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ABOUT IMPROVEMENT OF SCHEMES FOR PROCESSING OF RARE-METAL RAW STOCK WITH THE USE OF CHLORINATION PROCESSES

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A geological structure and mineralogical composition for Mazurovskj deposit of nepheline-rare-metal ores and results of works directed at resumption in processing of it raw material are considered. The thermodynamics analysis for reactions of chlorinating of niobium and tantalum oxides is executed. It is shown utility of testing for the intensificated technology of chlorinating with the use of gaseous repairer for processing of deposit rare-metal concentrates.

Keywords: rock, niobium, tantalum, concentrate, technology, rate of chlorinating, oxide of carbon, rectification

In 50-60th of the XX century rare-metal ore of deposit of mariupolies actively developed as a source of zirconium [1,2]. At a gravity scheme friable ores of residual soil are processed with goting zircon concentrate for the subsequent processing at the Donetsk chemical-metallurgical plant. Other rare metals were not extracted from subzero content and absence of technologies of their enriching. After working of a residual soil the booty of zircon concentrate wass stopped. At the end of 50th ore of deposit began to examine also and as a source of receipt of pyrochlor and feldspar foods.

At Mazurovsk deposit a technological proof was selected from private core proofs, the mass stake of components made in a test, %: Nb_2O_5 - from 0.01 to 1.80 (on the average – 0.11); Ta_2O_5 from 0.0005 to 0.075 (on the average – 0.057); ZrO_2 - from 0.02 to 6.0 (average – 0.470); correlation of Nb/Ta = 20.1; Zr/Nb = 3,7, that is characteristic for all deposit. As a result of works on enriching concentrates: zircon: (mas. stake ZrO_2 – 60.76 %), niobium-zirconium (mas. stake Nb_2O_5 - 9,63 %, Ta_2O_5 – 0.45 %, ZrO_2 – 6.46 %), nepheline-feldspar (mas. stake SiO_2 – 63.53 %) were got.

As a possible technological scheme of processing of the got niobium concentrate the method of chlorinating for the briquetted batch in mine chlorinators is examined [3]. Thus the division of niobium and tantalum in the process of chlo-rinating was foreseen with zirconium, as it mineral forms are unsealed at more high temperatures [4]. After factious distillation of got chloride product and subsequent steam hydrolysis, the receipt of commodity pentaoxide niobium was foreseen. Tetra-chloride of silicon, distinguished by the method of rectification, planned to use for the production of polycrystalline silicon on the chemical-phisics factory of OAJ the «Metallurgical combine the name of Ilich».

It is the serves preliminary restoration melting of concentrates by other possible direction of processing as with the receipt of ferrocolumbium, it subsequent chlorinating, and division of chlorides rectification [5]. Technology requires higher expenses at the stage of preparation for process chlorinating, but has the advantages at the stage of receipt of the prepared chloride foods.

On the basis of simple, but effective enough methods of study for mechanism and kinetics of heterogeneous processes at research of chlorinating process of magnesite, expediency of replacement of hard reducing material is set on gaseous an oxide of carbon [6]. The mechanism of co-operation of natural magnesite with mix-ture of chlorine and oxide of carbon was investigated, conformities to law of mass transfer in the reactionary system are studied, the diffusive presentation of process of chlorinating is set. The conditions of equal delivery of gas reagents to the surface of the chlorinated magnesite [7] are certain by calculation and experimental way, that allowed to attain in the chlorinating process to high-rate at the complete mastering of chlorine. The worked out technology is tested on a pilot apparatus for processing of natural magnesite in the chlorinator of mine type with the internal diameter of mine a 0.3 m.

As the intensifyed technology can be applied and to processing of rare-metal cocentrates of Mazurovsk deposit, we are realized the comparative thermodynamics estimation of chlorinating processes of penaoxides niobium and tantalum with the use of hard and gaseous (oxychloride carbon $COCl_2$) reducing material. Possibility of flowing of the stated below reactions are analysed:

$$Nb_2O_5 + 5Cl_2 \Rightarrow 2NbCl_5 + 2{,}5O_2 \ ; \qquad (1)$$

$$Nb_2O_5 + 3Cl_2 \Rightarrow 2NbOCl_3 + 1{,}5O_2 \ ; \qquad (2)$$

$$Nb_2O_5 + 5C + 5Cl_2 \Rightarrow 2NbCl_5 + 5CO \ ; \qquad (3)$$

$$Nb_2O_5 + 5CO + 5Cl_2 \Rightarrow 2NbCl_5 + 5CO_2 \ ; \qquad (4)$$

$$Nb_2O_5 + 5COCl_2 \Rightarrow 2NbCl_5 + 5CO_2 \ ; \qquad (5)$$

$$Nb_2O_5 + 3C + 3Cl_2 \Rightarrow 2NbOCl_5 + 3CO \ ; \qquad (6)$$

$$Nb_2O_5 + 3C + 4Cl_2 \Rightarrow 2NbCl_5 + NbOCl_3 + 2CO + CO_2; \qquad (7)$$

$$Nb_2O_5 + 4CO + 4Cl_2 \Rightarrow NbCl_5 + NbOCl_3 + 4CO_2; \qquad (8)$$

$$Ta_2O_5 + 5C + 5Cl_2 \Rightarrow 2TaCl_5 + 5CO \ ; \qquad (9)$$

$$Ta_2O_5 + 5CO + 5Cl_2 \Rightarrow 2TaCl_5 + 5CO_2 \ ; \qquad (10)$$

$$Ta_2O_5 + 5COCl_2 \Rightarrow 2TaCl_5 + 5CO_2 \ . \qquad (11)$$

The calculations of change of Gibbs energy allowed to set that for reactions

(3)-(11) range ΔG_T^0 depending on a temperature in considered is area of negative values: from - 118 to ~ is a 833 kJou/mol, id est flowing of reactions of chlorinating is thermodynamics credible both with the use of solid-phase and gaseous reducing material.

Executed kinetic researches [8] and the attained specific speed of chlorinating with the use of mixture ($CO + Cl_2$) showed that gasification of reducing material allowed approximately in three times to promote speed of process of chlorinating (at the temperature 900-1000 °C) as compared to a solid-phase reducing material.

Conclusions. The schemes of processing of rare-metal concentrates of Mazurovsk deposit can substantially modernize on the basis of the use of new technologies for chlorinating and renewal, promote economic efficiency of processing of concentrates, provide the substantial decline of capital costs and the prime price of the got chlorides and producible from them foods.

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