Gold in ash and slag material of the Primorsk hydroelectric power

Natalia Lavrik[1*] and *Peter* Henning[2]
[1] Mining Institute FEB RAS, 51 Turgenev st., Khabarovsk, 680000, Russia;
[2] SIEMAG TECBERG group, Haiger, Germany

Abstract. The paper shows the results of studies on the identification of noble-metal mineralization in various components of ash and slag formations: underburning, aluminosilicate microspheres, initial ash (fed to the magnetic separation of the technological section of Primorsk SDPP), magnetic and non-magnetic fractions – using analytical and mineralogical methods, electronic microscopy. An integrated approach made it possible to reliably establish significant concentrations of gold, to identify the factors of technological persistence of anthropogenic materials. All products contain free gold grains ranging in size from 50 to 230 micrometers and microscopic inclusions of 0.5-20 microns. The content of free grains of gold is from 0.4 to 1.37 mg / kg. The gold is pure or with an admixture of silver (up to 17% of the mass). Depending on the research materials, gold contains variable inclusions of magnetite, ilmenite, quartz, glass, amphiboles, pyroxenes, clay minerals, and carbonaceous formations. Gold grains have complex structure and morphology. Micronized inclusions, usually rounded, also contain an admixture of silver.

1 Introduction

In connection with the development of modern methods of analysis, an intensification is observed in large-scale and systemic studies of coal deposits and ash and slag formations as potential sources of noble and other metals; issues are being developed on the prospects for their extraction and the creation of technologies for integrated processing, as well as the ecology of coal mining and use [1, 2]. Noble metals are found in coals and coal ash from many coal deposits and basins of the world [3-6, etc.], Siberia [7, 8] and the Far East [9-16, etc.].

Over the past 20 years, studies of fossil coals in the south of the Far East for metal content have revealed gold, platinum, and platinum group metals, the content of which in coal ash often approaches commercial level (from 0.0n g / t to 3-7 g / t). It is not possible to extract gold and platinoids from coals by traditional methods. Ash and slag wastes are considered as alternative sources of mineral raw stock. However, in this case, there are problems associated with uneven distribution of metals in ash, with the presence of gold mainly in dispersed, microscopic and submicroscopic dimensions, close connection with carbonaceous matter and intergrowth with other minerals [17]. In the Institute of Mining of the

* Corresponding author: lavrik@igd.khv.ru

FEB RAS, on the basis of traditional and innovative methods of analysis, some methods are being developed for finding the concentration of noble metals in coals, in ash and slag formations of the Far Eastern region. Experimental studies are underway to identify the factor of technological refractoriness of the studied anthropogenic materials. When doing experimental studies using standard methods of gravity concentration using concentration tables and centrifugal separators, a loss of the valuable component into the tailings was up to 80%. According to electron-microscopic studies – gold in the gravity tailings, is, mainly, of the size class 0.5-1 microns or is inside other mineral formations, which explains the reason for a loss of gold.

2 Factual material and research methods

The material for research at this stage was: brown coal of the Luchegorsk open-pit mine, ash-and-slag material of Primorsk SDPP, formed during the combustion of high-ash brown coal 1B, 2B grades of the Bikin, Pavlovsky and partially Erkovetsky, Kharanorsky, Rakovsky deposits. The components of ash and slag formations were also investigated: underburning, aluminosilicate microspheres, initial ash, in addition, the magnetic fraction and tailings of magnetic separation (products of the technological section of Primorsk SDPP, receiving iron concentrate). The average content (g/t) of precious metals in coal ash (laboratory combustion) of the Bikin deposit according to the results of the atomic emission study at the Institute of Mining of the FEB RAS are as follows: Au – 0.05 [0.45; 1.8]; Ag 0.17 [13.4]; Pt – not found [0.08]; Pd – not found [0.9]; Pavlovskoe: Au – [up to 9.0], Pt – [up to 2.37], Pd – [up to 3.17], Ag – [up to 0.1] (the results by other authors are given in square brackets [3, 4, 18, 19, 20, etc.]).

