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Concentration of Gold from Ash and Slag Wastes of Energy Sector Enterprises of The Primorsky Territory.

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ABSTRACT

The study of a large array of ash waste from landfills of energy sector enterprises in Primorsky Territory was made. Data on the content of gold and silver in the ash and slug waste of some energy enterprises in Primorsky Territory was given. Group of samples with high content of gold and silver was found. Silver content was found within 0.5-29.7 g/t limits. Gold content was found within 0.004–0.45 g/t limits. The information on the chemical composition of the investigated slag samples was given. Based on these data, the method of separation of ash and slag waste in the individual mineral fractions was proposed. The possibility of gold concentration in the non-magnetic fraction of the slag cleared of silt, clay, black charcoal and magnetic minerals was shown.
Keywords: technogenic deposits, wastes of energy enterprises, ash and slag waste (ASW), gold, silver, atomic and absorption analysis, neutron-activation analysis, X-ray fluorescence analysis.

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INTRODUCTION

Ash and slag waste (ASW) is formed during coal combustion process in energy producing enterprises. For example, in recent years, yearly inflow of ASW into the ash and slag disposal areas of Primorsky Territory is up to 3.0 million tons. Result of this technogenic activity shows collection of huge amounts of ash. According to available literature [1], the total amount of waste from Russian energy enterprises is 1.5 billion tons.

Many researches on ASW conducted in a few developed countries have proved that ASW is a valuable mineral material that can be used in construction, including road construction, and agriculture. In Russia, the utilization level ASW does not exceed 5%. There are a number of reasons for such a low level of ASW utilization: for example, difference in chemical and phase composition of coals from different coalfields; difference in coal combustion conditions at different thermal power plants (TPP); lack of standard equipment for collecting ASW from the technological chain of TPP; lack of equipment for disposed ASW conditioning; unreadiness of energy-producing companies for ASW release; lack of legislative framework that would encourage using secondary materials; lack of market for materials made of ASW, etc.

Combusting coal, upon transformation into ASW during production in the energy enterprises, is a natural sorbent material. Also, it contains lots of components of precious elements, such as rare earth metals, gold, and platinum group metals (PGM) [2]. During combustion process the content of valuable elements in ash increases five to six times; therefore it can be of industrial interest [3].

Researches on the possibility of gold extraction from ash were conducted not long ago. Some information about the possibility of gold extraction from ASW appeared in 1998 [4]. The idea of using ASW as a nonconventional source of gold and platinum group metals is constantly discussed. Attempts of gold extraction from ASW from TPP were made [5, 6]. We also know successful experiments on concentrating and extraction of precious and rare metals from ASW [7, 8]. But still there is no extraction technology that would allow organizing sustainable industrial production of gold from ash and slug wastes. It can be explained by complicated form of the valuable components in ash and slag and by their micro- and nano-size [9]. For example, gold contained in the fly room is a fine-grained drop-like particles with size 0.01–0.2 µm on the surface of glass beads [10].

Because of nanometer and micrometer size of gold in coal, there is a necessity for developing a special extraction method. For efficient extraction of gold from ASW it is necessary to take into account the difficulties in both developing ash disposal areas and unearthing the form of gold in ASW. Also, it should be noted that the amount of noble and rare earth metals in ash disposal areas is not that high, so it is very important to create technologies that would not need large capital expenditures.

METHODS

Fifty-seven samples of ash and slag were selected on the territory of six ash disposal areas of Primorsky Territory (Vladivostok, TPP-2; Artem, TPP; Bolshoy Kamen, TPP; Arsenyev, TPP; Partizansk, State District Power Station; and Luchegorsk, Primorsky State District Power Station). On the first stage of the research to estimate the presence of gold, PGM in selected samples were identified by atomic and absorption analysis (AAA) and neutron activation analysis (NAA). For ascertainment of mineral composition the X-ray fluorescence analysis was done.

Content of noble and rare earth metals in ASW was determined by atomic absorption spectrophotometer (AAS) in the micro- and nano-research laboratories of analytical center of Far Eastern branch of Russian Academy of Sciences (FEB RAS) Geological Institute.

To determine Au, Pt and Pd content the samples were preliminarily decomposed by adding a mixture of acids ($HF + HNO_3$) and further by Te co-deposition using a method formulated by Central Geological Institute for Nonferrous and Precious Metals – 2005.

