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Aspects of Establishing Precious Metal Reserves in Waste of Heat-And-Power Engineering Enterprises.

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ABSTRACT

The literature on the presence of precious metals in ash and slag waste of thermal power plants (TPPs) was reviewed in this paper. Extraction of gold-containing concentrate from ash and slag waste was investigated. Three regularities were revealed: type regularities, content regularities, and gold distribution regularities in ash and slag waste of thermal power plants (TPPs). Pre-built theoretical model of the physical and chemical transformations that occur with gold in the process of coal burning was developed on the base of the discovered patterns. The process is implemented in a dry-bottom boiler with electric filter. Preliminary calculation of quantity content of precious metals for some Far Eastern TPPs was made. Solution for withdrawing ash and slag materials with increased gold concentration from ash-handling system without interrupting TPP's technical operation schedule was offered. According to the obtained data, collecting a part of ash and slag waste from slag baths and from electric filter prechambers before they reach TPP's ash removal system, presumably, allows getting material with gold concentration that is three to five times higher than in ash disposal area. The amount of recycled initial ash and slag waste decreases two to three times, and material and financial expenditures decrease correspondingly. In addition, forecasted data about gold content in ash and slag disposal areas of several Far Eastern TPPs was provided.

Keywords: technogenic deposits, wastes of energy enterprises, ash and slag waste (ASW), precious metals, gold distribution regularities, gold concentration from ash-handling system

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INTRODUCTION

Many authors [1-3] have recorded information about the presence of noble metals and rare earth metals in ash and slag waste of electric power plants. Moreover, the number of ash disposal areas of electric power plants where valuable components are found is growing with each year. That is why the extraction of noble metals from coal combustion wastes attracts special attention. It is well known that coal is a good sorbent and it collects significant amount of rare metals, rare earth metals, and noble metals. During coal combustion at electric power plants and during the production of electric and heat energy most parts of noble metals and rare earth metals get mingled with the combustion products or settle in the gas purification system. In addition, percentage of valuable components and their combinations in ash and slag waste of TPPs is higher than that in the source material (coal). Minimal content of elements that determine the possible industrial significance of commercial energetic coal and gravity separation products as a source of crude ore in coal and ash includes 0.02 g/t and 0.1 g/t of gold; 1 g/t and 5 g/t of silver; 0.05 g/t and 0.025 g/t of platinum; and 0.005 and 0.025 g/t of palladium [4].

Noble metals were found in ten fields in the south of the Russian Far East. Places of special interest are fields of germanium-bearing coals. It is observed that concentration of noble metals in the coal of Pavlovskoye, Bikinsckoye, Rakovskoye, and Luzanovskoye fields can reach hundreds of milligrams per ton [5].

Gold and platinum metals are interest by the organizations that seek profitable and sustainable production. First, the government acts as a guaranteed buyer of these metals. Second, the price of gold and platinum or their concentrates tends to increase. Third, huge amount of ash and slag is already collected. According to available data [6], the amount of collected ash and slag in Russia is 1,300 million tons. Annual ultimate yield during coal, schist, and peat combustion at TPPs and boiler houses of RAO *Energy System of East* is about 40 million tons [7]. Comparatively, there is a small amount of gold and platinum in ash and slag waste. But taking into account the vast collected amount of ash and slag waste and the amount of annual output of ash and slag, it can be said that the amount of precious metals that are already extracted from the earth and wait for processing is dozen or even hundred times more than that present in traditional mineral raw material [8].

