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Analysis of the Chemical Composition of Ash and Slag Waste of TPP in the Far East District of Russia as Technogenic Deposits of Precious Metals

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Abstract: Assessment of precious metals content in coals and ash and slag waste of thermal power plants is carried out. Methods of obtaining gold concentrate from ash and slag waste are considered. The data on amounts of precious metals, accumulated in ash dumps of large Far East thermal power plants are presented. The technology of selection of ash and slag materials with increased gold concentration from an ash handling system of thermal power plant for further enrichment is suggested.

Key words: Waste of power production industry enterprises, ash and slag waste, thermal power plant, precious metals, enrichment

INTRODUCTION

Information about the presence of precious metals and rare earth elements in Ash and Slag Waste (ASW) of Thermal Power Plants (TPP) is noted by many researchers (Kler *et al*., 1987; Leonov *et al*., 1998; Korneev, 2004). Year by year the number of TPP ash dumps, where in valuable components are detected, increases. Therefore, the problem of extracting precious metals from the coal combustion waste attracts increased attention. It is known that coals are good sorbents and accumulate significant amounts of the rare, rare earth and precious metals. In the process of coal burning at power plants, in the production of electric and thermal energy, the majority of precious and rare earth elements passes into combustion products or deposits in the gas cleaning system. At that, the percentage of precious components and their compounds in the ash and slag waste of TPP becomes higher than in original coals (Table 1).

In the south of the Far East of Russia precious metals are determined in ten coal deposits. Among them, deposits of germanium-bearing coals are of the particular interest. It was determined that the concentration of precious metals in coals of Pavlovsky, Bikinsky, Rakovsky and Luzanovsky deposits can reach hundreds of milligrams per ton (Seredin, 1998a, b). Gold and platinum, which can be extracted from ASW are of the greatest interest from the viewpoint of profitable and sustainable production organization (Korneev, 2004).

The origin of gold and platinum in coals is not sufficiently studied yet but their presence in combustion products of some coal types having the content which is of practical interest, can be considered proven (Leonov *et al*., 1998; Kler, 1987; Yudovich, 1989). An increased content of Ge, W, Au, Ag, platinum and rare earth elements in bituminous and brown coals of deposits in Siberia and the Far East of Russia is noted (Yudovich, 1989; Seredin and Magazina, 1999). Mainly used method of extracting gold from the ore is gravity concentration. Conducted semi-industrial and industrial experiments for enrichment of ash and slag raw materials by gravity method have shown the possibility in principle of fine gold extraction from ASW with preliminary obtaining an intermediate product with Au content of 500-600 g t^{-1} (Leonov *et al*., 1998). Subsequent operational development of the industrial product by

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Table 1: Assessment of of power generating coals and ASW as sources of ore raw materials by the minimum content of rare elements

	Content of elements (g ton^{-1})	
Elements	In coals	In coal ashes
Beryllium	5	20
Oron	2000	10000
Anadium	100	500
Ismuth	1	5
Tungsten	30	150
Gallium	20	100
Hafnium	5	25
Germanium	30	150
Old	0.02	0.1
Ndium	0.20	1
Yttrium	15	75
Ytterbium	1.50	7.5
Cadmium	1	5
Cobalt	20	100
Lanthanum	150	750
Lithium	35	175
Manganese	2000	10000
Copper	100	500
Molybdenum	6	30
Nickel	100	500
Niobium	10	50
Tin	20	100
Palladium	0.005	0.025
Platinum	0.005	0.025
Rhenium	0.100	0.500
Rubidium	35	175
Mercury	1	5
Selenium	1	5
Silver	1	5
Lead	240	1200
Scandium	10	50
Strontium	400	2000
Antimony	30	150
Thallium	1	5
Tantalum	1	5
Tellurium	1	5
Titanium	1500	7500
Chrome	1400	7000
Caesium	30	150
Zinc	400	2000
Zirconium	120	600

magnetic and flotation methods allows obtaining the conditioned concentrate with Au content of up to 1.5 kg ton^{-1}. In some researchers (Leonov *et al*., 1998; Yudovich, 1989) opinion, the gold extraction from the ash and slag waste is cost- effective when the content of gold in amounts of >0.2 g ton^{-1}.

