Extraction of useful components from ilmenite-titanomagnetite ores of Sikhote-Alin (Russia)

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Abstract. In the south of the Far East of Russia, a new source of critically important metals (titanium and iron) has been discovered - ilmenite-titanomagnetite ores of mafic-ultrabasic rocks of the Sikhote-Alin orogenic belt. On the example of one of these massifs, Kokshaarovsky, the possibilities of decomposition of mineral raw materials are conducted with using hydrometallurgy methods are considere. The opening of the studied mineral raw materials was carried out by means of using ammonium hydrofluoride $\text{NH}_4\text{HF}_2$ and ammonium sulfate ($\text{NH}_4\text{SO}_4$) with subsequent complete transfer of useful components into solution. It has been established that the use of a mixture of these reagents makes it possible to more fully open titanium-containing rocks. The experience of deep processing of ilmenite-titanomagnetite ores will allow outlining the ways for the industrial development of complex deposits of the Far East.

1 Introduction

There has been a sharp increase in interest in deposits of ilmenite-titanomagnetite ores all over the world, and especially in Russia recently because the last ones are an important industrial sources of titanium and iron. At the same time, the technologies used for processing mineral raw materials are most often suitable only for certain types of ores with strict requirements to the quality of their enrichment [1]. Thus, decrease in the concentration of titanium dioxide is an important condition for the usage of ilmenite-titanomagnetite ores as iron ore raw materials, in view of the fact that the amount of $\text{TiO}_2$ should not exceed 4% to maintain the normal course of blast-furnace smelting. The titanium-rich ores are the only ones used to obtain commercial titanium slag. They can be processed as high-quality titanium raw materials with an ilmenite content in the ore being equal to more than 5 percents. of Processing titanium ores with the sulfuric acid is traditionally the most common method which is due to the simplicity of usage of equipment and the availability and low cost of reagents [2]. On the other hand this method is characterized by a high degree of environmental impact with increased amounts of harmful liquid and solid wastes being released. Besides, the structure of domestic titanium-containing raw materials is distinguished by a large proportion of associated components, which makes in inferior to traditional sources of mineral raw materials, such as ilmenite and rutile, if the titanium content is considered. All this requires creating new technical
solutions that will allow conducting complex processing of mineral raw materials in compliance with the principles of rational use of natural resources and environmental protection.

The attention of researchers to the ways of processing mineral raw materials by fluoride methods using such reagents as ammonium fluoride and ammonium hydrodifluoride [3, 4] has increased recently. It is especially advantageous to use this approach in the processing of complex mineral raw materials, since it allows expanding the range and the degree of extraction of useful components [5]. According to the data from [6] obtained due to the comparing of the technical and economic indicators of existing methods for the production of pigment titanium dioxide the use of fluoride technology appeared to provide significant reduction of the pigment cost. The difference between the fluorination of samples with dry salts and the acid opening, in which the process temperature is limited by the boiling point of the solution, is that the first one can be carried out at temperatures of 230–250°C in open-ended vessels [7], which allows increasing the speed and completeness of fluorination significantly. The opening process is carried out with the usage of solid-phase interaction of ammonium fluoride/hydrodifluoride with elements of mineral raw materials. The fluorinated products are dissolved in nitric acid with a subsequent analysis of the solutions by instrumental methods, for example, such as using inductively coupled plasma mass spectrometry [8]. The interaction of minerals which rocks are composed of results in the formation of a number of the water-soluble complex fluoroammonium compounds of metals (such as iron, aluminum, titanium, zirconium, etc.), silicon and practically insoluble fluorides of calcium, magnesium and rare earth elements (REE).

On the other hand, as shown in [9, 10], sparingly soluble fluorides, such as calcium and rare-earth elements, can be transformed into more soluble sulfates by solid-phase interaction with ammonium sulfate.

