Concentrating precious metals from ash and slag waste of Far Eastern energy enterprises

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Abstract. This work represents the data on the content of gold, noble metals and rare earth metals in ash and slag waste taken from the ash disposal areas of the Far Eastern energy enterprises. Ash and slag objects with increased concentration of Au and Ag were found. The chemical content of samples from researched ash and slag disposal areas is represented in this work. A scheme of dividing ash and slag waste into different mineral fractions is offered in this work. The mechanisms of collecting and distribution of Au, Pt and Ag concentrations in ash and slag wastes were determined during the research. Also, the possibility of gold concentration in heavy non-magnetic fraction is shown.

1. Introduction
In the "Energy strategy of Russia for the period up to 2030" and "Long-term program for the development of the coal industry of Russia for the period up to 2030", an advanced development of coal TPPs is considered. Knowing that the existing TPPs mostly use non-enriched, low-quality, high-ash coal (such fuel makes almost 90% of all the fuels), it can be expected that the rate of ash and slag waste (ASW) generation will not be decreased [1].

Nowadays, the amount of Russian energy enterprises’ waste is around 1.5 billion tones. The ASW utilization level is extremely low – from 2 to 13%, according to different sources. Two-thirds of 172 working coal TPPs and GRES have run out of their ash dumps’ capacity.

In these conditions, an exacerbation of environmental problems associated with the organization of storage of ash and slag should be expected. So, for example, if to consider the planned 1.5-time increase in coal generation compared to the existing level by 2030, it can be expected that an additional annual production of ASW will be 35-36 million tons. Thus, the volume of stocked ASW may reach 1.7 billion tons by 2020, and 2.0 billion tons by 2030 [1-2].

At the same time, it is known that ash and slag wastes contain industrially significant quantities of valuable components. The chemical and mineralogical composition of ash and slag indicates that it is more correct to consider them as enriched raw materials for various industries (construction, road, cement, metallurgical, chemical) [3-7].
ASW can be a source of gold and noble metals. ASW obtained from the burning of many coals, and especially of brown coals, can be considered, in some cases, as conditional ore, particularly according to gold and platinum content [8-10].

Attempts to extract gold from TPP’s ASW are made from time to time. However, extraction technology, which would allow organizing stable industrial production, has not been developed, largely due to the form of useful components in ash and slag. Gold and noble metals can be presented in coals in both forms: in native fine-dispersed form and in the form of organic inclusions formed under the influence of microorganisms and the products of their metabolism [11-14].

Relatively low concentrations of gold and noble metals (NM) in coals, and ash, and slag, as well as the small size of particles of native gold and NM, require the development of special approaches of concentrating and extracting this class of valuable components from energy enterprises’ waste.

2. Research methods

Investigations of the qualitative composition of ash and slag wastes were carried out on lithogeochemical samples taken from a number of polygons of the energy enterprises of the Russian Far East: 1) ash dumps No. 1, No. 2 and No. 3 of TPP-2, Vladivostok city; 2) ash dump of the town boiler room, Bolshoy Kamenn town; 3) ash dump of the town boiler room No. 2, Arsenyev town; 4) ash dump №1 of TPP, Artem town; 5) sections of the ash disposal area No. 1, No. 2 and No. 3 of the GRES, Partizansk town; 6) ash dump of GRES, Luchegorsk town.

The chemical content of ash and slag samples was determined by X-ray fluorescence analysis (XRFA) with using the Shimadzu EDX 800 HS spectrometer (tube with rhodium anode, vacuum) in room temperature conditions. For determination of valuable components microparticles morphology scanning electronic microscope (SEM) JSM-6490LV (JEOL, Japan) was used, which is equipped with energy-dispersive spectrometer (EDS) INCA Energy and with the microanalysis system for the spectrometer with wavelength dispersion (WDS), Inca Wave.

The content of noble and rare earth metals in technogenic waste of energy enterprises was determined using of atomic-absorption spectrophotometry (AAS) on atomic-absorption spectrophotometer Shimadzu 6800. For the research, the 2g weighed portions were used. Before the analysis of Au, Pt, Pd content, the samples were decomposed by a mixture of acids HF+HNO$_3$ with further coprecipitation. For determination of Ag content, the samples were decomposed by a mixture of acids HCl + HNO$_3$.