To determine Ag content, the samples were also preliminarily decomposed by adding a mixture of acids ($HCl + HNO_3$).

Measurements of Au, Pt, Pd and Ag content were done using AAS (Shimadzu 6800). Samples 2 g were used for the experiments.

The main method of control used to estimate the finely dispersed gold content in the waste of energy enterprises was instrumental NAA (INAA). INAA was executed on small-sized unit developed by Chemistry Institute of FEB RAS. The small-sized unit has radionuclide excitation source on the base of ^{252}Cf. For samples of gold-quartz ore deposits the gold content was measured by NSAM method [11]. This method is also considered to be more appropriate for coal-containing samples [12]. Detection limit of Au for ^{198}Au isotope using INAA was 0.2–1 g/t for 50–100 g.

Chemical composition of ash and slag technogenic waste was determined by X-ray fluorescence analysis in Far Eastern Structural Researches Center of FEB RAS Chemistry Institute. The measurements were made by energy-dispersive X-ray spectrometer EDX-800HS (Shimadzu, Japan). Sensitivity for elements from Na to U was 1 ppm; standard deviation in diapason from 1 ppm to 1% did not exceed 5% and in the range higher than 1% did not exceed 1%.

RESULTS AND DISCUSSION

Researches on ASW from the energy enterprises of Primorsky Territory allowed determining the close connection of spatial gold distribution with surrounding mineral complexes.

Table 1. Gold content in ASW of Primorsky energy enterprises

№	Sample name	Au, g/t (NAA)	Au, g/t (AAS)	Ag, g/t (AAS)
1	TPP-2-1 hole (survey loop 1) (Vladivostok, TPP-2)	0.10	0.180	0.75
2	TPP-2-3 hole (survey loop 1) (Vladivostok, TPP-2)	< 0.05	< 0.001	2.44
3	TPP-2-5 hole (survey loop 2) (Vladivostok, TPP-2)	0.05	< 0.001	< 0.50
4	TPP-2-6 hole (survey loop 2) (Vladivostok, TPP-2)	<0.05	< 0.001	29.70
5	TPP-2-7 hole (survey loop 2) (Vladivostok, TPP-2)	<0.05	< 0.001	1.53
6	TPP-2-8 hole (survey loop 2) (Vladivostok, TPP-2)	<0.05	< 0.001	0.53
7	TPP-2-9 hole (survey loop 2) (Vladivostok, TPP-2)	<0.05	< 0.001	1.34
8	B-K-10 hole (Bolshoy Kamen, TPP)	<0.05	< 0.001	1.34
9	B-K-12 hole (Bolshoy Kamen, TPP)	<0.05	< 0.001	0.50
10	B-K-14 hole (Bolshoy Kamen, TPP)	<0.05	0.024	0.78
11	B-K-15 hole (Bolshoy Kamen, TPP)	<0.05	< 0.001	0.58
12	B-K-16 hole (Bolshoy Kamen, TPP)	<0.05	0.004	< 0.50
13	B-K-17 hole (Bolshoy Kamen, TPP)	0.10	< 0.001	< 0.50
14	ARS-19 hole (Arsenyev, TPP)	<0.05	< 0.001	0.54
15	ARS-23 hole (Arsenyev, TPP)	0.20	< 0.001	< 0.50
16	TPP-2-29 hole (survey loop 3) (Vladivostok, TPP-2)	<0.05	< 0.001	2.84
17	TPP-2-31 hole (survey loop 3) (Vladivostok, TPP-2)	0.45	< 0.001	< 0.50
18	TPP-2-33 hole (survey loop 3) (Vladivostok, TPP-2)	0.15	< 0.001	0.94
19	A-TPP-2-37 hole (survey loop 2) (Artyom, TPP)	0.35	< 0.001	< 0.50
20	A-TPP-2-39 hole (survey loop 1) (Artyom, TPP)	0.45	< 0.001	< 0.50
21	A-TPP-2-40 hole (survey loop 1) (Artyom, TPP)	0.20	< 0.001	< 0.50
22	P-GRES-48 hole (section 1) (Partizansk)	<0.05	< 0.001	< 0.50
23	P-GRES-50 hole (section 2) (Partizansk)	<0.05	< 0.001	< 0.50
24	P-GRES-54 hole (section 3) (Partizansk)	<0.05	< 0.001	< 0.50
25	L-GRES-57 hole (Luchegorsk)	<0.05	< 0.001	< 0.50

In the analysis conducted in FEB RAS Far Eastern Geological Institute (FEGI), gold was found in 3 ASW samples and the gold content was within 0.004–0.180 g/t limits (Table 1). At the same time silver was found in 13 ASW samples and the silver content was within 0.5-29.7 g/t limits (Table 1). The presence of PGM and rare earth metals was not found in any of the 57 samples during AAS analysis.

