GEOCHEMISTRY

## New Method of Gold Concentration and Extraction from Graphitic Ores of the Turgenevskoye Deposit, Primorye

Academician A. I. Khanchuk, M. A. Medkov, L. P. Plyusnina, and V. P. Molchanov

Received June 3, 2008

DOI: 10.1134/S1028334X08080278

Technological experiments in gold concentration and extraction from graphite-bearing rocks of the Turgenevskoye deposit located in the northern part of the Khanka terrain have been performed. A scheme of extraction of fine and ultrafine gold from large-sized samples including preparatory milling, flotation, and magnetic and electromagnetic separation of flotation tailings has been worked out. Pine oil as a foaming agent and long-chain amine as a collecting agent have been used. For leaching of gold from the concentrates obtained, it was suggested to use acid thiocarbamide instead of cyanides.

Over the past few decades, several deposits of noble metals (NMs) were discovered in carbonaceous strata in Eastern Siberia and the Russian Far East industrial exploration of which was restricted due to lack of technological methods of NM extraction from them. To these objects belong graphitized metamorphic complexes of the northern part of the Khanka terrane. Uplifted concentrations of gold and platinum were discovered within the previously known graphite deposits of the Tamgino-Turgenevsky group [1, 2]. Within this rock complex, an early stage of regional metamophism (with an age of 730 Ma) under conditions from epidote-amphibolite to amphibolite facies is distinguished [3]. The later stage of metamorphism (in conditions from greenschist to granulite facies) is connected with collision events on the boundary of the Cambrian and the Ordovician. The occurrence of regional graphitic mineralization located within the band stretched in the submeridianal direction for about 100 km and 3-4 km in width is connected with the later metamorphism stage. Among the largest objects belonging to this area are the following graphite deposits: Tamginskoye, Turgenevskoye, and Innokent'evskoye (Fig. 1). A close connection has been established between the NM mineralization and graphite occurrence at the Turgenevskoye deposit area [1, 2]. This was proved by the experimentally mea-

Far East Geological Institute, Far East Division, Russian Academy of Sciences, Vladivostok Chemical Institute, Far East Division, Russian Academy of Sciences, Vladivostok sured high sorption capacity of graphite in relation to gold and platinum [4]. As is known, NMs form stable metallorganic complexes, and this is the reason why their extraction from carbonaceous rocks is restricted. In experimental investigation of gold and platinum chemisorption onto graphite, data on replacement of hydrogen vacancies in aromatic rings by metals have been obtained. The metal– carbon bonds that generated from this process are the most stable, which further restricts noble metal extraction during ore enrichment. Moreover, graphite is a chemically thermostable mineral and belongs to hardly enriched types of mineral resources, which additionally complicates the task of NM extraction from such rocks.

The aim of the investigation is to work out the method of gold extraction from the graphitized ores of the Turgenevskoye deposit. For this purpose, it was necessary to solve the problem of concentration of fine and ultrafine gold from carbonaceous rocks. Graphite is



Fig. 1. Location of the Turgenevskoye deposit of graphite.

presented in the ores of the rocks investigated in monomineral veins and lenses as well as in the dispersed state. Graphitization is characteristic to all of the following varieties of rocks of the complex investigated: crystal shales, plagiogneisses, granite–gneisses, granites, lamprophyre dikes, marbles, and skarns. The most abundant graphitization resulting in formation of graphitic metasomatites occurs along the planes of granite–gneiss schistosity, which allows us to make a conclusion about the endogenic nature of graphitization [2].

According to an investigation with the help of atomic force microscope data, graphite has a globular microstructure. IR spectroscopy proved the absence of amorphous carbon, which is due to the high grade of metamorphism of the rocks investigated at temperatures of about 450–620°C [1, 2]. Along with the bonded invisible gold, microscopic native gold occurs in the graphite ore in the form of spheroid or, rarely, lamellar grains 70–100  $\mu$ m in size, and intergrowths of visible gold and graphite occur (Fig. 2). According to scanning electron microscope investigation of the gold and graphite composition, gold in this case has high assay values with alternative content (in wt %): Au, 93.3–100; Ag, 0–3.5; Cu, 0–6.2. The graphite composition from intergrowth with gold spheroid showed the presence (in wt %) of Cl, 0.25–2.5; O, 27.4–28.4; K, 0.2–1.7; Si, 0.3–0.5; and Au, 0.5–2.1 with the C content accounting for 67–71.6. Such a composition of graphite reflects the chemical composition of a high-temperature metamorphic fluid. The heterogeneity of the gold and graphite composition revealed in different points of crystals,



Fig. 2. Spheroid of native gold with graphite inclusions.

as well as the globular microstructure of graphite, indicates that their crystallization proceeded from gaseous fluid accompanied by chloride and oxygen components in gas transport of metals [5].