The method of instrumental neutron-activation analysis (NAA) was used as the method of control of fine-dispersed gold content in energy enterprise’s waste. This instrumental NAA was realized on a small-sized unit developed by the Chemistry Institute of FEB RAS. The small-sized unit has a radionuclide excitation source on the base of $^{252}$Cf. The gold content was measured by NSAM method [15] for samples of gold-quartz ore deposits. As previous researches using this method were correct, this method is proper for coal-containing samples [16]. Detection limit of Au for $^{198}$Au isotope for INAA was 0.2-1g/t, for 50-100g weights.

3. Results

The samples were researched according to the scheme represented in Figure1. Initial ash and slag material was selected from energy enterprises ash dumps. The selected samples were grinded, quartered, and were sent to analytical researches. The gold and noble metal content was determined by NAA and AAS methods, the chemical content of samples was determined by XRFA, morphology of gold micro-particles and noble metals micro-particles was determined by the SEM method.

The researches have revealed presence of gold and NM in a number of the examined samples. So, according to AAS data, gold was detected in 3 of 57 examined samples. The Au content varied from 0.04 to 0.18 g / t. At the same time, silver was found in 13 samples. The highest silver content was noted in the sample from the polygon of TPP-2 - 29.7 g / t. According to NAA, gold was detected in 7 out of 57 examined samples. The Au content varied in the range 0.10-0.45 g / t (table 1).
Figure 1. The scheme of studies of samples from polygons of the Russian Far East energy enterprises

Table 1. Gold and silver content according to NAA and AAS data, in ash and slag wastes from polygons of the Russian Far East energy enterprises

| Samplename                                      | Au, g/t (NAA) | Au, g/t (AAS) | Ag, g/t (AAS) |
|------------------------------------------------|---------------|---------------|---------------|
| TPP-2-1 hole (survey loop 1) (Vladivostok, TPP-2) | 0.10          | 0.18          | 0.75          |
| TPP-2-3 hole (survey loop 1) (Vladivostok, TPP-2) | < 0.05        | < 0.01        | 2.44          |
| TPP-2-6 hole (survey loop 2) (Vladivostok, TPP-2) | < 0.05        | < 0.01        | 29.70         |
| TPP-2-31 hole (survey loop 3) (Vladivostok, TPP-2) | 0.45          | < 0.01        | 2.84          |
| TPP-2-33 hole (survey loop 3) (Vladivostok, TPP-2) | 0.15          | < 0.01        | 0.94          |
| B-K-14 hole (BolshoyKamen, TPP)                  | < 0.05        | 0.025         | 0.78          |
| B-K-17 hole (BolshoyKamen, TPP)                  | 0.10          | < 0.01        | < 0.50        |
| ARS-19 hole (Arsenyev, TPP)                      | < 0.05        | < 0.01        | 0.54          |
| ARS-23 hole (Arsenyev, TPP)                      | 0.11          | < 0.01        | < 0.50        |
| A-TPP-2-37 hole (survey loop 2) (Artyom, TPP)    | 0.35          | < 0.01        | < 0.50        |
| A-TPP-2-39 hole (survey loop 1) (Artyom, TPP)    | 0.45          | < 0.01        | < 0.50        |
| P-GRES-48 hole (section 1) (Partizansk)          | < 0.05        | < 0.01        | < 0.50        |
| L-GRES-57 hole (Luchegorsk)                      | < 0.05        | < 0.01        | < 0.50        |

The studies conducted by the SEM method showed that the free gold particles and NM present in the ash and slag wastes are mainly represented by a thin and ultra-thin class of fineness (the size of the gold minerals from fractions of micron to tens of microns).

The morphology of the detected grains of gold is diverse, there are particles of xenomorphic, cloddy, dendritic-cloddy-shaped form (figure 2).

Studies of ash and slag samples, performed by the XRFA method, showed that the chemical composition of the studied samples is very similar. The bulk of samples are: silicon compounds - 40-50%, aluminosilicates - 25-35%, iron oxides - 5-10%, calcium - 4%, potassium - 3%, titanium - 2%; Sulfur - 1. In several investigated samples, the microcontent of chromium, copper, manganese, rubidium, strontium, vanadium, yttrium, zinc and zirconium were found. The presence of iron and titanium oxides in all the investigated samples suggests the possibility of conducting magnetic separation of the samples and separating the magnetic minerals into a separate fraction.
As the conducted studies showed, the average gold and NM content in the researched ASW is about 0.10-0.45 g / t. (table 1), and gold is represented mainly by thin and ultrathin sizes that are difficult to extract (figure 2). In this connection, it seems expedient to carry out preliminary enrichment of ash and slag samples for gold and PGM by dividing the initial material into separate mineral fractions, followed by the determination of mineral complexes in which gold is accumulated.

