GEOCHEMISTRY

The Refined Method of Sample Preparation and Chemical Analysis for Refractory Gold–Silver Ores: Case Study of the Maisk Deposit, Primorye

O. V. Loseva, V. I. Radomskaya, L. I. Rogulina, S. M. Radomskii, and Academician of the RAS V. G. Moiseenko

The Maisk gold–silver deposit is located in the Dal'negorsk ore district of the Primor'e region. In terms of geological setting, the deposit is confined to the southeastern part of the Dal'negorsk volcanotectonic dome in the Primor'e sector of the East Sikhote-Alin volcanic belt. The Dal'negorsk ore district is composed of Upper Cretaceous acid and intermediate effusives that are superimposed on Lower Cretaceous accretionary-folded rocks of the Taukha terrane including Late Cretaceous granite, granodiorite, and gabbrodiorite plutons. The Taukha terrane incorporates Early Cretaceous continental-margin turbidites and olistostromes coupled with Triassic–Jurassic oceanic formations [1]. Ores of the Maisk gold–silver deposit are confined to volcanic and volcanosedimentary rocks of the Cenomanian Petrozuev Formation (sandstones and conglomerates combined with tuffaceous conglomerates, sandstones, and siltstones) that grades upsection into volcanic–pyroclastic rocks of the Turonian–Santonian Primor'e Group (rhyolitic ignimbrites and boulder–agglomerate tuffs combined with tuffaceous conglomerates and siltstones). The strike of high- and low-angle crush zones exposed at the deposit varies from a northwestern to a nearly east–west direction. Fractures in this area are partly filled with rhyolitic and less common granodiorite porphyry dikes. Consequently, rocks in such zones contain a significant amount of secondary quartz, sericite, and limonite. The development of geochemical aureoles of As, Ag, and Au is typical for this area [2].

The ore field incorporates no less than ten linear crush zones filled with mineralized breccia of ignimbrites, rhyolitic tuffs, and quartz. Silicification is developed as the filling of free space between rock clasts or

the metasomatic replacement of minerals. In general, the silicified rocks have the typical texture of epithermal formations with the cockade–banded distribution of crystalline and chalcedony-type quartz particles. Miarolic cavities (1–2 mm across) in the rocks are filled with drusy aggregates of euhedral crystals.

Quartz-dominated orebodies are developed as thin veins and stringer zones. The well-known Maisk zone is observed as a NW- to EW-striking structure with a low-angle (25°–45°) northward dip. The ore zone is confined to the contact between acid volcanic rocks (with tuffaceous siltstones) and flyschoid sequences (intercalation of siltstones and sandstones). Ore mineralization is developed in veins, veinlets, and metasomatic zones filled with quartz, adular–quartz, and adular–chlorite–sericite–quartz assemblages.

Orebodies are irregularly developed as ore shoots and depleted sectors. Stringer–banded zones prevail, while brecciated, colloform–banded, and crustification zones are subordinate. The Ar–Ar adular dating yielded the Eocene age of mineralization in the Maisk ore zone.

These ores have the following composition (%): quartz 80–90, adular 10, chlorite and sericite (3 to 4), and ore minerals (~3–5). The major ore minerals are as follows: küstelite, electrum, acanthite, pyrargyrite, freibergite, sulfosalts of silver (stephanite, andorite, diaphorite, and sternbergite), gold, pyrite, galena, sphalerite, chalcocite, chalcopyrite, argentojarosite, cubanite, and cerargyrite. The accessory minerals are represented by the following specific assemblage: monazite, chromite, scheelite, cassiterite, apatite, zircon, titanite, and magnetite (with native iron inclusions). The microscopic examination revealed rare inclusions of osmiridium and sperrylite in the gold–silver concentrate.

Mineral assemblages of the Maisk ore zone can be divided into the pyrite–adular–quartz and chlorite–sericite–hydromica types. The first (pyrite–adular–quartz) assemblage includes quartz, adular, and pyrite completely replaced by jarosite in the oxidation zone.