Simultaneously the samples that were used in AAS method were also analyzed by NAA method. The results are shown in Table 1. While AAS method found gold only in 3 of 57 samples, NAA found gold in 9 out of 57 samples and the gold content was within 0.05–0.45 g/t limits.

Underestimation of the gold content that was determined by the AAS method can be associated with incomplete autopsy of gold from samples during grinding and dissolving. In some research was shown that methods involving acid decomposition and assay of the samples show very low co-holding precious metals, while non-destructive physical methods give out significantly higher concentration [13].

ASW testing by X-ray fluorescence analysis showed that all the samples have quite similar chemical composition. In Table 2 we provide average content of macro elements in the samples from ash disposal areas of different energy enterprises in Primorsky Territory.

Table 2. Average content of macro elements in the ash and slug samples from Primorsky Territory

Survey loop	Al	Ba	Ca	Fe	K	Mg	S	Si	Ti
TPP-2, Vladivostok	35.8	0.3	3.6	4.7	2.1	3.4	0.8	49.9	0.6
TPP, Bolshoy Kamen	35.6	0.5	4.4	5.6	1.9	0.1	1.2	49.9	0.6
TPP, Arsenyev	35.3	0.4	5.3	7.3	1.6	0.1	1.4	47.8	0.6
TPP, Artem	35.4	0.5	1.8	4.7	2.3	0.0	0.9	53.4	0.9
State District Power Plant, Partizansk	34.1	0.4	3.1	7.7	2.7	0.0	0.9	50.1	0.7

Mostly there are aluminosilicates, Fe oxides, and titanium oxides in the mass of the samples. In addition, the samples have macro content of barium, calcium, potassium, magnesium, and sulfur. In some other samples we have also found macro content of chrome, cuprum, manganese, rubidium, strontium, vanadium, yttrium, zinc, and sulfur. Presence of titanium oxide and Fe oxide macro contents allows supposing the feasibility of magnetic separation of the samples and creation of separate fraction of magnetic minerals.

As the waste obtained from the energy enterprises is a rather complicated technogenic object with small average content of gold, which is represented by difficult-to-extract thin and extra thin elements, it is reasonable to try to divide ASW samples into separate fractions in order to find out the gold-collecting mineral complexes.

Using the AAS and NAA analyses, we have determined the most promising objects for further investigations with the aim of utilizing ash and slag samples for extracting gold concentrate. The following samples were selected:

1. Vladivostok: TPP-2, TPP-2-1 hole; TPP-2-5 hole;
2. Bolshoy Kamen: B-K-17 hole;
3. Arsenyev: ARS-23 hole;
4. Partizansk: P-GRES-54 hole;
5. Luchegorsk: L-GRES-57 hole.

Research on the selected samples has been carried out using the following method (Fig. 1). Initial sample of 10 kg was grinded in a disk grinder (Fritsch Company) to 0.1 mm size. Then, the grinded sample was taken in a vessel, and water was poured into it. The sample was mixed thoroughly till it got settled. Then foam that consisted of pumice and soot was collected from the surface. The collected material was dried and accuracy was measured on a weighing scale of second-order class. Then, low-pressure water was poured into the vessel with steeped sample. Silt, clay, and grinded coal were washed out of the sample. Water overflowed the vessel and went into the settling tank, and suspended particles settled and collected there. After washing out silt, clay, and grinded coal, the residue in the form of small grained sand was received. The concentrate consisted of magnetic material, and non-magnetic material was received from the derived sand by using gold-washing pan. The derived material was dried in a dryer, and then, magnetic materials were taken out of it by using magnetic separation process.

Thus, as a result of gravity separation of ash and slag samples, the following fractions of metals were derived:

- Coal dust (pumice, soot);
- Clay, silt, coal underburning;
- Concentrate – heavy non-magnetic fraction;
- Concentrate – heavy magnetic fraction;
- Light non-magnetic fraction – sand;
- Underburning of coal.