The origin of gold and platinum in coal is yet to be thoroughly researched. However, we can say that the presence of these metals in combustion products of some coal types in amounts that are of practical interest is proven. There is information about extraction of gold from coal and ash in some literature [9-11]. Wyoming and South Dakota (the USA) are the most recognized states where gold is extracted from coal and ash; the average gold content in coal is 2.8 g/t, and that in ash is up to 17 g/t. High gold content is noticed in Japanese lignites and also in the coal available from thin coal beds of New Zealand. They are characterized by the presence of gold veins in enclosing rocks. In addition, there is information about incredibly high gold content in Czech anthracites – up to 35 g/t. Coal inclusions of carbonic sandstone of Canada, mineralized by Fe sulfides and Cu sulfides, contain 0.01–0.08 g/t of gold [1]. Some researchers [12, 13] have noticed high content of Au and Ag, platinum elements, and rare earth elements in black and brown coal of Siberian and Far Eastern coalfields. Leonov S.B. et al. have reported that there is gold content, within 0.1–0.6 g/t limits, in the ash samples of Revdinskaya State District Power Station (SDPS) in Sverdlovsk and also that gold can be extracted by using gravitational method. Many industrial and semi-industrial tests, as Leonov et al. have discovered, showed the possibility of fine gold extraction from ash and slag waste as well as intermediary product with 500–600 g/t Au content. Further processing of the product using magnetic and flotation methods gave conditional concentrate with Au content up to 1.5 kg/t. According to the authors, extraction of gold from ash and slag waste is economically effective with Au content not less than 0.2 g/t.

METHODS

Researches and practical works to calculate the content of precious metals in Far Eastern ash and slag waste were organized in Khabarovsk by Far Eastern Scientific and Research Institute of Mineral Raw Materials (FEIMRM) and in Vladivostok by Far Eastern Federal University (FEFU) in cooperation with Research and Production Enterprise Techno-Plasma (Vladivostok).

FEIMRM researched on the samples of ash from Khabarovsk TPP-1, TPP-2, TPP-3, and Birobidzhan TPP-2. FEFU in cooperation with Research and Production Enterprise Techno-Plasma researched on the samples of ash from Vladivostok TPP-2. Preliminary data about the content of precious metals in ash and slag waste of the largest TPPs were received.

During the field study of ash and slug wastes testing of the ash dump and burned at CHP coal were investigated. Testing of the ash dumps has been carried out through penetrations in accessible locations by a sparse grid of pits with the selection in them samples of the channel or the gross methods.

All samples after the standard preparation were subjected to semi-quantitative spectral and atomic absorption analysis for Au and Pt. In each sample 3 definitions of Au and Pt were carried out and the average content of precious metals in the sample was calculated. After determining the content of precious metals in selected ash and slag samples, they were divided into three parts. One part was analyzed by spectral, atomic absorption, and chemical methods. The second part was used as a small technology sample. The definition of useful components in technology sample was determined by using laboratory-technological researches. The third part of the ash and slag samples was washed on the tray or was processed on a laboratory concentrator. The heavy fraction obtained at the concentrator, was analyzed by mineralogical analysis. This analysis was used to study the ash and slug waste composition and to study the resulting concentrates, determination of output of precious metals and other products gain. Diagnosis of platinum-group minerals, native minerals and alloys was performed using electron microprobe analysis at the Institute of Volcanology FEB RAS (Petropavlovsk-Kamchatsky). Content of gold in some samples was determined by assay analysis.

Ash and slug samples were taken from the following places:

1. In Khabarovsk were tested the ash disposal areas of TPP-1 and TPP-3. At TPP-1 samples were taken from the ash dumps №1 (48 PCs), №2 (40 PCs), №3 (64 PCs). At TPP-3 samples were taken from the ash dumps №1 (82 PCs). For prevention conducted a pits network 100x200m and 100x100m depending on the dimensions of the landfill that were tested with trench method.
2. In Birobidzhan were tested the ash disposal areas of TPP disposal area 1 (34 PCs). The size of tested area is 350x400 m with a depth of 8-10 m. Varieties of ash and slug wastes transporting the pulp is combusted from TPP.
3. In Primorsky Territory were tested the ash disposal areas of Vladivostok TPP-2 (12 PCs), Luchegorsk SDPP (8 PCs), Artem TPP (2 PCs) and Partizansk SDPP (2 PCs).

