STUDY OF ACID LEACHING OF NIOBIUM FROM TITANIUM PRODUCTION SLUDGE

This article contains the results of acid leaching of titanium production sludge for the extraction of niobium into the solution. The material composition of sludge deposits from titanium-magnesium production was studied by methods of chemical, X-ray and electron-probe analysis. Studies of the sludge phase composition of the collector sludge showed that niobium was bonded mainly with aluminum and titanium. Electron-probe analysis showed that niobium in the form of fine grains is concentrated around the titanium particles. Agitation leaching was performed by two stages within a wide range of changing process parameters. The optimal leaching parameters were 4 % hydrochloric acid (HCl), S:L = 1:10; t=25 °C, agitation time 2 hours at the first stage. Optimal conditions for the second leaching stage were 20 % HCl, S:L = 1:5, t=25 °C, agitation time of 2 hours.

Keywords: sludge, niobium, hydrochloric acid, leaching, extraction.

INTRODUCTION

Niobium is a metal with high ductility, corrosion resistance, good weldability, and small thermal neutron capture cross-section. It is a microligating additive in alloys with high strength and considerable ductility, heat, cold, and corrosion resistance [1-2]. Global demand for niobium is approximately 120 000 tons/year, and its consumption increased by 25 % in 2018. [3]. There are currently about 4,3 million tons of niobium reserves available worldwide, ~95 % of them are in Brazil and the rest in countries including China and Canada [4]. The largest consumers of niobium are China, North America and Europe. Niobium prices currently range from $45 per kilogram for standard metallic ferroniobium to above $50 per kilogram for niobium pentoxide (Nb_2O_5). As analysts expect, niobium will be in demand, and prices for the metal will remain high [5].

Raw niobium stocks are quite limited, at the same time, 15-20 tons of niobium pentaoxide are lost annually only at Ust-Kamenogorsk Titanium and Magnesium plant JSC (UK TMP JSC) with titanium production wastes.

These wastes contain 0,4 to 2 % of niobium which is practically comparable with the niobium content in industrial ores of pyrochlore carbonatites [6]. Most recycling methods for these wastes are based on their dissolution in water to remove impurity metal chlorides from them. Sludges are washed out with water under the existing technology, the resulting chloride sludge is discharged into an acidic sewer and then neutralized with lime milk. In this case all valuable components in the sublimate are accumulated in the sludge collectors [7-9].

The niobium extraction from minerals is traditionally based on acid leaching where highly concentrated HF or mixed acid containing HF (~55 %) and concentrated H_2SO_4 (~98 %) is used as a leaching agent [10]. Although this method provides a decomposition efficiency and niobium extraction of over 90 %, it has a number of drawbacks. For example, about 6-7 % HF is lost in the decomposition process due to the high volatility of HF resulting in the discharge of toxic fluorine-containing waste gases. Besides, beneficiation concentrates characterized by high niobium content (~ 40-50 % Nb_2O_5) were used in the cited works as rare-metal niobium-containing raw materials. However, the described technologies do not guarantee a high degree of niobium extraction to process poor niobium-containing raw materials.

The analysis of available scientific, technical and patent literature shows that most studies were performed for conditioned niobium-containing raw materials, and very few studies - to extract niobium from titanium production waste [11-12], and there is no rational technology intended to produce intermediate products containing and concentrating niobium compounds in the amounts suitable for further use for titanium-magnesium production. Extraction of niobium from the sludge contained in a sludge collector into marketable concentrate will enble to extract the valuable component and dispose multitonnage waste.

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The purpose of this work was to study the extraction of niobium in solution from the sludge contained in a sludge collector and to establish the optimal regime of two-stage hydrochloric acid leaching.

MATERIALS AND METHODS

Materials and equipment

Hydrochloric acid, purity grade «chemically pure (C.P.)»; sludge from the sludge collector of titanium-magnesium production provided by UK TMP JSC. Contents of the main components in the sludge from the sludge collector of the titanium production, mass. %: 12,70 TiO_2; 0,73 Nb_2O_5; 32,90 CaO; 2,00 MgO; 3,40 Al_2O_3; 4,10 SiO_2; 2,70 Fe_2O_3; 0,26 MnO; 0,29 V_2O_5.

IV-6 Vibro distiller (Russia), IKA RW16 stirrer (Germany), Shimadzu scales (Japan), SNOL drying cabinet (Lithuania), distiller (Russia).

