UDC 543.054

Low-Temperature Fusion and Autoclave Processes for Decomposing Ores and Precious Metal Concentrates

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Abstract

Features of opening resistant materials in the open and closed systems are considered. A possibility is demonstrated for increasing the decomposition efficiency concerning refractory ores and precious metal concentrates in open systems with the application of low-temperature alkali fusion and acidic oxidative opening in closed systems such as autoclaves with the use of microwave radiation.

Key words: sample preparation, alkali fusion, autoclaves, microwave radiation

INTRODUCTION

The Krasnoyarsk Territory plays one of the leading roles in the world in storing, mining and processing ores and precious metal concentrates. A paramount task of the metallurgical branch consists in obtaining of a high-quality product meeting the requirements of world standards. The analytical composition control for ores and concentrates represents an important and crucial stage of the metallurgical cycle. The mentioned procedure includes preliminary chemical preparation such as opening a sample, *i. e.* the decomposition of samples providing the most complete passing the components under determination into solution, suitable for the subsequent instrumental analysis. Dissolution of analyzed material samples is based on the destruction of its structure as the result of reactions between components contained therein with the reagents introduced. Choosing the method of sample decomposition depends as on chemical analytical properties of a material and reagents used, as well as on the subsequent course of the analysis. In turn, the economic efficiency of the works, *i.e.* the cost and quality of the analysis depends on the method of opening.

In connection with the fact that the great bulk of ores and concentrates of precious metals is presented in the form of refractory materials, a great role is played by the development of new efficient, economic and ecologically safe methods for opening resistant materials.

The methods for dissolving of solid samples can be divided into the two groups [1] such as decomposition in open and closed systems (autoclaves). The advantage of open systems consists in the fact that they do not require for special equipment for realizing the process of opening. However, rather frequently the dissolution of refractory materials via the open method does not provide a sufficient decomposition level for carrying out the analysis of the material.

Such material includes aluminium silicate and sulphide matrices those are resistant under the conditions of acidic oxidative opening for the majority of samples. Besides aluminium silicate samples could possess great surface area, whereby an unpredictable adsorption of precious metals would result in worsening the results of analysis. In this connection, a universal method for opening is required for obtaining authentic results of the analysis of the majority of resistant ores and concentrates with the destruction of sulphides, silicates and aluminosilicates.

The second group of methods is based on carrying out the processes of sample preparation the materials under influence of high temperature and pressure. This could be achieved using the potentialities of autoclave technologies. Besides a high efficiency, the advantages of this method involve ecological safety and the absence of the loss of reaction mixture components due to the tightness of the system. The implementation of the process of autoclave opening any resistant precious metal ores and concentrates became one of the most serious achievements in the field of hydrometallurgy for last years [2]. Joint application of autoclave technologies and microwave radiation widely used for the last years as an intensifier of various physical and chemical processes including sample preparation [3, 4] is even more efficient.

The purpose of the present work consisted in the development of techniques directed on increasing the efficiency of chemical sample preparation, for opening resistant ores and precious metal concentrates in open systems with the use of low-temperature fusion as well as in autoclaves with the use of microwave radiation.

EXPERIMENTAL

In order to study the solubility in alkali fusion we used the basic rock-forming oxides: SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3. As the components of fusion-cakes we used alkali such as KOH and NaOH. All the reactants were of analytical grade.

Alloying these alkalis was carried out in carbon glass crucible at the temperature of 200 °C during 40 min in the mode of permanent stirring. The fusion obtained were gradually introduced with weighed portions of oxide samples by 0.5–1 % of a fusion mass until their dissolution stopped and the formation of solid phase was observed. The processes of dissolving oxides came to the end during 20–30 min. Crystallized fusion were dissolved in water. Basing on the amount of non-dissolved residue we estimated the decomposition level for oxides.

As a material for opening in autoclaves with the application of microwave field we used the concentrate of platinum group metals (CP-2) with the following content of precious metals therein, %: Pt 2.86, Pd 16.26, Rh 1.29, Ir 0.025, Ru 0.42, Au 0.65, Ag 48.32. The procedure of filling the autoclaves and carrying out the experiment is similar to the procedure described in [1].