RESULTS AND DISCUSSION

The technical team of FEIMRM conducted researches and discovered the presence of gold and platinum in some samples of ash and coal from Khabarovsk TPP-1, TPP-3, and Vladivostok TPP-2. The mass fraction of gold in ash was calculated executing a method that was developed by FEIMRM. The result fluctuated from 0.2 g/t to 24.5 g/t, and platinum content was 67 g/t in terms of initial material. Content of gold and platinum in combusted coals was confirmed by control sampling, but in much smaller amounts:

- In Khabarovsk TPP-1 the average and maximum gold content was 0.07 and 0.5–25 g/t, respectively, and platinum content was 0.1–0.5 and 0.3–2.5 g/t.
- In Khabarovsk TPP-3 the average and maximum gold content was 0.07 and 0.5–0.6 g/t, respectively, and maximum platinum content was up to 2 g/t.
- In Birobidzhan TPP, the average and maximum gold content was 0.13 and 2.13 g/t, respectively.

Data about noble metals content in ash and slag waste of some TPPs of Primorsky Territory were also received:

- Gold: 0.6–2.5 g/t (Artem TPP)
- Silver: 0.15 (Artem TPP); 0.4 (Vladivostok TPP-2); 0.14 (Luchegorsk SDPP); 0.2 (Partizansk SDPP)
- Platinum: 0.6–3.5 (Artem TPP)

Based on the analysis of the literature and the results that we had obtained during our experiment at Vladivostok TPP-2, we could identify three regularities: type regularities, content regularities, and gold distribution regularities in ash and slag waste of TPPs.

The data received during mineralogical analysis show that gold contained in ash and slag is mostly thin and dust-like, produced in grain size or sometimes in cloddy aggregates of 5–40 μM. Gold elements of 0.5×1.0 mm in size were found in singular samples. Gold content in new ash was less than that in old, dried ash disposal areas. We can claim that the gold elements become larger as time goes by. Though the process of mineralization of gold in ash disposal areas has not been studied thoroughly until now, we can say that in old ash disposal areas gold elements are purer. In fresh, new ash the gold elements have traces of melting and they are covered by different types of patina, often in alloys with other minerals and ash fragments. Gold is mostly found in ash class 0.071 mm.

During the investigation, we have observed the following:

− Smaller amount of gold, independent of combusted coal type, is found in fly ash of TPPs.
− Most of the gold elements are fused with slag component.
− Ash and underburning have increased sorption capacity compared to gold.

With this knowledge, we can create a preliminary theoretical model of physical and chemical transformations that happen with gold during the process of coal combustion. The process is executed in a dry-bottom boiler with an electric filter:

1. During coal preparation, in a mill of a TPP, on the grinding phase, gold gets evenly distributed in all volumes of grinded coal.
2. It is most likely that there is active coal redistribution between combustion products during coal combustion in boiler furnace. We can suppose that there are high-speed repetitive processes of gold smelting in the high-temperature flame zone. Gold smelts from combusting coal and there is also sorption of gold and its compounds. The combusting coal particles undergo the process of turning into coke and semi-coke – the so-called underburning – at the same time. Particles of gold and its compounds sediment on the small particles of underburning. Then, these particles of underburning with sedimented gold and its compounds reach the electric filter together with fly ash and small slag particles. Main amount of underburing is depositing in prechamber of electric filters together with small slag particles (particles of slag sand). Simultaneously, compounds of gold with other metals are created in the flame, and their sedimentation on the relatively large coal and slag particles falls into the furnace slag and gets removed. It is necessary to note that it is typical for most of the power plant boilers, built in the Far Eastern TPPs, to have the option of distributing underburning in ash and slag (until they are mixed in the hydraulic ash removal system, which is described below). Slag contains up to 65% of underburning in the form of particles of 3–10 mm in diameter. Slag sand in prechambers of electric filter contains up to 20% of underburning in the form of particles up to 2 mm in diameter. Other underburning gets distributed on the electric filter fields, decreasing along the way of combustion gas. Usually there is no more than 5% of underburning in the first field of electric filter, and no more than 0.5% in the last field. Taking into account the studies about gold content in slag, and the information about selective sorption characteristics of underburning, it can be considered that the maximum amount of gold is concentrated in underburning, slag, and slag sand. These elements of ash and slag waste are the initial gold-containing sources, before they come into the hydraulic ash removal system. In this case, for the first level of concentration, if there is a proper increase of gold concentration in the initial material, the volume of ash and slag material can be 30%–35%, which is transported to the ash and slag disposal area. It may be true that gold does not accumulate in slag sand, because slag sand consists of 70%–75% of silicon oxide grains. Grains are covered by firm and inert carbonate film. Indirectly it is proved that it is difficult to estimate the gold content in fly ash through experiments. Obviously, all the suppositions must be confirmed by researches with supporting facts.
3. All fractions of ash and slag get moved from the electric filter to the canals of hydraulic ash removal system, and an ash-handling pump drains them through tubes to the ash disposal area. The initial gold-containing concentrate (underburning, slag, and slag sand) gets distributed in all the ash and slag waste (or deconcentrates) in the canals of hydraulic ash removal system, in ash-handling pump, and in tubes. Simultaneously, active physical and chemical processes of gold redistribution on the ash and slag waste get started through the sorption of gold by fine mechanic-activated fly ash in ash-handling pumps and tubes. These processes go on while ash and slag waste gets transported to the ash disposal area, from where it pours into a repository and gets dried.