Methods of experiments. Agitation leaching of the first stage was performed in a wide range of changing of the process parameters. For this purpose a sludge sample was treated for 2 h at 20-50 °C and concentrations of hydrochloric acid 2-8 %. The ratio of acid to raw material was stoichiometric. The liquid phase was filtered after the process, the sediment was washed on a filter with water and prepared for the second leaching stage. The products obtained after each leaching stage were analyzed for calcium, iron, aluminum, niobium and vanadium.

Methods of analysis: X-ray phase analysis was performed on BRUKER D8 ADVANCE. X-ray fluorescence analysis was performed on a Venus 200 PANalyical B.V. spectrometer with wave dispersion (Holland). Chemical analysis of the samples was performed on Optima 2000 DV optical emission spectrometer (USA) with inductively coupled plasma. Mapping of elemental and phase composition of the samples was performed on JXA-8230 electron-probe microanalyzer by JEOL (Japan).

RESULTS AND DISCUSSION

The sludge was dried to a constant weight according to the known methodology before the study. Then, the waste was crushed to the size of -1 mm and averaged by quarting. X-ray phase and electron-probe studies were performed to study the composition of the main phase
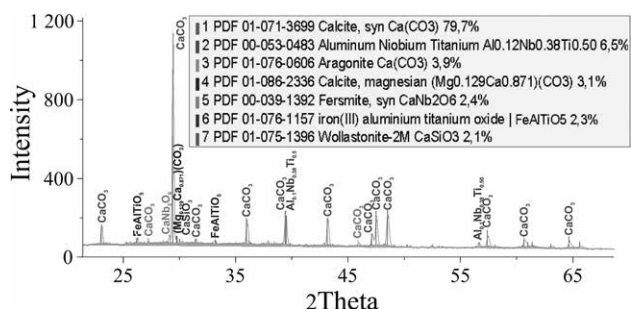

Figure 1 Diffractogram of a sludge sample

of the sludge and associated formations. The X-ray phase analysis result is presented in Figure 1.

It was found according to the results of phase analysis that most of the sludge from the sludge collector was calcium carbonate $CaCO_3$, niobium in its turn was found in compounds - $Al_{0,12}Nb_{0,38}Ti_{0,50}$ and $CaNb_2O_6$.

The electron probe examination of the sludge was performed in the WDS (Wave Dispersive Spectroscopy) mode. Figure 2 shows a section of the sample where significant accumulation of niobium and titanium is observed. Niobium in the form of fine grains is concentrated around titanium particles.
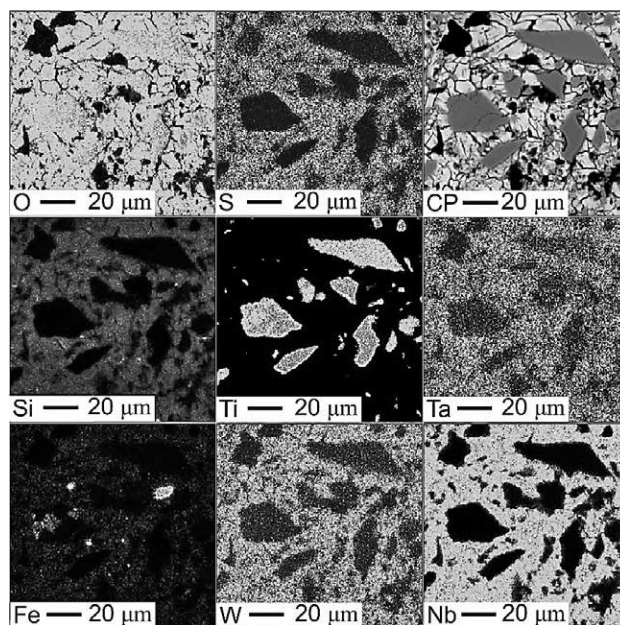

Figure 2 Distribution of elements in the sample area. WDS mode, × 500.

Thus, the physicochemical studies of the phase composition of the sludge collector showed that niobium was mainly bonded with aluminum and titanium. The particles of these compounds were very small and surrounded by clay and carbonate component of the sludge collector.

Study of the sludge leaching process with an acid solution

The study of the dependence of the extraction degree of calcium, iron, aluminum, niobium and vanadium from the sludge in the sludge collector into the solution on the initial concentration of hydrochloric acid solution within the range 2-8 %, at 22-28 °C and agitation time 2 hours showed (Figure 3) that the calcium extraction did not depend on the concentration of hydrochloric acid under these conditions, as it reached its maximum value already when 2 % HCl was used. The aluminum and iron extraction degree increased with increase of acid concentration in the solution. Moreover, an increase in concentration up to 4% did not result in the transfer of significant amounts of niobium and vanadium into the solution.

