On the possibility of autoclave desiliconization of ilmenite-leucoxene concentrates using lime milk

Y V Zablotskaya, G B Sadykhov, A S Tuzhilin and K G Anisonyan

Baikov Institute of Metallurgy and Materials Science, 49 Leninsky Avenue, Moscow, Russia

Corresponding author’s e-mail: zablotskay202@gmail.com

Abstract. This article presents the results of studies on the autoclave desilicization of silicon-titanium concentrates of the Pizhemskoye field. Leaching was carried out using burnt lime as a reagent in the presence of the initiator NaOH. The work was carried out on two types of concentrate - pseudorutyl (siliceous-ilmenite) and leucoxene concentrate, which differ in the content of SiO₂ (14.03 and 36.8%, respectively) and Fe₂O₃ (21.6 and 1.1%, respectively). The process was based on the selective binding of silica to calcium hydrometasilicate, which, upon subsequent calcination at 1050 °C, crystallizes into β-wollastonite.

1. Introduction

Russia has large reserves of titanium, but does not have titanium raw materials that meet the requirements of the titanium and chemical industry and for which there were standard processing schemes. This led to the almost complete dependence of the domestic titanium industry on imported raw materials. At the moment, the main importing countries of ilmenite and rutile concentrates to Russia are Ukraine, Australia, and India, but in the modern world with unstable political ties between the countries, this is extremely inconsiderate, which can negatively affect not only the existing enterprises for the production of metallic titanium and pigment TiO₂ (Berezniki TMK (AVISMA), Crimean TITANIUM), but also the future supply of the country with its own raw materials base. Since 2014 The Government of the Russian Federation has set an urgent task to find new opportunities for import substitution in the industry, in connection with which one of the promising sources of titanium raw materials can be large titanium deposits on the Timan (Komi Republic).

About 50 % of the domestic raw materials are represented by ancient titanium placers, which are located in the middle and southern part of the Timan of the Komi Republic. The South Timan placers are combined into the Yarega deposit and are mainly represented by leucoxene. It should be noted that the uniqueness of this field is that it is a reservoir of oil or asphalt. This is the largest domestic deposit in terms of proven titanium reserves. The Pizhemsksoye titanium deposit with ilmenite-leucoxene ores has also been identified and preliminarily evaluated in the Middle Timan [1]. The Pizhemsksoye deposit consists of titanium sandstones consisting of the weathering products of ilmenite-pseudorutyl, leucoxene, rutile, siderite, and goethite. These sandstones are characterized by a high iron content (up to 20%). One of the common distinguishing features of these Timan deposits is their complex polyminal composition and high silica content in concentrates (up to 40%), which leads to a significant decrease in the contrast between the physical properties of the minerals, making it difficult to enrich using known technologies. In this regard, the use of such concentrates without preliminary
desilicization as titanium raw materials will not be cost-effective, which is associated with significant technological difficulties in the production of titanium products from them.

Since the beginning of 2000, IMET RAS has been conducting research on the desilicization of silicon-titanium concentrates from the Yarega deposit to produce artificial rutile and synthetic wollastonite. According to the proposed technology, pre-enriched concentrates containing the main components 63,4-67,2% TiO₂ and 25,3-28,1% SiO₂ are selectively desilicinated in an autoclave with lime milk at a molar ratio of CaO/SiO₂=1 in the presence of 5 g/l NaOH. The most complete degree of desilicization is achieved when the process is carried out in the temperature range of 200-220°C for 2-3 hours, while the quartz is selectively dissolved from the leucoxene grains. As a result, the final product contains (%): 90,5-93,0 TiO₂; 1,5-2,5 SiO₂; 2,5-3 Al₂O₃; 2-2,5 Fe₂O₃; 0,35 Nb+Ta; 0,45 Rare Earth Metals. According to the content of TiO₂, this product is a synthetic rutile and is a valuable raw material for the production of titanium and pigment TiO₂ by the chlorine method. It concentrates rare and rare earth elements contained in leucoxene concentrate. It should be noted that the process also produces calcium metasilicate hydrate, which, after drying and calcination at 1000-1050°C, crystallizes calcium metasilicate with the structure \( \beta \)-wollastonite. The resulting wollastonite is an agglomerate consisting of needle-like crystals with the length and diameter of individual "needles", respectively, 2-5 μm and ~0,2 μm (figure 1) [2].

Figure 1. Photomicrographs of wollastonite, obtained by autoclave leaching of leucoxene concentrate with milk of lime, calcined at 1050°C.

2. Experimental

This paper presents the results of a search study of the possibility of using a similar process of chemical desilicization of silicon-titanium concentrates of the Pizhemskoeye deposit with lime milk to obtain a high-quality titanium concentrate and the possibility of simultaneously obtaining synthetic wollastonite. For the study of autoclave desilicization, two types of concentrates obtained after primary enrichment were used:

- pseudorutile (siliceous-ilmenite) concentrates, having the following chemical composition (%): TiO₂ – 56,4; SiO₂ – 14,03; Al₂O₃ – 3,2; Fe₂O₃ – 21,6;
- leucoxene concentrates having the following chemical composition (%): TiO₂ – 55,4; SiO₂ – 36,8; Al₂O₃ – 3,4; Fe₂O₃ – 1,1.