MATERIALS AND METHODS

Scientific and applied researches for determination of the content of precious metals in the Far East ASW were carried out in Khabarovsk by the Far Eastern Research Institute of Mineral Raw Materials (FEIMRM) and the Far Eastern Federal University, together with "Tekhno Plasma" SPE (Vladivostok).

Ashes of Khabarovsk TPP-1, TPP-3, Birobidzhan TPP and Vladivostok TPP-2 were investigated. At the ash dumps pits and mole-hole operations were sunk throughout the network of 100×200 and 100×200 m (depending on size) which were sampled by trench and tear method. In the field study of ASW, the sampling of ash dumps and coals burned at TPP, the ash sampling in systems of transportation from furnaces (boilers) to ash dumps with the analysis of combustion and transportation.technology were carried out. Testing ash dumps themselves was carried out by drifting in accessible places on a sparse network of mole-hole operations and pits with sampling therein by trench or bulk method.

All samples after standard sample preparation were subjected to the spectral semi-quantitative analysis and the atomic absorption analysis for Au and Pt. Diagnostics of Platinum Group Minerals (PGM), native minerals and alloys was carried out using micro-probe analysis at the Institute of Volcanology (the city of Petropavlovsk-Kamchatsky). Individual samples were studied for the presence of PGM in the city of Novosibirsk in United Institute of Geology, Geophysics and Mineralogy, Siberian branch of the Russian Academy of Sciences.

Preliminary data on the content of precious metals, which allow outlining directions for technological developments of ASW enrichment processes, were obtained by ash and slag waste of the largest TPP. Mass fraction of gold in the ash of studied TPP in Khabarovsk, determined according to the method developed in FEIMRM ranged from 0.2-24.5 g ton^{-1}, the platinum content is determined in the amount of 0.67 g ton^{-1} in terms of the original material. Obtained data are specified in Table 2.

At examined TPP the coal combustion takes place at the temperature 1, 100-1, 600°C. At combustion of the organic coal portion, volatile compounds are produced in the form of smoke and vapour and the incombustible mineral portion of a fuel escapes in the form of solid ash residues forming dust-like mass (ash), as well as lumpy slags. The amount of solid residues for bituminous and brown coals ranges from 15 up to 40%. Coal is ground prior to combustion and for a better combustion, the oil fuel is often added therein in a small (0.1-2%) amount.

At combustion of atomized fuel small and light particles are whirled with flue gases and they are called flue ash. The particle size of the flue ash ranges from 3-5 up to 100-150 um. The amount of larger particles usually does not exceed 10-15%. Flue ash is caught by ash collectors. At TPP-1 in Khabarovsk and Birobidzhan TPP ash collection is wet on scrubbers with Venturi tubes at TPP-3 and TPP-2 in Vladivostok-dry on electrostatic precipitators.

