

Investigation of the Mechanism of Decomposition of Artificial Scheelite in Nitric Acid

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Abstract

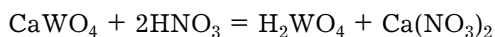
The mechanism of decomposition of artificial scheelite in nitric acid is investigated by recording the curves of anodic charging. This method involves fixation of temporal changes in the potential of platinum electrode in reaction medium. It is established that the reaction between artificial scheelite and nitric acid is not a solid-phase process but a usual exchange reaction in aqueous medium with the dissolution of scheelite and formation of precipitate which is tungsten trioxide monohydrate.

Natural minerals of high-melting metals are distinguished by high stability toward the action of acidic and alkaline reagents, which requires rather rigid conditions for their chemical decomposition: a high concentration of leaching agent, temperature rise, presence of oxidizers, *etc.*

For tungsten-containing minerals as xample (scheelite, wolframite), the mechanisms of their interaction with mineral acids were investigated. It follows from the published data [1] that there is no common opinion on the mechanism of transformations in non-yielding tungstates under the action of acidic reagents. The authors of [2–6] investigating the kinetics of nitric acid decomposition of scheelite paid major attention to the forms in which tungstate occurs and to obtaining the final product, tungstic acid, but did not take into account the formation of intermediate compounds which are the basis to obtain H_2WO_4 .

It is known that the traditional technological scheme of processing tungsten concentrates and other compounds into target products provides the stage of precipitation of artificial scheelite and its decomposition with mineral acids (often hydrochloric, and more rarely nitric).

It is accepted that this stage involves a simple exchange reaction between artificial scheelite and mineral acids (in particular, nitric acid) according to the following scheme:



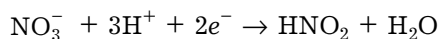
However, the reaction of scheelite transformation into tungstic acid does not take into account the specific behaviour of nitric acid in aqueous solutions in comparison with other inorganic acids, which results in some practical complications connected with the isolation of the final product of processing.

Thus, it is necessary to make an analytical review of literature data and investigate some properties of nitric acid in application to the scheme of processing of tungsten-containing raw material for the purpose of its rational use in the technology of high-melting metals. The mechanism of decomposition of artificial scheelite by nitric acid was investigated by studying the electrochemical behaviour of this acid depending on its concentration. Nitric acid can participate in both exchange and oxidative reactions [7].

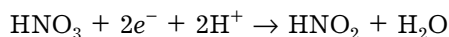
Electrochemical behaviour of nitric acid was determined by recording cathode polarization

curves at the given current density without exposure of platinum electrode till constant potential in nitric acid solutions of 1, 2, 5, and 10 mol/l within the range 10^{-6} – 10^{-2} A/cm² in a special volume according to [8] with the simultaneous analysis of the products of reduction of the indicated acid in the reaction medium.

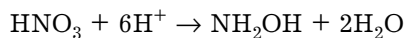
The analysis of polarization curves shows that their shape and behaviour depend on the concentration of the acid. In the solutions with low concentration, when the dissociation degree is close to unity (up to 3 mol/l), at low current density, in addition to hydrogen evolution, nitrate ion can get reduced on the cathode at low current density according to the reaction:



In nitric acid solutions with relatively high concentrations with high content of non-dissociated molecules, the evolution of hydrogen on the cathode can likely be preceded by direct reduction of nitric acid molecules according to the reaction:



or



Comparison between the data of polarization measurements and the data obtained in analysis of the products of nitric acid reduction gives grounds to assume that in dissociated solutions (that is, in diluted solutions, <5 mol/l) the kinetics of the process is determined by the joint reduction of nitrate ion and hydrogen ion, while in concentrated solutions (>5 mol/l) by the reduction of homopolar (ester) molecules of nitric acid resulting in the formation of HNO₂, NH₂OH and possibly NH₄OH, N₂. The results of investigations showed which concentration of nitric acid in solution is necessary for the exchange reaction, as well as which concentration is necessary for oxidative properties to start being exhibited [9]. Specific recommendations for the application of nitric acid in hydrometallurgic processing of mineral raw materials containing nonferrous and rare metals are absent from literature.