The present studies on the identification of noble metal mineralization in ash and slag formations are based on an integrated stage approach. To characterize and control the content of noble metals in coals and ash and slag formations, the most sensitive analyzes ICP-AS (atomic emission spectrometry with inductively coupled plasma), AAC (atomic absorption analysis), assay-atomic emission with inductively coupled plasma, MAES (multichannel atomic emission spectroscopy). Electron microscopic examination was carried out on a JEOL scanning electron microscope (Japan) equipped with a JCM-6000 PLUS energy dispersive analyzer. An accelerating voltage of 15 kV and a probing current of 7.475 nA were used.

The first stage included an analytical identification of the concentration of precious metals in coals and coal ash (laboratory combustion at 8,000°C) of the Bikin deposit.

At the second stage, the fraction of free gold grains in various components of ash and slag formations of Primorsk SDPP (underburning; aluminosilicate microspheres; original ash, magnetic and non-magnetic fractions) were found. The share of free gold was found using the method of reduced mineralogical analysis for gold (by engineer-mineralogist V.F. Stepanova).

At the third stage, visually undetectable gold was identified by chemical methods (MAES – Grand spectrometer; AAS-6200, AAS-7000 atomic absorption spectrophotometers).

The fourth stage was an electron microscopic study of gold grains isolated by mineralogical analysis and a search for fine micron particles of precious metals in fine fractions of ash and slag formations.

3 Results

At the SDPP, coal combustion occurs at a temperature of 1,100-1,600°C. When the organic part of coal is burned, volatile compounds are formed in the form of smoke and steam, and the non-combustible mineral part of fuel is released in the form of solid ash residues, forming a pulverized mass (ash), as well as lumpy slags. Small and light ash particles are carried away by flue gases – fly ash (the particle size of fly ash varies from 3-5 to 100-150 microns, the amount of larger particles usually does not exceed 10-15%). Fly ash is captured by ash collectors. Heavier ash particles settle on the subfurnace and are fused into lump slags, being aggregated and fused ash particles with a size of 0.15 to 30 mm. Slags are crushed and removed with water. Fly ash and crushed slag are first removed separately, then mixed, forming an ash-and-slag mixture. In the composition of the ash and slag mixture, in addition to ash and slag, particles of unburned fuel (underburning) are constantly present, the content being 10-25%. The amount of fly ash, depending on the type of boilers, the type of fuel and the way of its combustion, can be 70-85% of the mix mass, slag – 10-20%. Ash and slag pulp is removed to the ash dump through pipelines [9, 10].

The initial sample of ash and slag material from Primorsk SDPP visually has a dark gray to black color. It consists of microspheres, the smallest fragments of porous slag, rocks, minerals and intergrowths of minerals, and carbonaceous residues. According to the results of a mineralogical analysis, the original ash contains 11.79% magnetite and 10.86% magnetic spheres; 19.73% magnetic slag and 23% siliceous slag; 17.48% brown coal; 10.88% quartz; 2.48% intergrowths of quartz and feldspar; up to 1.35% coal with inclusions of magnetite. Clay minerals, amphiboles, pyroxenes, pyrite, marcasite, zircon, apatite, garnet, rutile, sphene, leucoxene, corundum, and barite are found in insignificant amounts.

Gold content in the initial ash and slag material of Primorsk SDPP is from 0.005 to 0.5 g/t; platinum 0.003-0.046 g/t; palladium within 0.001 g/t; silver 0.65-3.415 g/t. Osmium and iridium being at the sensitivity threshold of devices. The non-magnetic fraction contains some noble metals: Pt up to 0.015 g/t, Au 0.01-0.049 g/t, Ag up to 0.7 g/t. According to the results of spectral and chemical-spectral analyzes in the magnetic fraction, Au content is up to 0.4 g/t, in aluminosilicate microspheres Au is up to 0.013 g/t, Ag – up to 0.3 g/t.

It should be noted that the comparative analysis of coal and coal ash for gold (laboratory combustion) failed, because there is a variation of grades across samples: relatively high gold grades in a coal sample could give zero ash content and vice versa.

Difficulties in studying and extracting precious metals from coals and coal ash are uneven distribution, fine (0.1-0.5 mm) and micron size of particles, connection with carbonaceous matter, intergrowth and "cohesion" with other minerals, volatility of gold-organic formations. The total carbon content in the original ash and slag material is 4.7%; gradually increasing from 1.41% in fine grain sizes to 29.1% in the +2 mm size class. A sufficiently high carbon content in the upper size classes indicates the possibility of obtaining coal concentrate from these fractions.