The structure of solutions was determined using a PerkinElmer A Analyst 400 atomic adsorption spectrophotometer with electrothermal atomizer.

RESULTS AND DISCUSSION

Alkaline dissolution of refractory rock-forming oxides

For increasing the efficiency of opening resistant concentrates in the cases when the dissolution does not result in decomposition sufficient for carrying out the analysis of a material, one uses alloying the samples with corresponding fusion (inorganic substances intended for decreasing the temperature of ore or concentrate melting and for much easier separating the metal under treatment from burden). Alloying represents deep and vigorous means for influence upon the structure of the material under analyzing. In practice, wide application is found by alkali fusion such as alkali metal carbonates, borates, and hydroxides.

In order to destruct mineral raw material, the use alkali metal hydroxides is rather efficient, however a number of disadvantages of this method restrains a much wider use of alkaline alloying for the group separation of metals. In particular, sample alloying is usually carried out at the temperature lower than the red heat temperature, *i. e.* at 450–500 °C [5], which is caused, first of all, by the temperature values of proper hydroxide melting. At the same time at high temperature values, the majority of crucible materials are unstable. Hence, the problem of decreasing the destruction temperature for oxide and sulphide matrices under the conditions of alkali melting is urgent.

The amount of fusion under melting is 5–20 time higher than the amount of the material under analysis [6]. In practice, one uses 1.5 g NaOH at the alloying temperature of 800–850 °C in silver crucible for decomposing 0.1 g of silicates for determining SiO_2 therein [5]. The mass of the weighed sample amounts to 6.6 % the mass of NaOH. The decomposition of bauxite portion (2 g) for determining aluminium is performed with a fivefold amount of NaOH.

Molten NaOH and KOH interact with atmospheric oxygen. Long contact with oxygen already at 410 °C results in the formation of 3 % Na_2O_2 and 22 % KO_2, which is undesirable, too [5].

Thus, a question arises concerning the obtaining of highly efficient low-temperature alkali fusion and studying the solubility of metal oxides therein.

According to the state diagram of the KOH–NaOH system, the temperature values for NaOH and KOH melting are equal to 321 and 404 °C, respectively, whereas the eutectic composition containing 50 molю % KOH, melts at 170 °C [7]. This allows one to obtain low-temperature fusion with the composition mentioned. It should be noted that alkali fusion consisting of 25 % KOH and 75 % NaOH is used for the destruction of cement. With the use of pure components one can observe the formation of very viscous fusion-cake in the case of KOH and the destruction of platinum crucibles in the case of NaOH only.

Enough data are available in the literature concerning state diagrams of ternary systems such as water–alkali metal oxide–various oxides. At the same time, information is limited concerning the systems those include two and more oxides of alkali metals, water and oxides being a basis of matrices of minerals composing ores and concentrates.

A series of experiments carried out demonstrated that at the temperature of 200 °C the dissolution level in alkali fusion based on eutectic NaOH and KOH mixtures, amounts to 20 % for silica, 35 % for alumina, 3 % for calcium oxide, 2.4 % for magnesium oxide, 7.6 % for iron oxide with respect to the mass of the alkali fusion.

Opening of platinum concentrates under the action of microwave radiation

Nowadays different sample preparation methods with the use of MW radiation [3, 4] are widely distributed. However, serial units have two considerable disadvantages. They are, first, the impossibility to observe visually the processes; second, the absence of stirring of in the solid phase in the course of dissolving a material. The last factor can result in even more worse results than that with the use of traditional heating method, since as the result of microwave radiation effect on conducting materials there could occur "undermelting" of the solid phase. Thereof the access of reagents to the material under opening is limited.

The industrial use of MW radiation together with the autoclave hydrometallurgy to a considerable extent forestalls theoretical studies. Novel data concerning the behaviour of compounds at increased temperature values under the action of microwave radiation are to an extreme extent required for the further development of the scientific foundations of technological and analytical methods for opening platinum ores and concentrates. In particular, are of interest the studies on the potentialities of using MW radiation in the processes of opening platinum concentrates. Studying these processes is worthwhile by the example of opening iridium and rhodium (as the most resistant components of platinum concentrates) and their comparison with similar data obtained with usual heating technique.