Table 2: The content of rare elements in ASW of Khabarovsk TPP

	Content (%)				
	TPP -1		TPP -3		
Elements	Average	Max.	Average	Max.	Note
Mn	0.2500	0.4000	0.09000	0.2000	Maximum in the slag
Ni	0.0060	0.0100	0.00300	0.0080	Maximum in samples with increased Pt. content
Co	0.0014	0.0100	0.00055	0.0010	Maximum in samples with increased Pt content
Ti	0.3000	0.6000	0.30000	0.6000	Minimum in the foam
V	0.0080	0.0200	0.00800	0.0100	max in samples with increased Au content and in the foam
Cr	0.0080	0.2000	0.00600	0.0600	
Mo	0.0001	0.0008	0.00010	-	
W	-	0.0040	-	0.0100	Maximum in the slag
Nb	0.0008	0.0020	0.00100	0.0020	Minimum in the foam
Zr	0.1500	0.0600	0.04000	0.0800	Maximum in the slag
Ga	0.0015	0.0030	0.00200	0.0030	Minimum in the slag maximum in muddy deposits
Be	0.00040	0.0010	0.00025	0.0006	
Y	0.00450	0.0100	0.00200	0.0040	Maximum in the foam
Yb	0.00045	0.0010	0.00010	0.0003	
La	-	0.0100	-	0.0060	
Ce	-	0.0300	-	0.0300	
Sc	0.0010	0.0030	0.00080	0.0010	Maximum in the foam max in the foam
Li	0.0060	0.0300	-	-	Maximum in the foam
Au (g ton^{-1})	0.0700	25.000	0.07000	6.0000	In the slag of TPP-3 up to 6.67 g ton^{-1}
Pt (mg ton^{-1})	0.0800	5	-	2	
Ash dump of Birobidzhan TPP					
Au (g ton^{-1})	0.1300	2.130	-	-	In the slag up to 9.25 g ton^{-1}

Heavier ash particles settle on sub-fireboxes and are fused into lumpy slags representing aggregated and fused ash particles ranging in size from 0.15 up to 30 mm. Slags are ground and removed with water. Flue ash and pulverized slag are removed at first separately and then they are mixed forming a mixture of ash and slag.

In the composition of ash and slag mixture, besides ash and slag there are always present particles of unburned fuel (incomplete burning), the amount of which is 10-25%. The amount of a flue ash, depending on the type of boilers, fuel type and its combustion regime can be 70-85% by weight of the mixture 10-20% of slag. Ash and slag pulp is removed to the ash dump via pipelines.

The ash and the slag at hydraulic transport and at dump of ash and slag interact with the water and carbon dioxide of the air. Therein take place processes, similar to diagenesis and lithification. They rapidly yield to weathering and at drying they begin to produce dust at a wind speed of 3 m sec^{-1}. ASW colour is dark grey, layered in section due to alternation of uneven-grained laminas as well as deposition of white foam, consisting of aluminosilicate hollow micro-spheres.

RESULTS AND DISCUSSION

Carried out analysis allows marking out some regularities by type, content and distribution of precious metals (on the example of gold) in TPP ASW: According to the data of mineralogical analysis, the gold in ASW is mainly thin and dust-like. It is represented by grains, more rarely cloddy aggregates with the grain size of 5-40 um, rarely larger. In singular samples the gold particles with the dimensions of 0.5×1.0 mm are found. In fresh ashes the amount of relatively large, extracted gold is the smallest and in the old, dried ash dumps, larger. It is possible to assume that in due course time an agglomeration of gold particles sizes takes place in ash dumps. Processes of gold mineralization in ash dumps were not studied in detail to date but in "old" ash dumps gold grains are cleaner. In the fresh ash, gold particles have traces of melting are covered by various films, often in intergrowths and alloys with other minerals and ash particles. Gold is revealed predominantly in the ash class 0.071 mm. Regardless of burned coal rank, the lowest content of gold is observed in TTP flue ash; In all studies it is noted that the most portion of the gold is connected

Table 3: ASW composition and gold content in the different ASW fractions of Vladivostok TPP-2

Name of ASW components	Amount (tons)	Gold contents (g ton^{-1})	Calculated gold amount (kg)	ASW (%)
Annual yield of ASW	432000	0.600	259	100
Annual yield of the clean slag	38880	1.934	75.20	9
Annual yield of the incomplete burning	43200	1.933	83.50	10
Annual yield of the slag sand	52840	1.898	100.3	12
Annual yield of the flue ash	298080	Not determined	-	69

Table 4: Distribution of gold by ASW fractions of Vladivostok TPP-2

Name of gold-containing components	Amount (tons)	Gold contents (g ton^{-1})	Calculated gold amount (kg)	ASW (%)
Annual yield of the mix of the slag sand with the unburned fuel	69120	1.936	133.8	16
Annual yield of the mix of the the unburned fuel	64800	1.936	125.4	15

with the slag component; It is determined that ash and incomplete burning have increased sorption capacity relatively to gold (Table 3 and 4).

