Prospects and possibilities of using ash and slag wastes of power enterprises of Primorsky Krai as technogenic mineral raw materials

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Abstract. The results of an investigation of ash and slag wastes (ASW) of enterprises of the energy sector of Primorsky Krai are presented. The averaged contents of the main elements and mineral complexes in Primorsky Krai are given. It is shown that the mineral composition of the ASW data makes it possible to separate the primary raw materials into fractions with different compositions. A scheme is proposed for dividing the initial ash extractors into separate mineral fractions by the particle size and by their physical properties. The predominant concentration of gold, platinum, rare earth elements (REE) and a number of other valuable components in the heavy non-magnetic fraction isolated from the primary ASW was detected. Almost complete absence of gold, noble metals and REE in underburning of coal, magnetic and micro-dispersed fractions of ASW has been demonstrated. A device was offered for complex processing of ash and slag wastes of enterprises of the power industry of Primorsky Krai, which makes it possible to divide the initial ASW into mineral fractions, being raw materials for various industries.

1 Introduction

One of the main problems facing the energy industry, producing electricity and heat using coal, is the problem of waste generated from the combustion of fuel. According to the Federal Agency for Technical Regulation and Metrology, in 2017, the annual increase in ash and slag wastes in Russia is about 21.3-26.7 million tons [1], while the volumes of secondary use of ASW do not exceed 6.3 million tons [1], which led to the situation when the total volume of ASW accumulated at the landfills in Russian Federation is about 1,300 million tons [2], and the area occupied by ash and slag polygons exceeds 22,000 ha [2].

The share of coal in the fuel balance of Russian power plants in 1980 – 2010. did not fall below 25%. At the moment, according to the "Energy Strategy of Russia for the period until 2030", the share of coal in the fuel balance of power plants is forecast to increase to 36-38% with a further increase in coal consumption in physical terms by 64%, while reducing consumption of gas and fuel oil [3]. And this is not surprising, since Russia has huge resources of various quality coals - from brown to anthracite. The total resources are

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estimated at 4,089 billion tons, and the balance reserves are about 272.7 billion tons [4], most of these reserves being energy coals – 3,641.9 billion tons (89%), and only 447.1 billion tons (11%) being coking [4].

Meantime, the volumes of ASW processing in Russian Federation remain one of the lowest in the world today, which leads to further growth of ASW stocks stored in landfills. This fact adversely affects the ecological situation in the ash disposal areas. The main danger is the penetration of effluents from the ash dump into the ground, leading to the entry of polluting substances (heavy metals, radioactive elements, etc.) into groundwater, and then - into rivers and aquatic bodies and, ultimately, human food [5].

At the same time, ASW can serve as a valuable source of various minerals. The ash included in the ASW of energy enterprises contains the following mineral complexes: aluminosilicate microspheres (1-2%), magnetite (5-9%), aluminum oxide (Al_2O_3 20-27%), silicon dioxide (SiO_2 49%), underburning coal (5-15%); oxides of rare earth elements (5-7%), which can find the widest application in industry [6, 7]. In the literature there are numerous reports on the presence of increased contents of precious metals and rare earth metals in ash and slag waste from energy enterprises [8-10]. There have been some attempts to extract from ASW gallium, germanium [11] and scandium [12].

The mineral composition and properties of ASW differ significantly depending on the composition of the coals from which they were obtained, the specifics of combustion technology and other factors [13]. According to the data of Yarmolinskaya [14], for ASW from CHP of the Far East, the following features are characteristic: a relatively small amount of active oxides (CaO + MgO); increased content of sesquioxides ($Al_2O_3 + Fe_3O_4$); insignificant content of sulfuric and sulfuric compounds: (in terms of SO_3) - 0.36%; acidic surface of particles due to the increased content of amorphous silica (basicity module <1), specific composition of organic waste compounds, increased porosity (41-56%) and bitumen capacity. Existing studies of physical and chemical properties and natural activity of the Far East ASW indicate the possibility of using these materials as raw materials for the production of building materials [15-17].

ASW from energy enterprises can become a promising reserve for replenishing the country's mineral and raw materials base and require comprehensive study with the aim of organizing ASW comprehensive processing that can simultaneously solve both the ecological task of large-scale utilization of ASW by creating building materials, and achieve economic profitability of the process, due to the extraction of valuable components.

2 Materials and Methods

To study the prospects and possibilities of using ASW as technogenic mineral raw materials, samples from the landfill sites of the Primorsky Krai largest cities were taken: CHPP-2 (Vladivostok); CHPP (Artem); CHPP (Bolshoy Kamen); CHPP (Arsenyev); GRES power plant (Partizansk); Primorsky GRES power plant (Luchegorsk). Mechanical sampling was carried out at various depths from the surface (from 0.5 m to 1.5 m) in accessible locations of ash dumps. The distance between the sampling points was from 20 to 100 m, the sample seats were fixed by the navigation system.

