INTRODUCTION

Since the raw materials resource of rich ore-metallic deposits, including molybdenum, decreases on a global scale, the necessity to treat poor ores appears more frequently in recent years. Poor ores cannot be used to produce highly enriched concentrates for further processing into standard molybdenum-containing products or this process is unprofitable. Analogous problems arise for processing of artificial deposits, which are more frequently developed by metallurgists, because the content of basic metals in old industrial dumps often approaches and sometimes exceeds their cutoff grade in ores developed by modern ore mining and processing enterprises.

One of the ways to the solution of this problem is an industrial use of poorly enriched concentrates and intermediate products (hereinafter, industrial products). Due to a decrease in the number of technological enrichment procedures, the cost of processing decreases substantially and, which is the main point, the losses of a base metal from ore also decrease. This way can be accomplished in practice in combination with the development of roasting-free technologies of treatment of molybdenum concentrates. Another way is to involve a flotation concentrate with a low content of the base metal and nonstandard compositions of copper, iron, silicon, sulfur, and other impurities in a direct treatment in parallel with the molybdenum concentrate treatment.

These methods include the oxidative autoclave leaching of sulfide molybdenite concentrates. An advantage of this method is that its use allows one to process products with any molybdenum content, including a very low one (<15% Mo) and to efficiently extract molybdenum even in the presence of a considerable amount of impurities of nonferrous metals, iron, and silica. A practical development of this process since the beginning of the last century provided its wide modern application on industrial scales [1–4].

The hydrometallurgical opening of molybdenite concentrates provides high-quality products following a short ecologically safe technological chain with procedure expenses several times lower than those during roasting. At present, this scheme was performed, for example, at the Molymet enterprise (Chile), where the autoclave opening of a molybdenite concentrate in the form of a water pulp is carried out at 240°C and an oxygen pressure of 4.4 MPa. Under such working conditions, an autoclave is made of an expensive high-strength steel. The autoclave is leaded inside, and the lead is brick-lined (two layers, the brick is acid-resistant). Autoclaves for molybdenite leaching operate according to an analogous technology in the United States, Republic of South Africa, Australia, and Canada [1–8]. We developed scientific technological principles and tested the technology of autoclave oxidative leaching (AOL) of molybdenites in the presence of nitric acid, which is a substantial intensifier of the process and makes it possible to considerably increase the...
kinetic parameters of leaching and to decrease the temperature and pressure of the working process. This principle is known for more than ninety years [1, 5–7, 9–15]. However, it has not been accomplished on industrial scales until now, at least for the processing of sulfide molybdenite products, because of the absence of a scientific substantiation and understanding of the mechanism of the effect of nitric acid on the AOL processes of sulfide concentrates and industrial products.

Specialists in the field of hydrometallurgy believe that an addition of nitric acid to the AOL process can result in uncontrolled foaming of a pulp and the formation of a considerable amount of nitrogen oxides, creating the well-known problems for the environment in the case of their atmospheric emission. Although this possibility was not checked in practice and there are no quantitative and qualitative calculations and scientific substantiations. Practical characteristics of approbation of this process are also lacking.

At the same time, the AOL technology has a doubtless advantage: almost any, including low-grade and dirty (with impurities), molybdenite raw materials from dumps or enrichment tails and wastes of other production processes can be processed with the achievement of high parameters of extraction of the obtained products and ecological safety of production. The most attractive feature of the use of this technology is the practical easiness of controlling the qualitative and quantitative parameters of the AOL process by monitoring the supply of nitric acid, which makes it possible to vary the kinetic parameters (in the case when the time of the process should be shortened) or (when the process duration is unchanged) to considerably decrease the working parameters [2, 5, 9, 10, 12, 13] with a simultaneous increase in the degree of extraction of molybdenum from a sulfide product.

Although the AOL technology of molybdenites in the presence of nitric acid is evidently advantageous, its industrial use is mainly prevented by risks of uncontrolled formation of large amounts of nitrogen oxides during leaching and a danger of their emission into the atmosphere. In addition, there is a danger of too vigorous occurrence of the reaction upon the introduction of nitric acid and uncontrolled foaming of a pulp during leaching.

For experimental checking of the technological parameters of the oxidative leaching of the molybdenite concentrate in the presence of nitric acid, in May 2008 we carried out industrial tests at the experimental pilot base of OOO Institut Gipronikel’ (St. Petersburg).

THEORETICAL FOUNDATIONS AND STATEMENT OF THE PROBLEM

The main reaction of sulfide minerals with acidic solutions is as follows:

\[
3MS(s) + 2HNO_3(l) + 3H_2SO_4(l) \rightarrow 3MSO_4^2- + 2NO(g) + 4H_2O. \tag{1}
\]

It is considered that the NO\(^+\)/NO pair possesses a very high oxidation potential; therefore, this is NO\(^+\) that is the main oxidant of sulfides [1, 3, 5, 6, 8]. It is most likely this is valid for the formation of sulfide solutions of metals. In addition, intermediate nitrogen compounds serve as oxygen carriers, transporting oxygen to the surface of solid mineral particles; as a result, they favor a significant acceleration of the leaching process. As a consequence, it is experimentally possible to decrease the working temperatures and pressure in an autoclave, which substantially decreases the cost of the equipment and increases the economical parameters of sulfide processing [5].

From the generally accepted point of view [1, 4, 6–8], the main purpose of reaction (1) between sulfide minerals and acidic solutions and oxygen is the maximum dissolution of a leached metal in a sulfate solution accompanied by the formation of elementary sulfur. It should be mentioned that the studies of leaching of the sulfide concentrates upon the action of nitric acid were carried out in many works, in particular, by Prof. C.G. Anderson (Canadian Institute of Mining, Metallurgy and Petroleum, Montreal) for the minerals of iron, gold, silver, nickel, copper, and other metals [2, 5, 7, 8], but not for molybdenum.

When it is necessary to completely oxidize molybdenite and other sulfides, a specific feature of molybdenite leaching is that this process requires no complete transfer of a metal to a solution, since molybdic acid exists in the solid state and can be processed from this state. Another specific feature is a necessity to take into account the presence of rhenium, which is also a valuable component, in the initial raw materials when choosing the technology of processing of a molybdenite concentrate.

The conclusions of a classical theory concern the oxidation of sulfides at high temperatures and oxygen pressures (so-called mild oxidation) with the formation of elementary sulfur. When the process occurs under more severe conditions (temperature above 160°C), the elementary sulfur content is low and part of nitric acid is recovered in the reactions

\[
MoS_2 + 6HNO_3 \rightarrow H_2MoO_4 + 2H_2SO_4 + 6NO, \tag{2}
\]

\[
2NO + O_2 \rightarrow 2NO_2, \tag{3}
\]

\[
2NO_2 + H_2O \rightarrow HNO_3 + HNO_2, \tag{4}
\]

\[
2HNO_2 + O_2 \rightarrow 2HNO_4, \tag{5}
\]

\[
MoS_2 + 4.5O_2 + 3H_2O \overset{\text{HNO}}{\rightarrow} H_2MoO_4 + 2H_2SO_4. \tag{6}
\]