This approach is especially beneficial in the processing of complex mineral raw materials, since it allows expanding the range and degree of extraction of valuable components [5]. In addition, a comparison of the technical and economic indicators of existing methods for the production of pigment titanium dioxide showed that the use of fluoride technology allows reducing the prime cost of the pigment by several times [6].

The purpose of our work is to study the possibilities of opening ilmenite-titanomagnetite ore with a mixture of ammonium sulfate and ammonium hydrofluoride and to find out if the subsequent complete transformation of valuable elements into solution is possible.
2 Materials and methods

The ore-bearing intrusions of mafic-ultramafic rocks of the Sikhote-Alin orogenic belt which are a new source of high-tech metals (titanium, platinum group metals, rare earth elements, niobium, tantalum, hafnium, vanadium, cobalt, antimony) have been discovered in the south of the Russian Far East [11]. The Koksharovsky ultramafic massif located in a densely populated center of Primorye with a developed infrastructure facilitating the usage of up-to-date methods of production and extraction of minerals is a prominent representative of this group. The formation of the massif occurred in several phases, with pyroxenites relating to the earliest one and compositing the main body of the intrusion [12]. Titanomagnetite and ilmenite are the essential minerals constituting up to 30 percents and 5-10 percents of the rock mass, respectively. Titanomagnetite (nFeTiO$_4$ · (1-n) Fe$_3$O$_4$) is found in the form of small rounded grains of disturbed octahedral and sharply-angular fragments and represents a solid solution with isomorphic inclusion of titanium into the magnetite lattice. Ilmenite (FeTiO$_3$) often develops grains with well-defined crystallographic forms resembling thin plates. According to X-ray fluorescence analysis calculated in terms of oxides, the content of the main components in the studied rock sample was (wt.%) as follows: SiO$_2$-33.0; TiO$_2$-8.8; Al$_2$O$_3$-3.6; Fe$_2$O$_3$-17.7; FeO-11.7; MgO-11.3; CaO-14.2. The industrial development of Koksharov titanium ores is constrained by the lack of technology for extracting useful components, which predetermined the line of our research.

The opening of the studied mineral raw materials was carried out by means of using ammonium bifluoride NH$_4$HF$_2$, ammonium sulfate (NH$_4$) and concentrated nitric acid HNO$_3$, each belonging to “chemically pure” grade. The previously mentioned components were mixed in various mass proportions to study the possibility of interaction of ore samples with a mixture of ammonium sulfate with ammonium hydrodifluoride. The resulting mixture poured in glassy carbon or platinum crucibles was placed in a muffle furnace-controller produced by Nabertherm GmbH (Germany) and equipped with an electronic controller with a digital display. The mixture was heated at the rate of 2.5 K/min to a predetermined temperature kept for 4–6 h. The quantities weighted 10–40 g.

The changes that the sample underwent during heating were controlled by the weight loss of the initial mixture, X-ray phase and X-ray fluorescence analyses of the products obtained during processing, and atomic absorption analysis of leaching solutions.

The leaching process of the samples treated with a mixture of ammonium sulfate and ammonium hydrodifluoride was carried out at room temperature by using 4-fold dissolution of the resulting product in water at the ratio of T : L equal to 1:10 with duration of 15–30 min and subsequent filtration through a blue ribbon filter. Leaching of samples obtained by the interaction with NH$_4$HF$_2$ was carried out in fluoroplastic cups and the ones obtained by the interaction with the mixture of NH$_4$HF$_2$ and (NH$_4$)$_2$SO$_4$ underwent the procession in glass cups.

The content of the main components of the fractions at various stages of processing was determined by X-ray fluorescence analysis using a Shimadzu EDX 800 HS spectrometer (tube with a rhodium anode, vacuum) at the room temperature with a tablet containing polytetrafluoroethylene (PTFE) being used. The quantities weighing 1 g were ground in an agate mortar with 0.5 g of PTFE, then placed in a mold of 20 mm in diameter, and pressed for 2 min at the pressure of 20 MPa.