For the separation of ash and slag samples, the following scheme was used:

1. The initial sample in the amount of 10 kg was ground in the disk grinder to 0.1mm size. Then, the grinded sample was put into a vessel, and the water was conveyed into it. The sample was mixed thoroughly and settled.

2. The foam that consisted of micro sized minerals (suggestively – microspheres) and particles of unburned coal (underburning) was collected from the surface. The collected material was dried and measured on weighing scales of the 2nd accuracy class.

3. Water under small pressure was conveyed into the vessel with soaked sample. Light clay particles were washed out of the sample. Water overflowed the vessel and went into the settling tank, and suspended particles settled and collected there.

4. After washing out of light particles, the residue in the form sand was received. The concentrate of heavy minerals was received from the derived sand, by using a gold-washing pan. Derived material was dried, and then it was divided into magnetic and non-magnetic fractions by using magnetic separation.

Thus, from ASW sample following fractions were received:
- coal underburning; light fraction;
- heavy non-magnetic fraction; heavy magnetic fraction.

Derived fractions were analyzed by NAA method for determination of gold content.

Realized studies have shown that gold concentrates mainly in the heavy non-magnetic fraction (table 2).

Figure 2. Microparticles of complex shaped gold, shot under SEM
Table 2. Gold content in various fractions of ash and slag samples from polygons of Primorsky region enterprises (after classification), g / t

| Sample | Initial | Light fraction | Heavy non-magnetic fraction | Heavy magnetic fraction |
|--------|---------|----------------|----------------------------|------------------------|
| TPP-2-1 hole (survey loop 1) (Vladivostok, TPP-2) | 0.10 | 0.26 | 0.39 | <0.05 |
| B-K-17 hole (Bolshoy Kamen, TPP) | 0.10 | <0.05 | 0.35 | <0.05 |
| ARS-23 hole (Arseniev, TPP) | 0.11 | <0.05 | 0.36 | <0.05 |
| P-GRES-54 hole (section 3) (Partizansk, GRES) | <0.05 | 0.12 | 0.37 | <0.05 |
| L-GRES-57 hole (Luchegorsk, GRES) | <0.05 | <0.05 | 0.15 | <0.05 |

A research (by AAS method) of ASW fractions, obtained from a sample collected at the Vladivostok TPP-2 polygon, showed almost a twofold concentration of platinum in the heavy non-magnetic fraction of ASW in comparison with the light fraction (table 3). Platinum was not found in the underburning of coal and the magnetic fraction of ASW.

Table 3. Content of platinum and silver in ash and slag waste of Vladivostok TPP-2, in g / t

| Sample | Ag  | Pt  | Pd  |
|--------|-----|-----|-----|
| TPP-2-1SH-MC (sample 1) heavy non-magnetic fraction | <0.50 | 0.015 | <0.001 |
| TPP-2-1SH-MC (sample 2) heavy non-magnetic fraction | <0.50 | 0.015 | <0.001 |
| TPP-2-1SH-SSH (sample 1) light non-magnetic fraction | <0.50 | 0.008 | <0.001 |
| TPP-2-1SH - SSH(sample 2) light non-magnetic fraction | <0.50 | 0.006 | <0.001 |

4. Conclusion
The presence of noble metals in ash and slag and their quantity depends on the type of burned coal, and, ultimately, on the metallogenic features of the regions where coal deposits are located. The obtained data show the presence of gold and NB in a number of ash and slag samples selected at the survey loops from the enterprises of the Primorsky Region energy complex. Particles of free gold and NB, presented in ash and slag waste, are mainly of thin and ultra-thin size. A significant part of gold is closely associated with the surrounding minerals. Gold and NM in ash and slag are classified as difficult to extract and require the use of special measures for concentration and additional opening.

The conducted studies show the possibility of efficient separation of ash and slag wastes into certain mineral fractions and the separation of a preliminary concentrate of precious minerals, in which most of the gold and noble metals, will be collected.

5. Acknowledgments
This paper has been done with the financial support of the Ministry of Education and Science of the Russian Federation, state task in the field of scientific activity, № 10.3706.2017/PCH.

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