Table 1. Results of short mineralogical analysis for gold

Sample name	Sample weight, kg	Au content, mg
Primary ash and slag	1.000	0.60
Magnetic fraction	1.249	0.56
Aluminosilicate microspheres	1.129	0.46
Underburning	1.000	1.37
Non-magnetic fraction	1.480	1.28

Analysis of gold content by size class did not bring positive results. During the gravitational enrichment of individual ash size classes using a laboratory concentration table, it was not possible to obtain products with a significant gold content. However, the washing of the ash and slag material using a manual tray made it possible to obtain visible results (Table 1, Fig. 1). Table shows the results of an abbreviated mineralogical analysis for gold of samples of the primary ash and slag material, magnetic and non-magnetic fractions, aluminosilicate microspheres, underburning.

By mineralogical analysis, grains of free gold were identified in all products of the ash and slag material of Primorsk SDPP (Fig. 1). The shape of gold grains is varied: bizarre, lumpy, tabular and lamellar, flattened with smoothed edges, irregular with a porous structure. The color is yellow, reddish and greenish-yellow with characteristic black sooty patches.

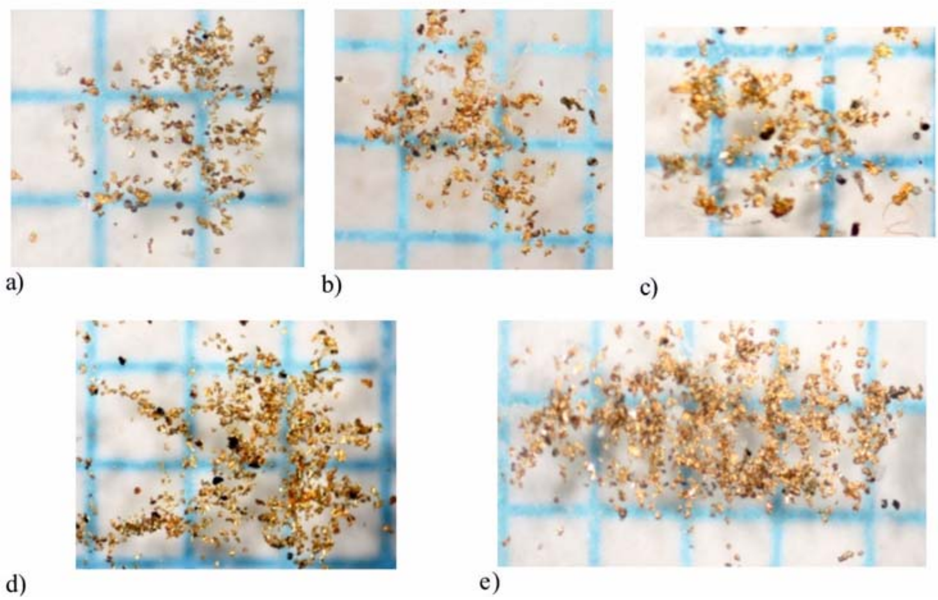

Fig. 1. Gold grains isolated by mineralogical analysis from the ash and slag material of Primorsk SDPP and the products of magnetic separation: a) initial ash; b) magnetic fraction; c) aluminosilicate microspheres; d) underburning; e) tailings of magnetic separation. *Cell size is 1 mm*.

According to the results of electron microscopic studies of gold grains, isolated by mineralogical analysis from all samples, the composition of gold can vary from pure gold to electrum, kustelite is less common. In some cases, gold grains contain an admixture of copper, iron, while a minor admixture of platinum and iridium was occasionally noted. The structure of all studied gold grains is complex – it is an alloy or accretion of small cubic crystals or irregular grains or plates. The size of the inclusions is from 50 micrometers to 230 microns. Recesses between individual grains can be filled with porous aluminosilicate glass, quartz, magnetite, titanomagnetite, carbonaceous matter (Fig. 2, 3, 4, 5).