Figure 3 shows that the concentration of niobium and vanadium compounds in the cake increases with increase in HCl concentration while the extraction of iron and aluminum in the cake decreases significantly.
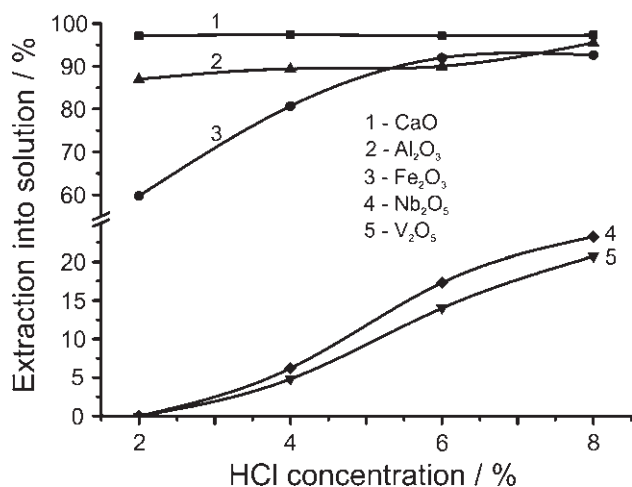

Figure 3 Effect of HCl concentration on the extraction of sludge components (S:L = 1:10; t = 25 °C)

Consequently, at the first leaching stage the optimal concentration of hydrochloric acid was 4 % to avoid significant losses of niobium, with sufficiently high extraction of calcium, aluminum and iron in the solution.

Study of the dependence of extraction degree of calcium, iron and aluminum in the solution on the ratio of liquid and solid phases when 4 % hydrochloric acid was used at 20 °C showed (Figure 4) that with the S:L ratio = 1:8 the extraction degree of calcium and iron in the solution reaches only 71,5 and 75,5, respectively.
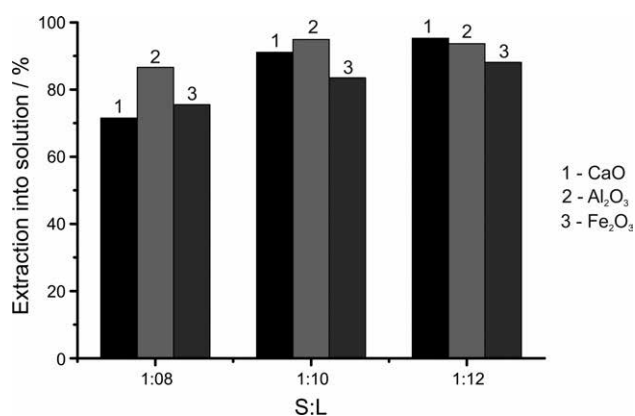

Figure 4 Influence of the S:L ratio on extraction of CaO, Al_2O_3, Fe_2O_3 in solution (t = 20 °C, 4 % HCl)

The extraction degree of controlled components in the solution increases with the increase of S:L ratio in the sludge leaching. The extraction degree of the main component - calcium - is more than 90 %.

The results of studies intended to identify the optimal conditions for the first sludge leaching stage showed that the sludge cound be subject to hydrochloric acid leaching with almost complete extraction of calcium, aluminum and iron in the solution. The optimal

leaching parameters were 4 % HCl, temperature 20 -25 °C, S:L = 1:10÷12 and agitation time 1,5-2,0 h.

Further studies were devoted to the study of optimum conditions of the second stage of cake leaching of the first stage of sludge collector. Cake composition wt. %: CaO 4,2; Al_2O_3 1,9; Fe_2O_3 3,7; SiO_2 8,0; Nb_2O_5 3,54; V_2O_5 2,24.

The technological experiments for the first stage leaching conducted during 2 hours at S:L = 1:5 using 20 % HCl showed that the extraction of niobium and vanadium remained practically unchanged, reaching 92-97 %, in the temperature range of 20-95 °C.