The X-ray diffraction patterns of the samples were taken on a D-8 ADVANCE automatic diffractometer with sample rotation in Cu K$_\alpha$ radiation. The X-ray phase analysis was performed using the EVA search program with the PDF-2 powder database.
The induced activity was measured on a spectrometric box monitor on GC2018 coaxial Ge detector basis manufactured by Canberra. The energy resolution of the detector was 1.8 keV with the radiation energy being equal 1332 keV. The relative detection efficiency in the 1332 keV peak was 20%. In addition to the detector, the spectrometric box monitor consists of SBS-75 information processing unit and a 2002CSL preamplifier with a cooled head stage and 3 m cables. The eSBS Version 1.6.7.0 program and the Gamma Analyzer for semiconductor detectors (SPD)" version 1.0 were used was measuring the gamma spectra and processing the results of the measurements, respectively.

The thermogravimetric studies were performed on a Q-1000 derivatograph in platinum crucibles in air at a heating rate of 2.5 K/min and weighed quantities of 100–200 mg.

3 Results and discussion

While interacting with ammonium hydrodifluoride, the oxygen-containing compounds of transitional and most of non-transitional elements form ammonium fluoro- or oxofluorometallates, which facilitate the solubility of the products due to their physicochemical properties and allow transforming the main part of the complex salts into solution upon subsequent leaching of the product with water, which makes the use of NH₄HF₂ very perspective for the usage usage with the purpose of opening of mineral raw materials [13].

According to [7] the procedure for preparing samples for analysis includes the following sequence of actions: mixing a weighed quantities of the analyzed sample with NH₄HF₂ in a ratio of 1:1-6, heating the resulting mixture for 1-6 hours, dissolving the resulting product in nitric acid, evaporating the solution to dryness and re-dissolving in nitric acid when heated for 6 hours. There were cases of incomplete dissolution of fluorinated samples containing aluminum by the passivation of the gibbsite surface by fluorine in this case [14], the same happened with alkaline earth and rare earth elements [3]. As noted above, the solid phase interaction of the calcium fluoride and REE with the ammonia sulphate at the temperature of 350-400°C leads to the formation of sulfates of these elements. It should be mentioned that these substances are more soluble than fluorides [9, 10]. Accordingly, the comparison between the degree of decomposition of the studied geological samples and the transformation of their constituent components into solution was made using the hydrodifluoride of NH₄HF₂ and the mixture of the last one with ammonium sulfate (NH₄)₂SO₄.

According to the data obtained as a result of the experiment, the fluorinated titanium-containing ore proved to dissolve much worse in nitric acid without preliminary leaching with water in case of processing the mineral raw material by NH₄HF₂. Better solution is achieved due to the processing of the ore by the mixture of hydrodifluoride and ammonium sulphate firstly at the temperature of 190°C followed by heating up to 350°C. This mode was chosen based on the analysis of the thermal behavior of a mixture of hydrodifluoride and ammonium sulfate.

The thermogravimetric study showed that heating the mixture of NH₄HF₂ and (NH₄)₂SO₄ is accompanied by both thermal decomposition in the temperature range from 125 to 430°C and almost complete transformation of the products into the gas phase. The first endothermic effect on the given thermogram refers to the melting of NH₄HF₂ (tₘ=126.2°C). The weight loss is observed during the further heating of the mixture, which is caused by insignificant evaporation of NH₄HF₂ at the temperature kept within the range from 126-to 200°C. The subsequent heating over 200°C leads to the decomposing of ammonium sulfate accompanied by the release of ammonia NH₃ and the formation of ammonium hydrosulfate NH₄HSO₄. According to X-ray phase analysis the product released at 220°C, appeared to be the mixture of (NH₄)₂SO₄, NH₄HF₂ and NH₄HSO₄. Two
endothermic effects overlapping each other occur within the temperature range of 220-280°C, they are as follows: boiling of NH₄HF₂ (t_{boil} = 238°C), accompanied by decomposition into NH₃ and HF, and melting of NH₄HSO₄ (t_{melt} = 251°C). The further increase in temperature is accompanied by two more endothermic effects, proceeding at the maximum rate at 330 and at the temperature of 425°C being caused by the stepwise decomposition of ammonium hydrosulfate NH₄HSO₄ into sulfuric anhydride, ammonia and water.