After having revealed some technologically important characteristics of nitric acid, we examined the mechanism of decomposition of artificial scheelite with this acid by means of recording the anode charge curves [10]. Experiments were performed under the conditions of the works of Uzbek Plant of High-Melting and Heat-Proof Metals (UzPHMHPM) using 56 and 28 % nitric acid without heating and with heating, but with compulsory mixing with a magnetic mixer. The method used involves recording of changes in the potential of platinum electrode in the reaction medium *vs.* time. The formation of phases of compounds on the surface of electrode (platinum) is accompanied by the appearance of the corresponding plateaus on charging curves. When soluble forms of the compounds appear in the reaction medium, a plateau passes into a sloping region of some length.

The results of measurements of the dependence of electrode potential on time for the decomposition of scheelite by nitric acid under heating are shown in Fig. 1. The curves have a clearly exhibited three-step character due to the formation of one or another phase of individual compounds on the electrode surface.

Region I is likely to correspond to the dissolution of artificial scheelite in this solution with the formation of the most stable dissolution products: Ca(NO₃)₂ and WO₂(NO₃)₂ or WO₂(OH)NO₃. When the near-electrode layer gets saturated

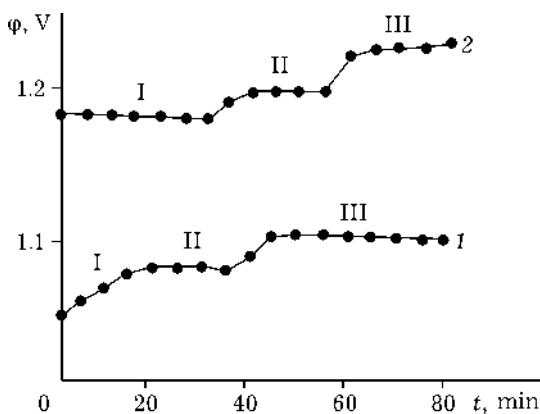
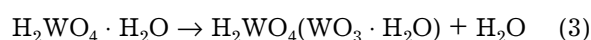
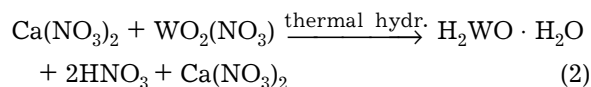
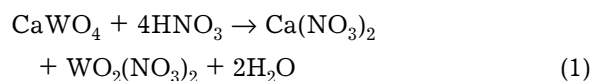


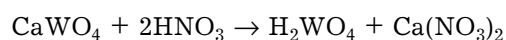
Fig. 1. Changes in the potential of platinum electrode *vs.* time for the decomposition of artificial scheelite by nitric acid. HNO₃ concentration, %: 28 (1), 56 (2); temperature: 80 °C.

with the soluble products, various deposits (layers) can be formed on the surface of the electrode and in the vicinity of it; these include tungsten trioxide dihydrate ($\text{WO}_3 \cdot 2\text{H}_2\text{O}$ or $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$) which is a white colloid form of tungstic acid (region II); the anode will start to be passivated, its potential will become more positive till the values at which a new electrode process arises at the anode, namely, the deposition of tungstic acid as a yellow form, tungsten trioxide monohydrate ($\text{WO}_3 \cdot \text{H}_2\text{O}$, region III).

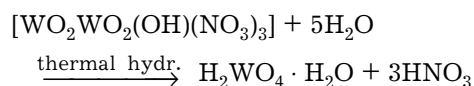
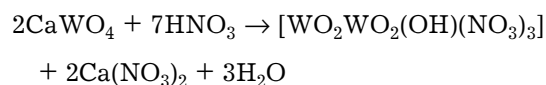
On the basis of these investigations and literature data on the ion status of nitric acid and tungsten in strongly acidic media [11, 12], the mechanism of the decomposition of artificial scheelite by nitric acid with the formation of tungsten trioxide monohydrate can be represented as follows:



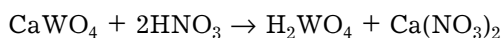
or total process:



Taking into account the fact that $\text{WO}_2(\text{OH})^+$ ions coexist with WO_2^{2+} ions, according to the data of [11, 12], the reaction can proceed *via* the scheme:



or total process:



So, three plateaus on the curves depicting the dependencies of electrode (anode) potential on time are the evidence of the formation of intermediate compounds on the electrode surface under these conditions. It should be concluded that the reaction between artificial scheelite and nitric acid is not a solid-phase process but a usual exchange process in aqueous medium with the dissolution of initial product followed by the formation and precipitation of tungsten trioxide monohydrate.

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