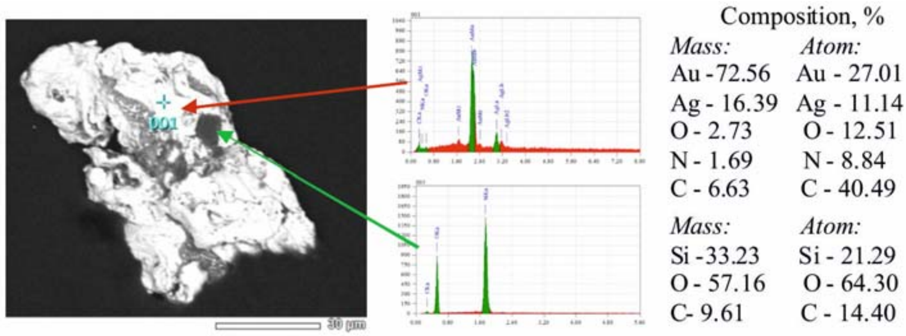

Fig. 2. Gold grain from primary ash and slag material of Primorsk SDPP; contains inclusions of quartz and other rock-forming minerals, plaque of carbonaceous formations.

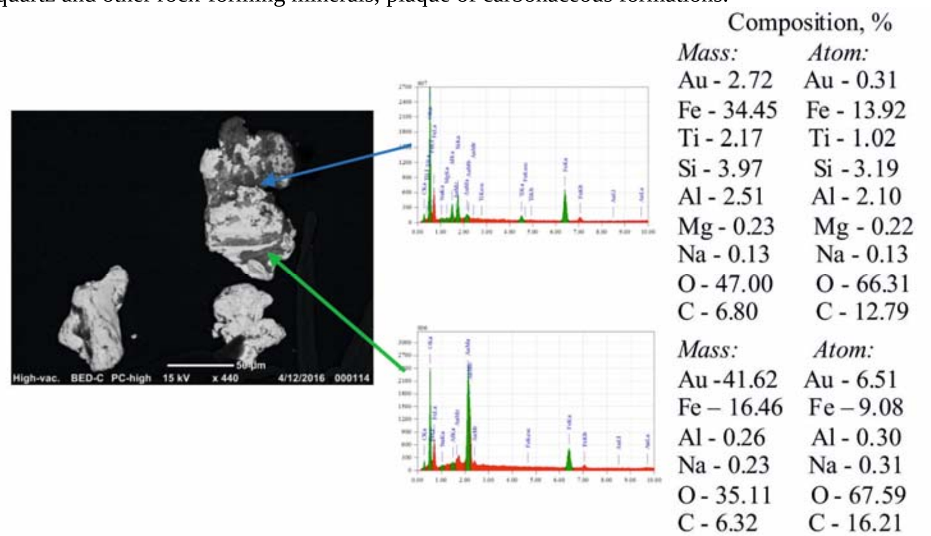

Fig. 3. Gold grains from the magnetic fraction: inclusions of magnetite, ilmenite, amphiboles.

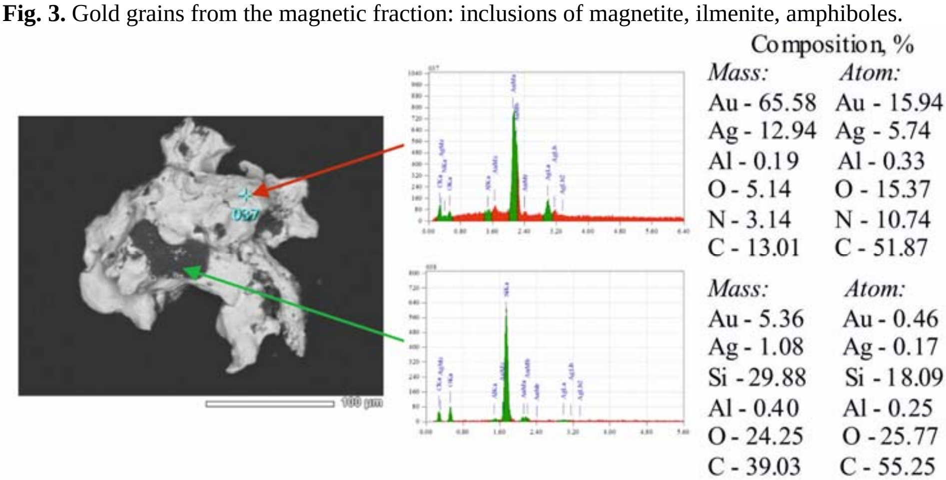

Fig. 4. Gold grain from aluminosilicate microspheres; contains inclusions of glass, clay, K-feldspar.