Institute of Geology and Nature Utilization,
Amur Research Institute, Far East Division, Russian
Academy of Sciences, per. Relochnyi 1, Blagoveshchensk,
Amur oblast, 675000 Russia; e-mail: losevao@rambler.ru

Table 1. Mineralogical composition of ores of the Maisk deposit

Component	Content, %
Quartz	85
Feldspar	14.65
Magnetite	0.0075
Zircon	++
Cerargyrite	+
Limonite + Ag	+
Limonite + Au	++
Gold	28.5 g/t (dendritic (0.1–0.05 mm) and lumpy (0.3–0.2 mm) grains)

Note: (++) Rare; (+) very rare.

Table 2. Mineralogical composition of ores of the Maisk deposit after fluorination

Component	Content, %
Quartz	0.2
Feldspar	1.3
Magnetite	–
Zircon	0.56
Cerargyrite	+
Goethite with Au dissemination	1.98
Clay minerals	4.32
Ag–Pb oxides	0.27
Cassiterite	0.015
Rutile	+
Limonite + Ag	0.057
Limonite + Au	90.5
Gold	85.5 g/t (lumpy grains and flakes, 0.6 × 0.1 mm)

Note: (+) Very rare; (–) not detected.

Confinement of this assemblage to cataclastic breccia suggests its formation at the early stage of mineralization. Quartz and adular–quartz aggregates contain an abundant dissemination of ore material. The concentration of ore material is maximal in recrystallized quartz particles (growth zones) and chalcedony-type quartz aggregates. Polished ore sections show a distinct rearrangement of ore material in the course of metasomatism of ores and its coarsening up to the point of the formation of gold veinlets at the subsequent metasomatic stage. Argentite and proustite-pyrargyrite are subordinate minerals. In the polished sections, ore minerals account for 1–3% of the pyrite–adular–quartz assemblage.

The second (chlorite–sericite–hydromica) assemblage is developed in the ore breccia matrix, quartz veinlets, and cracks. This assemblage is characterized by the abundance of gold, the development of veinlets, and the dissemination of larger gold and silver particles associated with argentite, freibergite, proustite-pyrargyrite, and stephanite. The ore minerals account for no more than 1% of the mineral assemblage. Intensely chloritized areas contain wood tin, prismatic cassiterite, and titanite. Sericite–hydromica aggregates are commonly disseminated in quartz particles. In the oxidation zone, pyrite is intensely replaced by goethite, hydrogoethite, jarosite, and argentojarosite. The oxidation zone also contains pyrolusite, plumbojarosite, anglesite, massicot, and nontronite-montmorillonite.

Gold particles (primarily, 0.001–0.1 mm in size) often make up intergrowths with cerargyrite, quartz, and adular. The gold particles have a typical coating of limonite and manganese oxides. The fineness of gold varies from 850 in the core of particles to 280 in the küstelite rim.

Thus, ores of the Maisk deposit are characterized by fine-grained irregular structures and rim textures. The refractory property of these ores is related to the fine dissemination of gold in quartz and sulfides, as well as the presence of As and Sb [3].

The concentration of Au in ores can be determined by various methods, but the calculation of reserves is only based on the assay analysis data. However, the assay analysis requires high-temperature heating over a long time (~1h) leading to the loss of gold nanoparticles (the melting temperature of gold is 350°C [4]). Therefore, the Au content is often underestimated in refractory ores.
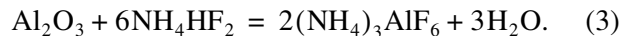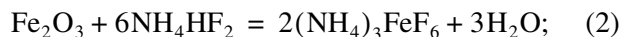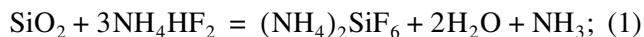
We can increase the accuracy of Au determination by the fluorination of larger samples (no less than 200 g) at a lower temperature and the subsequent leaching of gold with thiourea solution. The fluorination promotes the decomposition and removal of the mineral matrix, the consequent concentration and coarsening of gold particles, and the transfer of gold microparticles into macroparticles. The method of gold extraction with the thiourea solution has several advantages, such as low toxicity, high selectivity (relative to noble metals), kinetic activity, and possibility of industrial implementation.