The derived fractions were weighed and sent for reanalysis – NAA (to determine gold composition) and X-ray fluorescence (to determine material composition). Results of gold content in various ASW fractions are given in Table 3. The analyses showed that gold concentrates were mostly found in heavy non-magnetic fraction and partly in light non-magnetic fraction. An optimal, three-staged way of organization of ASW recycling was developed, considering the peculiarities of chemical composition.

Table 3. Gold content in various fractions of ASW samples from the survey loops

Sample name	Original	Soot, pumice	Silt, clay	Light fraction	Non-magnetic fraction	Magnetic fraction
TPP-2-1 hole (survey loop 1) (Vladivostok, TPP-2)	0.10	<0.05	<0.05	0,26	0.39	<0.05
TPP-2-5 hole (survey loop 2) (Vladivostok, TPP-2)	0.05	<0.05	<0.05	<0.05	0.21	<0.05
B-K-17 hole (Bolshoy Kamen, TPP)	0.09	<0.05	<0.05	<0.05	0.35	<0.05
ARS-23 hole (Arsenyev, TPP)	0.11	<0.05	<0.05	<0.05	0.36	<0.05
P-GRES-54 hole (section 3) (Partizansk)	<0.05	<0.05	<0.05	0.12	0.37	<0.05
L-GRES-57 hole (Luchegorsk)	<0.05	<0.05	<0.05	<0.05	0.15	<0.05

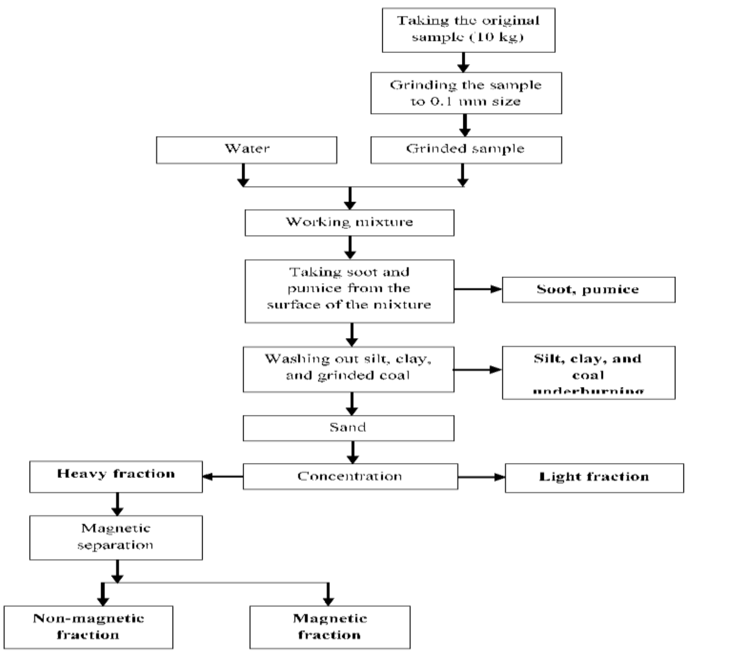

Figure 1: The proposed method to separate ASW samples from the energy enterprises of Primorsky Territory

The first stage is the material stage. At this technological conversion, ASW is divided into fraction and purified from underburning and iron oxides. At this stage commercial output with sustainable liquidity is already produced – high-energy fuel, iron concentrate, and sand. The second stage includes extraction of valuable concentrate components. The third stage is production of construction materials, including materials for road and cement industries.

CONCLUSION

Presence and amount of noble metals in ash and slug wastes depend on the type of combusted coal and on peculiarities of coalfields location. Nevertheless, the available data show that precious metals in a number of ash disposal areas reach a level that is of commercial interest. Silver content was found by atomic absorption analysis within 0.5-29.7 g/t limits. Gold content was found within 0.004–0.180 g/t limits. Gold content was found by neutron activation analysis within 0.05–0.45 g/t limits. Underestimation of the gold content that was determined by the AAS method can be associated with incomplete autopsy of gold from samples during grinding and dissolving.

Particles of free gold and other noble metals in ASW are mostly in the thin and extra thin form. Most part of gold strongly fuses with surrounding minerals. ASW's gold and noble metals are difficult to extract and hence they need special procedures of concentrating and additional extraction.

The recommended method of ASW separation allows obtaining the fractions that are sustainably linked with zones of higher gold concentration. In future, it will allow obtaining the concentrate that would be not only of scientific but also of practical interest for gold extraction.

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