On the basis of these regularities the theoretical model of physical and chemical transformations which takes place with gold in the process of coal combustion in the furnace of a boiler with solid slag removal, equipped with electrostatic precipitator was proposed: At the preparation of coal to burning, at the stage of coal grinding in TPP mills, gold is distributed uniformly throughout the volume of the milled coal. When the coal burning in the boiler furnace, it is most likely that there takes place an active redistribution of gold between products of combustion. It can be assumed that in the high temperature flame zone take place repetitive, high speed processes of melting gold from the burning coal and sorptions of gold and its compounds for slag particles and not yet burned coal particles, which in the same time are subjected to transformation into the coke and the char, so called incomplete burning. Fine particles of incomplete burning with deposited on them gold particles and its compounds get into the electrostatic precipitator together with the flue ash and fine particles of slag. Main volume of entrained incomplete burning together with fine particles of slag (slag sand) is deposited in pre-chambers of electrostatic precipitators. Simultaneously, formation of gold compounds with other metals, their deposition on relatively large particles of coal and slag precipitating in the furnace zone of slag removal take place in the flame. Is necessary to note that for the majority of power boilers, mounted on Far East TPP is characteristic the following distribution of incomplete burning in the ash and the slag while they are not mixed in the Hydraulic Ash Removal system (HAR): Slag contains up to 65% of incomplete burning in the form of particles with diameter in the range of 3-10 mm; slag sand in pre chambers of electrostatic precipitators contains up to 20% of incomplete burning in the form of particles with a diameter up to 2 mm.

The rest incomplete burning is distributed by fields of electrostatic precipitators decreasing along the flue gas flow. Usually not >5% of incomplete burning is contained in the first field of the electrostatic precipitator and not >0.5% in the last field. Considering the research data on the content of gold in the slag and sorption properties of incomplete burning, it is possible to assume that the main amount of gold is concentrated in incomplete burning, slag and slag sand and these ASW components, before entering HAR are the primary gold-containing concentrate. In this case, the amount of ash and slag material for the first stage of enrichment can be 30-35% of the total ASW amount transported to the ash dump with a corresponding increase in the primary material of gold concentration. It is quite possible that gold also does not accumulate in the slag sand, since the slag sand for 70-75% is represented by grains of silicon oxide, closed with strong and inert carbonate film. This is indirectly confirmed by the gold content in the flue ash at sensibility limit of methods.

From electrostatic precipitators all the factions of the ash and the slag get into HAR channels and are pumped with ash-handling pumps through pipes to the ash dump. The primary gold-containing concentrate (incomplete burning, slag and slag sand) is distributed throughout the entire ASW volume, i.e., deconcentrates, in HAR channels ash-handling pumps and in pipelines. Active physical and chemical processes of gold redistribution throughout the entire volume of ASW begin simultaneously through gold sorption by the flue ash, fine-dispersed, mechanically activated in ash-handling pumps and pipelines. These processes are continued all the time while ASW are transported to the ash dump, poured out into a container of the ash dump and dried.

Physical-chemical and biological processes of self-purification and agglomeration of gold and its compounds, i.e., the secondary concentration, begin in the ash and slag solid mass after stabilization of ash and slag waste at the ash dump. Perhaps, in the course of time there takes place a formation of ASW gold-bearing formation at some level in the body of the ash dump.