The process of solid-phase interaction of ilmenite-titanomagnetite ore of the Koksharovsky massif with both NH₄HF₂ and the mixture of NH₄HF₂ and (NH₄)₂SO₄ and subsequent leaching of the resulting product with water (see the table below) was used to illustrate the above said. The complete dissolution of the sample does not occur in this case. According to the X-ray diffraction data, the insoluble residue contains magnetite Fe₃O₄, which is most likely due to the positive values of the change in the Gibbs energy of the fluorine process of the ilmenite-titanomagnetite ores caused by the usage of the hydrodifluoride of ammonium [15]. The complete dissolving of the interaction product in this particular case is observed only after additional leaching of the first one by the nitric acid solution.

A comparative analysis of the data (table) obtained under various processing conditions of titanium-containing mineral raw materials indicates that the use of a mixture of hydrodifluoride with ammonium sulfate allows better opening of the mineral raw material compared with the usage of ammonium hydrofluoride alone. Accordingly, better transformation of the resulting product into the solution will be obtained during the water leaching. At the first stage, when the ore interacts with NH₄HF₂, prodestruction of the crystal structure minerals to form metal fluorides or their complex fluoroammonium compounds, and at the second stage - sulfatization with the formation of ion of acid-soluble metal sulfates.

Table 1. Influence of processing conditions of ilmenite-titanomagnetite ore on the degree of transformation of the sample into solution during leaching.

<table>
<thead>
<tr>
<th>Number of the experiment</th>
<th>T, °C</th>
<th>Ore: reagent relation</th>
<th>Leaching conditions (the concentration of the solution)</th>
<th>The residue weight, in % to the initial weighed quantity of the ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>220</td>
<td>Ore: NH₄HF₂ = 1:4</td>
<td>Water HNO₃ (16%)</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13,1</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>Ore: NH₄HF₂:(NH₄)₂SO₄ = 1:3:5:5</td>
<td>Water HNO₃ (16%)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0*</td>
</tr>
</tbody>
</table>

The usage of the mixture of NH₄HF₂ and (NH₄)₂SO₄ for water leaching of the product of the interaction of titanium-containing mineral raw materials allows transferring almost the whole of titanium and the bulk of iron into the solution of highly water soluble double salts. When the leaching solution having pH equal to 1-2 is heated (up to 50-60°C), the process of hydrolysis of the titanium salt (NH₄)₂TiO(SO₄)₂ starts accompanied by the formation of titanium dioxide in the form of anatase. This method allows complete separation of titanium and iron from the leaching solution. The resulting filtrate, which is a mixture of phases of NH₄HSO₄ and NH₄Fe(SO₄)₂, can be separated by stepwise neutralization.

4 Conclusion
The performed experiments on the decomposition of ilmenite-titanomagnetite ores of basic-ultramafic rocks of the Sikhote-Alin showed that the mineral raw material proved to open better in case of using the mixture of ammonium sulfate with ammonium hydrofluoride in comparison with the usage of ammonium hydrofluoride alone. Combining the processes of fluorination and sulfatization allows effective opening of rocks, including silicate ones, due to the breaking of Si–O bonds with the participation of NH$_4$HF$_2$ and the transformation of insoluble fluorides into soluble sulfates (NH$_4$)$_2$SO$_4$. The proposed technical solutions for the extraction of useful components from titanium ores worked out in compliance with the principles of environmental management and environmental safety are only the first step in the development of minerals in the south of the Russian Far East. Further research should be carried out in the direction of the quality improvement of the processing degree, which will allow reducing the cost of obtaining individual products and ensure higher production efficiency.

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References