size of 74 μm (100%). Ore leaching was carried out with nitric acid in laboratory rotating autoclaves, 100-mL capacity, made from quartz and fluoroplastic, in an air thermostat at temperatures between 120 and 250 °C at various solid:liquid ratios. After leaching, the autoclave was quickly cooled with water, the pulp was filtered, and the precipitate was washed with water. Then the solid and liquid phases were analyzed.

The liquid–liquid extraction testwork was carried out under static conditions by mechanical mixing of the organic and aqueous phases

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Table 1
Promising rare earth metals deposits in Siberia (Russia).

Deposits	Content, % oxides of REE (REEO)	Nb_2O_5	Positive factors	Negative factors
Kii (Krasnoyarsk region)	5.9	0.1	The ore is relatively easily broken down	The ore is difficult to beneficiate and is characterized by high radioactivity
Tomtor (the Arctic shore of Yakutiya)	10.2	6.7	High content of rare earth elements and niobium, large ore reserves	The ore cannot be beneficiated. There is an absence of infrastructure and transportation to processing plants is complicated
Chuktukon (Krasnoyarsk region)	7.1	0.5	Quite a high content of rare earth elements, large ore reserves	The ore has a complex composition. The ore cannot be beneficiated.

for 5–10 min at 20–25 °C. The volume ratios of the organic and aqueous phases were varied.

The ore reduction treatment was carried out in a PL 5/16 oven at temperatures between 900 and 1500 °C in 100 mL and 500 mL graphite crucibles. Commercial coke was used as the reducing agent. The concentration of elements in the aqueous phase was determined using a spectrometer, ICP-MS 7500c from Agilent, and an AAnalist 400 atomic absorption spectrometer from Perkin Elmer. Solid products were analyzed using an Axious X-ray fluorescence spectrometer from PANalytical.

3. Processing of rare metal ores

3.1. Characterization of the Chuktukon and Tomtor rare metal deposit

With regard to composition (Table 2), the Tomtor ore is distinguished by quite a high aluminum and phosphorus content, and iron and manganese oxides are prevalent in the Chuktukon ore.

Crandallite, monazite, pyrochlore, titanium and iron oxides, kaolinite and siderite are the main ore mineral species of the Tomtor deposit. The rare earth elements are mainly concentrated in monazite, and the niobium with a small amount of tantalum is found in the pyrochlore. All in all, the ore can be considered as a rich natural mixture of two concentrates – monazite and pyrochlore. The investigations carried out by different authors showed that physical liberation and separation of these constituents of the ore is practically impossible due to the reasons mentioned above, i.e. the high dissemination of the ore and intergrowth of the mineral species.

The ores of the Chuktukon deposit, unlike the Tomtor ores, are characterized by a high content of iron and manganese oxides. The average REE content is also high; however the niobium concentration is ten times less than that in the Tomtor ores.

The ore body of the Chuktukon deposit is located on the surface in the form of a cupola. The area of the ore zone is relatively small and characterized by its large thickness which increases to the dome part of the deposit up to 300 m.

Table 2
The chemical composition of the ores of the Tomtor (1) and Chuktukon (2) deposits.

Element (oxide form)	Content, % (mass)	
	1 (Burannyi site)	2
ΣREEO, including Y_2O_3	10.2	7.1
Nb_2O_5	6.7	0.5
TiO_2	5.0	0.9
Al_2O_3	17.1	4.9
P_2O_5	16.0	4.8
Fe_2O_3 (+ FeO for Tomtor)	12	51.4
MnO_2	~0.15	12.4
CaO	2.6	0.9
SrO	3.8	0.4
BaO	3.2	2.5
SiO_2	3.8	4.8
SO_3	0.5	–
CO_2	1.5	–

The ore is complex and principally consists of iron-manganese oxides (composition: 40.0–70% Fe_2O_3 and 1–20% MnO). It is important for processing technology to note that the ore contains about 1–2% phosphorus in the form of REE phosphates and apatite. Iron and manganese oxides and hydroxides form the main rock-forming minerals.

The REE in the Chuktukon ore are mainly present as florensite, monazite and cerianite. Phosphorus is relatively evenly distributed in different fractions throughout the ore.

The granulometric composition of the ore is characterized by the presence of finely dispersed particles with a grain size of 0.074 mm which constitute more than 50% of the material. The ore consists of agglomerates composed of particles of less than 1 μm in size. The particular dissemination of the minerals and intergrowth of the mineral species cause problems for the enrichment of these ores (Kuzmin et al., 2006).

This essentially complicates ore processing as compared to the ores from the Bayan–Obo deposit (China) which also are ferruginous, but, unlike the Chuktukon ores, they do not contain any phosphorus (the REE are presented as bastnesite) and can be beneficiated. Accordingly, it allows the Chinese producers to separate the rare-earth and iron-containing minerals at the enrichment stage and to produce REE oxides and steel, respectively (Wu Qifan et al., 2010).

3.2. Analysis of hydro-pyrometallurgical schemes for processing of the Chuktukon ores resulting in the production of rare-earth and niobium products

The uniqueness of the Chuktukon deposit, together with its large ore reserves, the compact nature of the ore body and favorable location of the deposit, rests in its high REE and niobium content. Therefore, the possibility for production of rare earth and niobium products was investigated.

The rare-earth elements in the Chuktukon ores are mainly present as monazite and florensite (phosphates). Various methods for the breakdown of the minerals are known and used. Monazite can be broken down using a direct acid treatment. As applied to rare-earth concentrates, leaching with sulfuric acid is the most widely known method (Clark and Furry, 1946; Katz and Rabinowitch, 1951). The process includes treating monazite with sulfuric acid at a temperature of 200 °C, dissolution of the sulphate in water and sequential recovery of the phosphate concentrates of thorium, REE and uranium by gradual neutralization of the solution. For the breakdown of the ores with high iron content, this method is not suitable due to the large consumption of sulfuric acid. For processing of the apatites (phosphorites) containing monazite, a number of processes for direct leaching with nitric acid has been developed (Aly and Mohammed, 1999; Esmaeil et al., 2011; Konvisar et al., 1991). Bunus and Dumitrescu (1992) found that the rate of recovery of REEs from phosphorites with nitric acid is essentially higher than when using sulfuric acid. Besides, nitrate solutions are more preferable for extraction and separation of the REEs. However the phosphoric acid impurities, which, according to the data reported by Peppard et al. (1953), suppress the REE recovery, are a problem.