Thus, the internal technological cycle "preparing material to separation of the gold concentrate (fuel

Table 5: Predictive gold resources in TPP ash dumps of Khabarovsk, Birobidzhan and Vladivostok

TPP (ash dump)	Amount of ASW (million tons)	Ag content (g ton^{-1})	Predictive Au resources (ton)	Extractable resources at the extraction ratio		
				0.3	0.4	0.5
TPP-1 Kubyaka, Khabarovsk	5.5	0.9	5.0	1.48	1.98	2.48
TPP-1 Amurkabel, Khabarovsk	4.5	0.7	3.2	0.94	1.26	1.58
TPP-1 Ilyinka, Khabarovsk	3.0	1.1	3.3	0.99	1.32	1.67
TPP-3 Fedorovka, Khabarovsk	3.0	0.6	1.8	0.54	0.72	0.90
TPP old ash dump,Birobidzhan	0.7	1.8	1.3	0.38	0.50	0.63
Total “Khabarovskenergo”	16.7	0.9	14.5	4.33	5.78	7.23
TPP-2, Vladivostok	20.2	0.6	12.0	3.61	4.83	6.02

grinding)-obtaining the primary gold-containing concentrate-concentrate dilution” is formed at the method of pulverized-coal combustion of solid fuel at TPP. It is necessary to consider the task of extracting the primary concentrate from the ash handling system of TPP prior to its distribution, having determined for this concentrate sampling locations from HAR system. Technical constraints to solve this problem do not exist. Ash removal system of any power plant is constructed in such a way that it allows selecting any ASW faction without both affecting the technological cycle of electric power production and reducing the reliability of TPP operation.

Initially, slag and ash flows are divided in the ash removal system at TPP. The first probable component of the concentrate, watered slag-coal mix, accumulates in the slag baths at the bottom part of the boiler furnace (for variant of the boiler with solid slag removal). Then this mix is unloaded with augers into HAR channel. At that it is not technically difficult to direct it through pipes into the intermediate hopper as it is done at many foreign TPP. Selection of slag-coal mix from slag baths can be individual for each boiler or one for several boilers. An additional advantage of this slag removal method is the abandonment of HAR channels within the boiler. The second probable component of the concentrate, slag sand and incomplete combustion, is stored in collecting hoppers of pre-chambers of electrostatic precipitators. According to the existing technology, this fraction is removed from hoppers in HAR channels through ash sluicing devices. By connecting to the hopper of pre chamber the pneumatic (vacuum, pressure-vacuum, pressure) selection system, it is possible to collect this fraction in a separate hopper. Such selection schemes operate at many TPP including Russian and are used for selection of the flue ash for the construction industry. Experimental and calculated data on the mass content of gold in some ASW fractions were obtained. Quantitative indices of the probable content of gold in the ASW on the example of Vladivostok TPP-2 are shown in Table 3 and 4.

It was ascertained that the selection of the ASW portion from slag baths and pre-chambers of electrostatic precipitators prior to their entering into the ash removal system of TPP allows obtaining a material with 3-5 fold higher gold concentration than at the ash dump. At that, the amount of processed initial ASW is 2-3 fold reduced respectively, material and financial expenditures for processing are reduced. For comparison, Table 5 shows the predictive assessment of gold resources in ash dumps of Khabarovsk TPP and the data on gold content obtained as per results of the study of Vladivostok TPP-2 ash dump. Calculated content of elements by ash dumps is accepted as an average by samples with the calculation of content by the mass balance.

CONCLUSION

Predictive resources of extractable gold at different extraction rates are determined for the Far East TPP. Presented resources by their quantitative indices correspond to an average deposit of the ore gold. Total in the Far East Region about 3 million tons of ASW annually enter the ash dumps of TPP >60 million tons of ASW are accumulated, predictive gold resources therein are 33-38 tons. Considering that 500-600 thousand tons per year of ASM enter ash dumps from examined TPP, gold resources in ash dumps increase annually by 300-400 kg of gold. Developed and patented technologies of ASW selection and enrichment allow considering TPP ash dumps as a source of precious and rare earth metals.

According to the data of Department for Subsoil Management in Far Eastern Federal district of Russia (Dalnedra), there were produced >100.8 tons of gold in 2011 in the Far Eastern Federal District, about 2 tons from them were produced in the Primorsky Territory. Using ash dumps resources, it is possible to increase production of only gold in the Primorsky Territory by 20-25% without causing environmental damage.

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