For primary ores of the Maisk deposit, we tested the fluorination method based on the reaction of ammonium fluorides with silicate minerals and the subsequent leaching of gold with the thiourea solution.

The distribution of Au and Ag was checked by the atomic absorption analysis of the water phase with a Hitachi 180-50 spectrophotometer. The chemical analysis of ore samples was performed using the fluorination method based on ammonium dehydrofluoride ($T < 200°C$) [5]. After separating fluorinated concentrates, Au and Ag were extracted from them by thiocarbamide analysis in the hydrosulfuric medium [6].

According to the mineralogical analysis data, the primary ore is mainly composed of quartz (85%) and feldspars (14.65%). The free gold (28.5 g/t) is observed as dendritic and lumpy grains (Table 1).

Fluorination of ore is accompanied by breakdown of the mineral matrix according to the following equations:

$$SiO_2 + 3NH_4HF_2 = (NH_4)_2SiF_6 + 2H_2O + NH_3; \quad (1)$$

$$Fe_2O_3 + 6NH_4HF_2 = 2(NH_4)_3FeF_6 + 3H_2O; \quad (2)$$

$$Al_2O_3 + 6NH_4HF_2 = 2(NH_4)_3AlF_6 + 3H_2O. \quad (3)$$

Application of the ammonium dehydrofluoride is restricted by a rather narrow temperature range (190°C). At $T < 170$°C, the reaction requires more time because of the insufficient rate of fluorination. Higher temperatures (>190°C) provoke the thermal breakdown and evaporation of the ammonium dehydrofluoride.

The amount of ammonium dehydrofluoride was chosen on the basis of stoichiometric composition so that silicon oxide could be dissolved in the solution. Kinetic experiments showed that SiO_2 reacts most rapidly with the ammonium dehydrofluoride. Thus, the ammonium dehydrofluoride is completely consumed in the reaction with SiO_2 and does not react with other oxides. Si is removed from the ore as a result of sublimation of the reaction product (ammonium hexafluorosilicate) at $T > 320$°C.

Duration of fluorination was experimentally determined. The run duration varied from 1.5 to 8 h. The optimal duration turned out to be 2 h. Minerals of the ore are incompletely fluorinated if the run duration is 1.5 h. In contrast, unproductive losses in energy and material are significantly higher if the duration is more than 2 h.

In our fluorination procedure, the ore mass decreased by 78% due to the loss of the major SiO_2 portion as $(NH_4)_2SiF_6$ and the breakdown of mineral-concentrators of Au. Gold particles concentrated and coarsened in the samples after fluorination (Table 2). Free gold (85.5 g/t) was extracted from the samples as lumps and flakes 0.6×0.1 mm in size. Iron hydroxides with tiny gold droplets were also detected.

The sublimation residue was treated by the thiocarbamide hydrosulfuric (ThiO) solution. It is well known that the thiocarbamide dissolves gold in an oxidant-bearing acid solution and forms a cationic complex:

$$2Au + Fe_2(SO_4)_3 + 4ThiO$$

$$= [Au(ThiO)_2]_2SO_4 + 2FeSO_4. \quad (4)$$
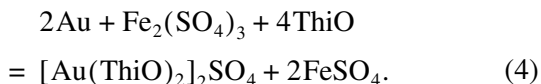
In order to find optimal conditions for the dissolution of gold, we examined the dependence of the thiocarbamide concentration on reaction duration.