4. After stabilization of ash and slag waste in the ash disposal area, self-purification of gold occurs through physical and chemical processes and its compounds are enlarged (secondary concentration) in all the mass of ash and slag. Possibly, in time, gold-bearing lay of ash and slag is formed on all the levels of ash and slag disposal area.

The technical cyclic process – "preparation of material for extraction of gold-containing concentrate (fuel grinding) – receiving of initial gold-containing concentrate – dilution of concentrate" – is initiated for the combustion of solid fuel. It is reasonable to set the task of extracting initial concentrate from the ash handling system of TPPs before its redistribution. This task includes collecting the concentrate from the hydraulic ash removal system. There are no technical limits for solving that task. The structure of ash removal system of any TPP allows collecting any fraction of ash and slag waste without disrupting the technical cyclic process of producing energy and without decreasing reliability of the TPP's work.

From the very beginning, flows of ash and slag are separated in the ash removal system of a TPP. The first supposed component of the concentrate is watered slag-and-coal mix. It is collected in slag bath in the lower part of the boiler furnace (if it is a dry-bottom boiler). Then the screw conveyor delivers this mixture to the hydraulic ash removal canal. Sending this mixture through the pipes to the surge bin is not a difficult technical task – a process that many Western European TPPs perform. Gathering slag-and-coal mix from the slag baths can be done separately for every boiler, or it can be done once for several boilers. An additional advantage of removing slag in such a way is liquidation of hydraulic ash removal canals within the boiler. The second supposed element of the concentrate is slag sand and underburning. These components are collected in the storage bins of the electric filter prechambers. According to existing technology, this fraction is removed from the bins and gathered into the hydraulic ash removal canals through ash-sluicing devices. This fraction can be collected into separate bins by connecting a pneumatic collection system to the bin of the prechamber. Such collecting schemes are used in many Russian and foreign TPPs. These schemes are also used for collecting fly ash for construction industry.

The data that we have obtained on the content of gold in ash and slag waste allow us to create a preliminary table of gold distribution in some ash and slag waste fractions. Quantity indicators of possible gold content in ash and slag waste are presented in Tables 1 and 2. These quantity indicators were used in the study of Vladivostok TPP-2 in 2004.

Thus, collecting a part of ash and slag waste from slag baths and from electric filter prechambers before they reach TPP's ash removal system, presumably, allows getting material with gold concentration that is three to five times higher than in ash disposal area. The amount of recycled initial ash and slag waste decreases two to three times, and material and financial expenditures decrease correspondingly.

Table 1. Ash and slag waste composition of Vladivostok TPP-2 in 2004

Name of ash and slag waste components	Amount (tons)	Gold content (g/t)	Calculated volume of gold (kg)	Percentage ration of ash and slag waste
Yearly output of ash and slag waste	432,000	0.60	259	100
Yearly output of pure slag	38,880	1.68	65	9
Yearly output of underburning	43,200	1.92	83	10
Yearly output of slag sand	52,840	1.91	101	12
Yearly output of fly ash	298,080	0.01	10	69

Table 2. Calculated distribution of gold in fractions of ash and slag waste from Vladivostok TPP-2

Name of gold-containing components	Amount (tons)	Gold content (g/t)	Calculated amount of gold (kg)	Percentage in ash and slag waste
Yearly output of slag sand and unburned fuel mixture	69,120	1.94	134	16
Yearly output of slag and unburned fuel mixture	64,800	1.94	125	15

For comparison we present data of gold resources in ash and slag disposal areas of Far Eastern Generating Company's TPP (FGC TPP), which were obtained, during the experiments [14]. In addition, gold and platinum content data, obtained as a result of investigation of Vladivostok TPP-2, are also given.