In order to carry out technological experiments on the concentration of gold, graphite-bearing rocks were sampled; their compositions are shown in Table 1. The gold content in these rocks were first detected by atomic-emission spectroscopy with preliminary fluoride decay at the Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences; in the sam-

Component	MT-04/50	MT-04/34	MT-03/1a	MT-03/3	MT-04/29
SiO <sub>2</sub>	70.82	50.52	38.61	38.56	43.07
TiO <sub>2</sub>	0.22	1.23	0.02	0.32	0.39
$Al_2O_3$	12.61	13.99	20.19	8.95	5.56
Fe <sub>2</sub> O <sub>3</sub>	0.32	0.69	0.69	2.18	0.36
FeO	0.26	7.08	0.64	0.85	3.97
MnO	0.02	0.13	0.02	0.06	0.13
MgO	0.32	8.86	0.56	2.16	1.53
CaO	3.04	9.96	4.12	2.51	25.24
Na <sub>2</sub> O	0.95	1.84	2.18	1.83	0.49
K <sub>2</sub> O	7.9	3.02	2.92	1.58	0.15
$P_2O_5$		0.62		Traces	0.43
$H_2O^-$	0.1	Traces	0.2	5.97	Traces
$H_2O^+$	0.98	1.15	2.16		3.98
С	2.08	0.53	27.41	34.57	13.95
$Cr_2O_3$		0.3			0.26
Total	99.62	99.65	99.72	99.54	99.51

Table 1. Chemical composition of rocks (wt %) in samples used in the gold concentration technological experiment

Note: Sample 04/50, graphitized leucocratic granite–gneiss; 04/34, lamprophyre; 03/1a, graphite metasomatite replacing biotite granite– gneiss; 03/3, biotite–feldspar schist; 04/29, quartz–carbonate–graphite metasomatite. Analyses were performed at the Far East Geological Institute, Far East Division, Russian Academy of Sciences.

Number of sample	τ, min	Product	Yield, %	Content of Au, ppm	Extraction of Au, %
		foamy	20.8	6.68	92.6
MT-04/34	20	chamber	79.2	0.14	7.4
		original	100	1.5	100
		foamy	36.1	4.32	69.9
MT-04/34a	20	chamber	63.9	1.05	30.1
		original	100	2.23	100
MT-04/34a		foamy	52.0	3.7	87.3
	30	chamber	48	0.64	13.7
		original	100	2.23	100
MT-04/29		foamy	11.5	3.1	23.8
	10	chamber	88.5	1.29	76.2
		original	100	1.5	100
MT-04/50	30	foamy	50.4	12.1	11.1
		chamber	49.6	98.6	88.9
		original	100	55.0	100

Table 2. Results of the experimental flotation of large-sized samples

Note: Gold contents were detected by NAA with Cf source at the Institute of Chemistry, Far East Division, Russian Academy of Sciences.

Table 3. Results of leaching of sample MT-03/03 by the thiocarbamide solution

Original material	Content of Au in leaching solution, g/l	Extraction of Au into solu- tion, %	Thiocarbamide concentra- tion in leaching solution, g/l
50 grams of sample + 50 grams of gold-bearing concentrate	0.098	89.9	49.47
100 grams of gold-bearing concentrate	0.194	89.2	49.5

ples 04/29, 1.45 ppm; 04/34, 1.5 ppm; and 04/34a, 2.23 ppm. The gold content detected in the samples by physical methods of ionic mass spectrometry (IMS) and neutron activation (NAA) at the Institute of Chemistry, Far East Division, Russian Academy of Sciences, shows higher values of Au concentrations (in ppm): 04/29, 15.2 (NAA), 15.0 (IMS); 04/50, 55 (NAA). Such discrepancy in different gold analysis results is due to significant losses with volatile metallorganic complexes during chemical sample preparation. As was noticed before, optimal gold concentrations were obtained by physical methods without preliminary chemical decay [2].