The dependence of niobium and vanadium extraction on the concentration of hydrochloric acid was studied at S:L = 1:5 due to the possibility to lower the leaching temperature 20 °C, Figure 5.
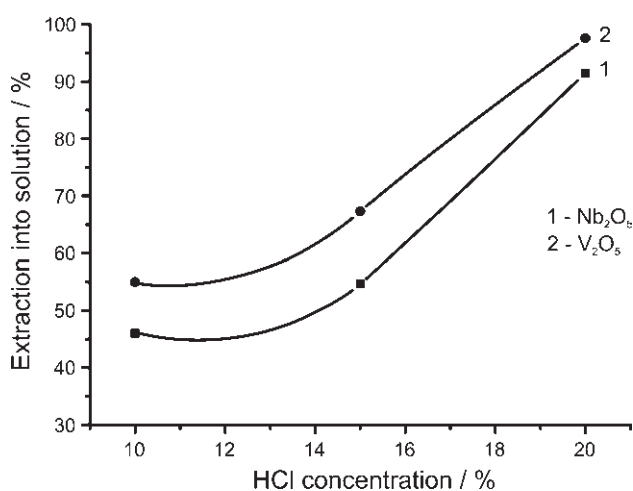

Figure 5 Effect of HCl concentration on recovery Nb_2O_5 and V_2O_5 in the solution

Experiments showed that with increase in hydrochloric acid concentration the niobium extraction degree increases as anionic forms of niobium are formed only in concentrated hydrochloric acid solutions (HCl > 17 % content) [13] resulted in an increase in solubility of niobium compounds.

The study of the effect of the initial S:L ratio in the pulp on the extraction of niobium and vanadium in the
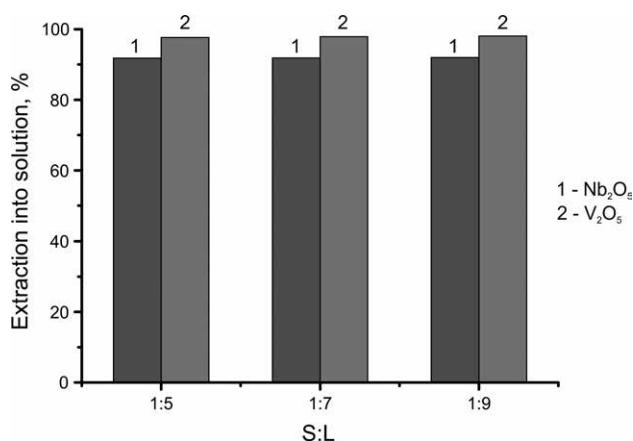

Figure 6 Influence of the S:L ratio on extraction Nb_2O_5 and V_2O_5 in solution

solution at temperature 22 °C, agitation time 2 hours with 20 % hydrochloric acid solution showed (Figure 6) that the extraction degree of niobium and vanadium from the cakes of the first leaching stage did not depend on the S:L ratio within the range of 1:5÷9 which seems to be caused by solubility of their compounds. The content of niobium and vanadium in the solution can be regulated by changing S:L.

Thus, the optimal conditions for the second stage is the S:L ratio = 1:5, the concentration of hydrochloric acid 20 %, agitation time of 2 hours, temperature 20-25 °C.

CONCLUSIONS

Chemical and X-ray fluorescence analyses determined the content of the main components of the sludge reservoir, wt %: 12,70 TiO_2; 0,73 Nb_2O_5; 32,90 CaO; 2,00 MgO; 3,40 Al_2O_3; 4,10 SiO_2; 2,70 Fe_2O_3; 0,26 MnO; 0,29 V_2O_5. X-ray phase analysis showed the presence of the following phases: Calcite $Ca(CO_3)$, aluminum niobium titanium $Al_{0,12}Nb_{0.38}Ti_{0,50}$, Fersmite $CaNb_2O_6$, aragonite $Ca(CO_3)$, calcite, magnesian $(Mg_{0,129}Ca_{0,871})(CO_3)$, iron aluminium titanium oxide $FeAlTiO_5$, Wollastonite-2M $CaSiO_3$. The electron probe study of the sludge showed that the niobium was concentrated as fine grains around the titanium particles.

Agitation leaching was performed in two stages within a wide range of process parameters. The optimal leaching parameters were 4 % HCl, S:L = 1:10; t = 25 °C, agitation time of 2 hours at the first leaching stage at sufficiently high extraction of calcium, aluminum and iron in the solution to avoid significant losses of niobium. Optimal conditions for the second leaching stage was the S:L ratio = 1:5, 20 % HCl, agitation time of 2 hours and temperature 20-25 °C.

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