Content of elements in ash disposal areas is calculated by averaging the content of chemical compounds in studied samples. For FGC TPP we declare that the resources of possible extracted gold have different extraction ratio. Given quantity of resources corresponds with large/average gold-bearing placer deposit (in quantitative indicators). Taking into account the fact that annual output of investigated TPPs is 500,000–600,000 tons of ash and slag material, we can say that resources have 300–400 kg increase of gold. All in all, considering the fact that FGC TPPs produce about 1 million tons of ash and slag material every year, and the amount of already collected ash and slag material in ash disposal areas is about 30 million tons, we can conclude that possible gold resources in them is about 18–20 tons (Table 3).

Table 3. Forecasted gold resources in ash and slag disposal areas of TPPs of Khabarovsk, Birobidzhan, and Vladivostok, as of January 1, 2001

TPP ash disposal area	Amount of ash and slag waste, mil. tons	Au content, g/t	Forecasted resource, t	Extracted resources if extraction ratio is		
				0.3	0.4	0.5
TPP-1 Kubyaka	5.5	0.92	4.95	1.48	1.98	2.48
TPP-1 Amurkabel	4.5	0.70	3.15	0.94	1.26	1.58
TPP-1 Ilyinka	3.0	1.10	3.30	0.99	1.32	1.67
TPP-3 Fedorovka	3.0	0.63	1.80	0.54	0.72	0.90
Birobidzhan TPP, old ash disposal area	0.7	1.82	1.26	0.38	0.50	0.63
Total	16.7	0.86	14.46	4.33	5.78	7.23
Vladivostok TPP-2	18.5	0.61	11.00	3.30	4.40	5.50

CONCLUSION

Extraction of gold-containing concentrate from ash and slag waste was investigated on base of literature data and carried out analyses of waste ash and slug wastes from landfills of Khabarovsk TPP-1, TPP-2, TPP-3, and Birobidzhan TPP-2. The following patterns were revealed as the result of the research:

- Fly ash of thermal power plants contains smaller part of gold irrespective of the type of burned coal;
- Slag component of TTPs waste contains major part of the gold;
- Ash and underburning have increased sorption capacity compared to gold.

Pre-built theoretical model of the physical and chemical transformations that occur with gold in the process of coal burning was based on the discovered patterns. The main provisions of the developed model are following:

– During coal preparation, in a mill of a TPP, on the grinding phase, gold gets evenly distributed in all volumes of grinded coal.
– The combusting coal particles undergo the process of turning into coke and semi-coke – the so-called underburning – at the same time. Particles of gold and their compounds have sediment on the small particles of underburning. Then, these particles of underburning with sedimented gold and its compounds reach the electric filter together with fly ash and small slag particles. Main amount of underburing is depositing in prechamber of electric filters together with small slag particles (particles of slag sand).
– All fractions of ash and slag get moved from the electric filter to the canals of hydraulic ash removal system, and an ash-handling pump drains them through tubes to the ash disposal area.
– After stabilization of ash and slag waste in the ash disposal area, self-purification of gold occurs through physical and chemical processes and its compounds are enlarged (secondary concentration) in all the mass of ash and slag.

The data that we have obtained on the content of gold in ash and slag waste allow us to create a preliminary table of gold distribution in some ash and slag waste fractions. According to the obtained data collecting a part of ash and slag waste from slag baths and from electric filter prechambers before they reach TPP's ash removal system, presumably, allows getting material with gold concentration that is three to five times higher than in ash disposal area. The amount of recycled initial ash and slag waste decreases two to three times, and material and financial expenditures decrease correspondingly.

In addition, forecasted data about gold content in ash and slag disposal areas of several Far Eastern TPPs was provided.

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