The phase composition of the material obtained in the process of desiliconization of a leucoxene and further heat treatment, were determined by x-ray diffraction, which was performed on the diffractometer DRON-3M in CuKα-radiation. Transcript of diffraction patterns was carried out using the PDF (POWDER DIFFRACTION FILE). To study the leaching of concentrates, a 50 ml capsule mini-autoclave was used. The autoclave was a capsule, namely a steel cup with a wall thickness of 7 mm and closed with a jacket with a screw cap. To move the reagents inside the capsule during the experiment, it was fixed in a special rotating device placed in a resistance furnace. The set temperature was automatically maintained with an accuracy of ±2°C. After leaching, the pulp was diluted with water and divided into fractions. The pulp was divided into three fractions: overflow (water), slurry (calcium silicate) and heavy (titanium-containing concentrate). After clarification, the overflow was returned to the leaching process; as a result, we reached the overflow water cycle. The leached
concentrate was first washed with slightly acidic solutions and water to remove the residual silicate, and then dried at a temperature of 100-120°C. The amount of silicon dioxide fixed in CaSiO\(_3\) was determined by weighing the solid residue and chemical analysis of the product to determine the SiO\(_2\) content. Calcium silicate hydrate was calcined at temperatures of 1050-1100 °C c with an isothermal exposure of 1 hour in the Nabertherm GmbH HTCT 03/16 furnace.

3. Results and discussion

Based on previous studies on desiliconization of silicon-titanium concentrates Yarega oil field, autoclave leaching siliceous and siliceous pseudorutile-leucoxene concentrates Pizhemskaya field was proposed at a temperature 220°C for 2 hours and the molar ratio CaO/SiO\(_2\)=0,9÷1 in the presence of 5-10 g/l NaOH. The degree of desilicization was estimated by the amount of bound silicon dioxide in CaSiO\(_3\), which was determined by weighing the solid dry residue after leaching, as well as by chemical analysis of the dried product. The results are presented in table 1. Microscopic analysis of leaching products was also carried out to control the process of quartz dissolution (figure 2), mainly the residual silica content is associated with free quartz grains, which, due to the directional selective nature of desilicization, remain practically unaffected by dissolution.

Table 1. The degree of desilicization of concentrates Pizhemskaya field at autoclave leaching (220 °C, τ -2 h).

| NaOH, g/l | Siliceous-ilmenite concentrates | Leucoxene concentrates |
|-----------|--------------------------------|-------------------------|
|           | CaO/SiO\(_2\)=0,9               | CaO/SiO\(_2\)=1         | CaO/SiO\(_2\)=0,95       |
| 5         | 16,1                            | 18,6                    | 24,0                     |
| 10        | 18,9                            | 19,8                    | 34,9                     |

Figure 2. Micrographs of the initial (a, b) and leaching products in the presence of 10 g/l NaOH at 220° C and a duration of 2 h (c, d) : individual grains in siliceous-ilmenite (a, c ) and leucoxene concentrate (b, d).
Comparison of the obtained results showed that almost complete removal of fine quartz from
titanium-containing grains occurs at a NaOH concentration of 10 g/l. As shown by chemical analysis,
in the leached concentrate, the content of TiO$_2$ reaches 91 %, and SiO$_2$ 3.1%. The resulting calcium
hydrosilicates after calcination at 1050°C for 1 h crystallize and acquire the structure of wollastonite,
which is confirmed by X-ray phase analysis of the calcined silicate product (figure 3). It should be
noted that the residual presence of Na$_2$O (0.5-1.0%) in the calcium metasilicate hydrate contributes to
the crystallization of wollastonite during subsequent calcination of the autoclave product [3].

**Figure 3.** Diffractograms of calcium metasilicate obtained by autoclave leaching of silicon-titanium
concentrates of the Pizhenskoye deposit with lime milk, calcined at 1050 °C for 1 h (Cu Ka).

**Conclusion**

In the searching result of the study demonstrated the possibility of hydrometallurgical selective
desiliconization of silicon-titanium concentrates Pizhenskaya field in the process of autoclave
leaching with milk of lime with the participation of NaOH getting quite rich in titanium product, and
wollastonite. At the same time, it is shown that lime leaching can be effectively used to desilicate
various types of silicon-titanium concentrates from Timan deposits.

**Acknowledgements**

The work was supported by the program of the Presidium of the Russian Academy of Sciences (R & D
registration number AAAA-A18-118032090120-7).

**References**

[1] Ignat’ev V and Burtsev I (1997) *Leucoxene of Timan* (St. Petersburg: Nauka) p 216.
[2] Zablotskaya Yu V, Sadykhov G B, Goncharenko T V, Olyunina T V, Anisonyan K G and
Tagirov R K (2011) Pressure leaching of leucoxene concentrate using Ca(OH)$_2$ *Russian
Metallurgy (Metally)* 11 pp 859–864.
[3] Martirosyan G G, Manvelyan M G, Hovsepyan E B, Grigoryan K G (1977) Obtaining synthetic
wollastonite *Armenian Chemical Journal* 11 pp. 890-897.