To control the gold content in ASW, the instrumental neutron activation analysis (NAA) method was used at the compact facility developed at the Institute of Chemistry of the Far East Division of Russian Academy of Sciences (FED RAS) with a radionuclide excitation source based on ^{252}Cf. Identification of the gold content was carried out according to the NSAM method No. 242-yaf.

To find the chemical composition of ASW, X-ray fluorescence analysis (XFA) was used. The investigations were carried out at the Laboratory of Molecular and Elementary Analysis of the Institute of Chemistry, FED RAS, a member of the Center for Collective

Use, Far East Center for Structural Research (FECSR). An energy dispersive X-ray fluorescence spectrometer EDX-800HS made by Shimadzu, Japan, was used for the measurements. The sensitivity for elements from Na to U was up to 1 ppm.

The identification of rare-earth elements was carried out by inductively coupled plasma mass spectrometry (ICP-MS) using the Agilent 7700 spectrometer (Agilent Technologies, USA) at the analytical center of the Far East Geological Institute of FED RAS.

The content of precious metals in ash and slag technogenic wastes was determined by the method of atomic-adsorption spectrophotometry (AAS) in the laboratory of micro- and nano-investigations of the analytical center of the Far East Geological Institute of FED RAS, on the atomic-absorption spectrophotometer Shimadzu 6800.

In order to identify the chemical and elemental composition of individual fractions of ASW and for the subsequent identification of chemical and technological methods for processing these fractions, the initial ASW sample was divided into individual mineral fractions by particle size and by their physical properties. The general scheme for separating the ASW sample into individual mineral fractions is shown in Figure 1. To separate coal underburning coal, FML-12 unit was used. To separate the magnetic minerals, PBM-32/20 unit was used.

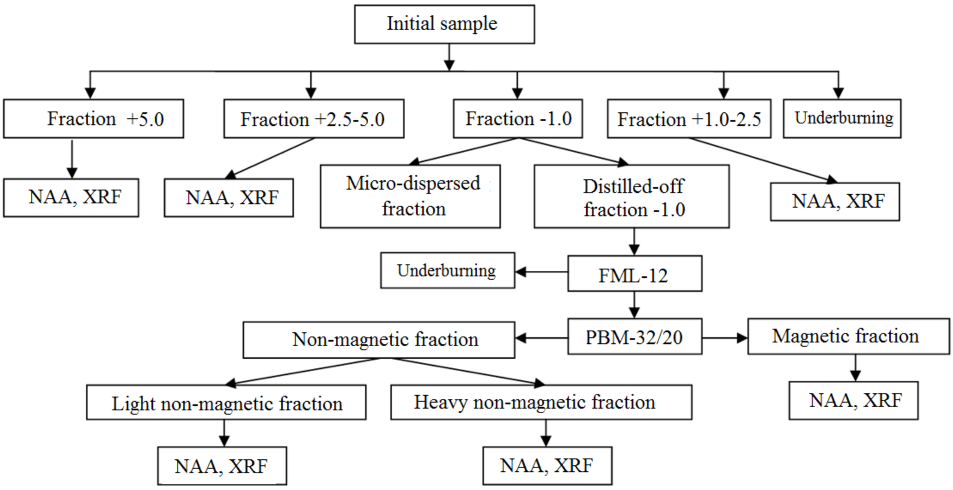

Fig. 1. Scheme of separation of initial ASW sample into individual mineral fractions.

3 Results and Discussion

A survey of ash and slag wastes from the landfill sites of Primorsky Krai showed that 90-95% of the samples consisted of free and bound oxides of silicon, aluminum, iron, calcium, magnesium, potassium, and sodium in chemical compounds. In selected samples, in small amounts (> 1%), the following trace elements are present: boron; fluorine; arsenic; zinc; nickel; molybdenum; germanium; gallium; vanadium; cobalt; mercury; lead; uranium. The chemical composition of ASW is highly dependent on the type of fuel burned from various fields, but for the site of a separate CHP plant, the chemical composition can be considered stable for practical use, being guided by the median value.

The work on the separation of initial ASW samples according to the scheme shown in Figure 1 was carried out and the following fractions of bulk material were obtained: aluminosilicate microspheres; microdispersed fraction; underburning of coal; magnetic fraction; light non-magnetic fraction; heavy non-magnetic fraction.

The distribution of the separated mineral fractions by volume (% of the total mass) was studied, as a result: the magnetic fraction (iron-containing concentrate) accounts for 5-10%;

underburning of coal of 2 types - 8-20%; microspheres of various composition 0,5-1,5%; microdispersed fraction – about 15-20%; light non-magnetic fraction, which is a purified aluminosilicate fraction, accounts for 70-80%.