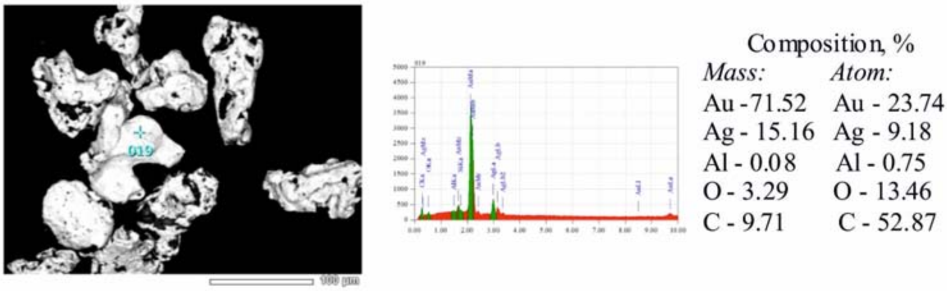

Fig. 5. Gold grains from underburning contain inclusions of carbonaceous matter, silicates.

Electron-microscopic study of fine fractions (below 40 microns) of ash and slag material products allows noting the following: all samples contain micron-sized gold (0.5-5 microns), silver, platinum and platinoids. Native platinum with an admixture of copper, less often silver; cooperite in accretion with tenardite. Silver is noted as native silver and kerargyrite. Micron-sized grains of precious metals are irregular or round in shape. Gold and other minerals (up to 2 microns) are found not only in the form of individual grains, but more often in the form of solder on the surface of aluminosilicate and ferruginous microspheres, in the composition of native metals and intermetallic compounds [18]. For example, gold is found in native copper and chromium-ferrous alloy.

In addition to gold and platinum in micron dimensions, other native metals are also noted: iron, nickel, cobalt, tungsten, copper; and intermetallic compounds of the type Fe_7Cr, Fe_4CrNi, Fe_3Al, Cu_2Sn. Ferberite, magnetite, titanomagnetite, barite, celsian, monazite, stronziobarite, cassiterite, sylvin, halite, brookite and some undefined mineral formations are also noted.

4 Conclusions

As a result of the studies carried out to identify noble metal mineralization in ash and slag formations of Primorsk SDPP on the basis of an integrated approach, it has been shown that gold is present in at least 3 states: 1 – free gold grains, 50-230 micrometers in size; 2 – microscopic grains of 0.5-20 microns in the form of solders and inclusions in other minerals, in porous surfaces of aluminospheres and magnetite spheres and 3 – visually undetectable forms of gold in the lattices of minerals, in organometallic compounds, etc.

The content of *free gold* in the original ash and slag material is 0.6 mg/kg; in the magnetic fraction 0.45 mg/kg; in aluminosilicate microspheres 0.41 mg/kg; in underburning 1.37 mg/kg; in the non-magnetic fraction 0.86 mg/kg. Gold, with a variable silver content (up to 17% by weight), complex grain morphology and structure, contains impurities of petrogenic elements, inclusions of rock-forming minerals, magnetite and carbonaceous matter. Apparently, the amount and nature of inclusions in gold determine its presence in a particular fraction or product.

In a microscopic form, in addition to gold, native platinum, silver, as well as copper, nickel, tungsten, cobalt, etc. are noted. Noble metals are also localized in other mineral phases and formations, for example, in sulfides, chlorides.

The results of a spectrochemical analysis of gravity tailings show that up to 80% of gold goes to tailings. According to electron microscopic studies, gold in the tails of gravity is mainly of the size class 0.5-1 microns or is included in other mineral formations, which explains the reason for the loss of gold.

For forms of visually undetectable gold, located in the lattices of minerals, in organometallic compounds, etc., in coal ash or in coals, special methods of identification and extraction are being successfully developed [19].

The applied set of analytical and research methods allows quite reliably identifying the concentration of precious metals in ash and slag material and primary products of their processing; revealing the factors of persistence, finding the main directions of technological solutions for the recovery of metals.

Based on the geochemical specialization of the region [20, 21], all coal deposits of the Russian Far East and, accordingly, ash and slag waste should be considered as potential alternative sources of precious metals, regardless of the level of concentration of precious metals known at the moment.

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