During working out of the method of extraction of gold from 50-kg weight samples, preparatory milling was used up to 0.044 mm size with further flotation on the laboratory flotomachine during one stage lasting from 10 to 30 min without repurifying and control flotation. Pine oil was used as a foaming reagent, and a long-chain amine, as a collecting agent. Because fine and ultrafine gold has high buoyancy features [6], gold concentrations in different samples in foamy and chamber products vary with the dimension of dispersed gold (Table 2). Magnetic and electromagnetic separation of flotation tailings of sample 04/50 with high Au content allowed us to obtain a concentrate with 253.6 ppm of gold. After flotation of sample 04/34a, the main amount of gold passed into the foamy product, and a flotation concentrate with Au content of 6.2 ppm was obtained.

Gold extraction from carbon-containing concentrates is a rather difficult task. Sorption of gold from cyanide solutions onto different carbonaceous materials has been investigated adequately. As a substitution for cyanides, it was suggested to use acid thiocarbamide solutions for leaching gold from the concentrates [7]. For investigation of gold and thiocarbamide losses while leaching graphite-containing concentrates, an experiment with a model system was used. For this aim, an additional amount of gold in the form of gold-containing concentrate in 50 g of sample 04/33 was introduced. This mixture was leached by a solution containing 100 g/l of thiocarbamide, 10 g/l of sulfuric acid, and 20 g/l of ammonium persulfate at the room temperature for 5 h. The filter cake was further washed first by the primary thiocarbamide solution, and then by water. Experiment results showed that in leaching gold and thiocarbamide losses did not occur (Table 3).

Thus, one may conclude that thiocarbamide acid solutions are more preferable than cyanide solutions when leaching gold from concentrates with a high carbon content. In order to leach gold from samples with a low gold content (04/34a), we used the method of fluoridation by ammonium hydrofluoride under heating up to 600°C with a rate of 2°C/min. From the pulp during decanting, the sediment was separated, the yield of which accounted for 16.5% from the initial mass. The gold content in it reached 38 instead of 6.2 ppm in the initial sample.

Thus, it was proved experimentally that the dimension of microscopic, fine and ultrafine gold affected the method of its extraction from carbonaceous rocks. For the first time, the method of thiocarbamide usage for gold concentration was suggested, which is more promising from the ecological point of view than the cyanides usually used in gold mining. The methods of gold extraction from graphite ore presented may be used successfully for creation of low-waste technology for processing mineral resources.

DOKLADY EARTH SCIENCES Vol. 423 No. 8 2008

## **ACKNOWLEDGMENTS**

This work was supported by the Far East Division, Russian Academy of Sciences, project nos. 15-IN-07, 06-3-A-8-235, 06-2-CO-08-029, and 06-1-OKhNM-134.

## REFERENCES

- 1. Khanchuk, A. I., Plyusnina, and L. P., Molchanov, V. P., *Doklady Earth Science*, 2004, vol. 397A, no 4, p. 820.
- Khanchuk, A. I., Plyusnina, L. P., Molchanov, V. P., et. al., *Tikhookean, Geol.*, 2007, vol. 26, no 1, pp. 70–80.
- 3. Mishkin, M. A., Khanchuk, A. I., Zhuravlev, D. Z., et. al., *Doklady Earth Science*, 2000, vol. 375, no 8, p. 1283.
- Khanchuk, A. I., Molchanov, V. P., Medvedev, E. I., et. al., in *Nanogeokhimiya zolota* (Nanogeochemistry of Gold), Vladivostok: Dal`nauka, 2008, pp. 33–36.
- Plyusnina, L. P., Kuz`mina, T. V., and Avchenko, O. V., *Geochemistry Int.*, 2004, vol. 42, no 8, pp. 775.
- Nanomineralogiya (Nanomineralogy), N. P. Yushkin, A. M. Askhabov, and V. N. Rakin, Eds., St-Petersburg: Nauka, 2005.
- Meretukov, M. A., Orlov, A. M., *Metallurgiya blagorodnykh metallov. Zarubezhny opyt* (Metallurgy of Noble Metals. Foreign Experience), Moscow: Metallurgiya, 1991.