We changed the thiocarbamide content in the solution from 0.5 to 9% (according to [6]), while other conditions were constant (3% H_2SO_4, 0.5% $Fe_2(SO_4)_3$, $T = 20$°C, and $t = 10$ h). The results obtained showed that extraction of gold from the solution is maximal (125 g/t) at a thiocarbamide concentration of 1% (Fig. 1). Further increase in thiocarbamide concentration is unpro-
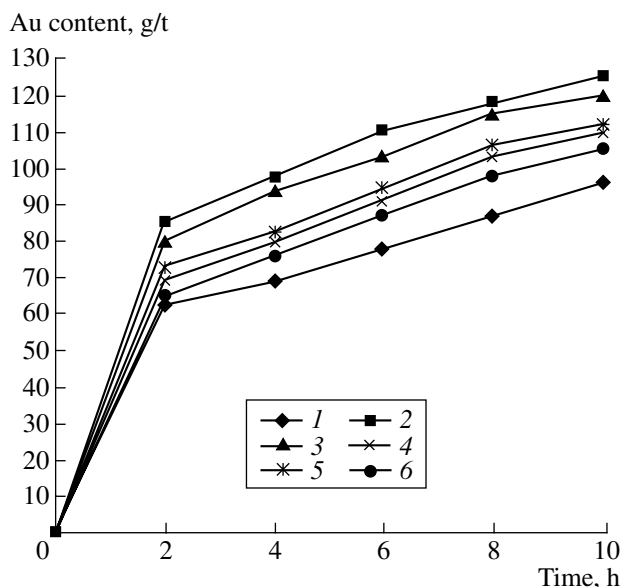
Influence of the duration of the leaching stage on the extraction of gold into the thiocarbamide solution: (1) C_{ThiO} 0.5%; (2) C_{ThiO} 1%; (3) C_{ThiO} 2%; (4) C_{ThiO} 3%; (5) C_{ThiO} 5%; (6) C_{ThiO} 9%.

ductive. If the thiocarbamide concentration is lower (0.5%), gold recovery decreases to 95.8 g/t, probably, because thiocarbamide is mainly consumed for bonding with other elements (Cu, Mn, Fe, and others) prior to the formation of gold complexes with the thiocarbamide.

The degree of gold recovery depends on the duration of leaching. Variations in the run duration from 2 to 10 h yielded the following results.

At the first stage of leaching (duration 2 h), more than 50% of Au contained in the sample is transferred to the thiocarbamide solution (figure). If the duration increases to 10 h, 125 g/t of gold is transferred to the thiocarbamide solution. According to our method, contents of Au and Ag in ores of the Maisk deposit vary from 125 and 2022 g/t, respectively. According to the assay analysis data, the contents are 113 and 2160 g/t, respectively.

Thus, our method of sample preparation and chemical analysis makes it possible to determine more precisely the Au content in refractory ores of the Maisk deposit.

CONCLUSIONS

(1) Auriferous ore of the Maisk deposit includes easily fluorinated Si-bearing minerals. Interaction with the ammonium dehydrofluoride provokes their breakdown and the release of gold. Fluorination of samples leads to a decrease in their mass and the consequent concentration and coarsening of gold particles.

(2) Optimal conditions have been found for the leaching of gold from fluorinated ore concentrates with

the application of thiocarbamide hydrosulfuric solution.

(3) The proposed method is expensive, but it provides a more complete determination of Au content in refractory ores of the Maisk deposit.

REFERENCES

1. 1. V. I. Kemkin and R. A. Kemkina, Geotektonika, No. 5, 71 (2000). [Geotectonics, No. 5, 407 (2000)].

2. Yu. P. Yushmanov, Tikhookean. Geol. **16** (2), 32 (1997).

3. V. G. Moiseenko and L. V. Eirish, *Gold Deposits of the Russian Far East* (Dal'nauka, Vladivostok, 1996) [in Russian].

4. M. A. Meretukov, Tsvet. Metally, No. 9, 24 (2005).

5. E. I. Mel'nichenko, V. G. Moiseenko, V. V. Sergienko, D. G. Epov, V. S. Rimkevich, and G. F. Krysenko, RF Patent No. 2 120 487, Byull. Izobret. Polezn. Modeli, No. 29 (1998).

6. V. I. Radomskaya, O. V. Loseva, and S. M. Radomskii, Vest. Dal'nevost. Otd. Ross. Akad. Nauk, No. 1, 80 (2004)