For this purpose, we have developed an autoclave system for the operation in MW field, allowing one to carry out both visual supervision over the processes, and stirring of liquid and solid components (Fig. 1).

In developing the autoclave design, the main difficulty was connected with the extremely limited choice of the material for the autoclave since it should be transparent for MW radiation as well as inert with respect to the components of a reaction mixture. The majority of commercial laboratory autoclaves for operation in a MW oven are made of Teflon. However, they do not allow one to perform visual supervision over the process.

The device we have developed consists of a quartz test tube (*1*) with a cylindrical channel for inserting a thermocouple (*2*). The test tube is plugged with Teflon cover (*3*) with a Teflon cup (*4*) (fixed by means of screw joint) intended for separating the components of the reaction mixture prior to beginning the action of microwave radiation. One of the components of reaction mixture was placed into the cup. In order to provide tightness in the quartz test tube, the Teflon cover is fixed by means of a clamping Teflon screw/nut (*5*, *6*) which is tightened to a thread bushing. The autoclave is attached to a shaft within the chamber of a MW oven which shaft in the course of experiments

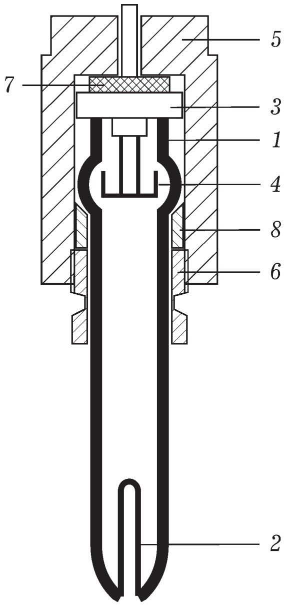

Fig. 1. Schematic diagram of autoclave arrangement. Designation see text.

rotates in the vertical plane, which is especially important in the studies concerning heterogeneous processes.

It was established earlier that using the autoclaves with a common heating method the concentrates can be completely opened at the temperature of 180 °C during 2 h [1, 8]. In the case of MW radiation used the experiments were carried out at the temperature of 110 °C. The choice of lower temperature values is caused by the necessity to demonstrate the effect of MW radiation on the processes under investigation. The results of comparative analysis for different methods of heating are presented in Table 1.

Materials and minerals containing iridium and rhodium belong to one of the most refractory objects of analysis. Hence, the rate of their dissolution determines to a considerable extent the rate of opening entire concentrate. In this connection, the comparison between different heating methods such as common heating and MW heating is worthwhile to perform by the example of these metals. It is established that the course of reaction and visually observed effects in both cases are similar. At the same time, it follows from data presented in Table 1 that a complete extraction of these metals occurs for 1 h with the use of MW radiation. With the use of common heating, as much as 90 % of rhodium and 95 % of iridium passes into solution during the same time interval. In this case, for the first 15 min of the experiment with the use of MW radiation. As much as about 75 % of rhodium and iridium pass into solution, whereas with the usual heating method about 50 % of these elements pass into solution. The passing of platinum and palladium into solution almost does not depend on heating method being determined only by the temperature and the time of experiment.

CONCLUSION

Techniques are developed aimed at increasing the efficiency of chemical preparation for samples containing precious metals, for opening resistant ores and concentrates of these metals in open systems with the use of low-temperature fusion and autoclaves with the application of MW radiation.

The analysis of the results for alloying rock-forming oxides with low-temperature alkali fusion demonstrated that there is possibility of their decomposition at the temperature values low enough.

The studies concerning the processes of opening platinum concentrate with the use of different heating methods demonstrated the advantage MW radiation: with the use of the

TABLE 1

Data concerning the content of precious metals in the solution after the opening depending on heating method (usual or MW), mg/L

Opening time, min	Rh	Ir	Pt	Ru
15	39/56	0.34/0.52	66/100	11/18
60	68/75	0.68/0.71	120/130	21/22
120	78/78	0.70/0.71	130/130	22/22

Note. The first value corresponds to common opening method; the second one corresponds to MW heating.

latter, the processes mentioned proceed not only at a lower temperature, but also to a much more complete extent.

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