Conducted by the NAA method, a study of the distribution of gold in the mineral fractions obtained showed a predominant concentration of the metal in heavy non-magnetic fraction (see Table 1), where the gold content increased by 3-4 times compared to the initial samples. At the same time, gold was not found in the underburning of coal, magnetic fraction and microdispersed fraction.

Table 1. The gold content in various mineral fractions ASW, in g / t. (according to NAA)

Sample	Initial sample	Coal under-burning	Micro-dispersed	Light non-magn.	Heavy non-magn.	Magn.
Vladivostok, CHPP-2,	0.10	<0.05	<0.05	0.26	0.39	<0.05
Vladivostok, CHPP-2,	0.05	<0.05	<0.05	<0.05	0.21	<0.05
CHPP Artem, polygon 2	0.12	<0.05	<0.05	0.09	0.28	<0.05
Bolshoi Kamen, CHPP	0.09	<0.05	<0.05	<0.05	0.35	<0.05
Arseniev, CHPP	0.11	<0.05	<0.05	<0.05	0.36	<0.05
Partizansk, GRES, section 3	<0.05	<0.05	<0.05	0.12	0.37	<0.05
Luchegorsk GRES polygon	<0.05	<0.05	<0.05	<0.05	0.15	<0.05

Similar results are observed for other noble metals. Thus, an additional study conducted on samples from the Vladivostok CHPP-2 landfill site using the AAS method showed almost a twofold concentration of platinum in the heavy non-magnetic fraction of ASW compared to the light fraction of ASW (0.006-0.008 to 0.015 ppm). In addition to precious metals, in the heavy non-magnetic fraction ASW, the concentration of rare and rare-earth elements predominates (see Table 2-3).

Table 2. The content of rare metals and rare earth elements in light non-magnetic fraction of ASW of CHPP-2, Vladivostok (according to ICP-MS)

Element	C, mg/kg	Element	C, mg/kg	Element	C, mg/kg
Be	2.01	**Nb**	14.83	**Dy**	4.20
Sc	7.2	**Mo**	3.46	**Ho**	0.93
V	55.3	**Cd**	0.21	**Er**	2.80
Cr	140.7	**Ba**	597.4	**Tm**	0.40
Co	8.8	**La**	29.5	**Yb**	2.77
Ni	60.7	**Ce**	57.4	**Lu**	0.50
Cu	31.3	**Pr**	5.41	**Hf**	6.49
Zn	46.3	**Nd**	23.66	**Ta**	1.35
Ga	10.98	**Sm**	4.98	**W**	3.89
Rb	103.6	**Eu**	0.57	**Pb**	19.04
Y	28.7	**Gd**	4.64	**Th**	11.88
Zr	205.6	**Tb**	0.72	**U**	4.32

Table 3. The content of rare metals and rare earth elements in heavy non-magnetic fraction of ASW of CHPP-2, Vladivostok (according to ICP-MS)

Element	C, mg/kg	Element	C, mg/kg	Element	C, mg/kg
Be	4.86	**Nb**	26.74	**Dy**	8.52
Sc	19.9	**Mo**	4.04	**Ho**	1.86
V	100.4	**Cd**	0.34	**Er**	5.42
Cr	64.96	**Ba**	943.7	**Tm**	0.75
Co	11.64	**La**	60.2	**Yb**	5.97
Ni	30.25	**Ce**	116.5	**Lu**	0.91
Cu	27.82	**Pr**	11.76	**Hf**	7.56
Zn	84.8	**Nd**	50.74	**Ta**	2.24
Ga	20.31	**Sm**	9.51	**W**	4.92
Rb	122.7	**Eu**	1.15	**Pb**	26.37
Y	57.6	**Gd**	9.70	**Th**	22.45
Zr	264.1	**Tb**	1.47	**U**	9.51

Since the studies show the predominant concentration of most valuable components in the heavy non-magnetic fraction of ASW, this fraction can be considered as a consolidated source of valuable elements. The remaining mineral fractions obtained from the separation of the original ASW can be used as a mineral raw material for various industries. In particular, on different equipment, technologies were developed for the making of commercial products with stable liquidity-briquetted high-calorie smokeless fuel based on the coal under-burning (see Figures 2-3), magnetite concentrate, microsphere concentrate, fine-grained sand and magnetite pellets.

Fig. 2. Briquettes of coal underburning, made on a screw press

Fig. 3. Briquettes of coal underburning, made on a roll press

The research conducted by the FEFU and FED RAS in the period from 2008 to 2017 [18-19], allowed developing a technological scheme for a device for comprehensive waste processing at power enterprises of Primorsky Krai. This technological scheme consists of separately functioning blocks connected in a single technological line (see Figure 4-5). In each block a certain intermediate product is extracted: concentrate of precious metals, iron oxides, coal underburning and an aluminosilicate residue.

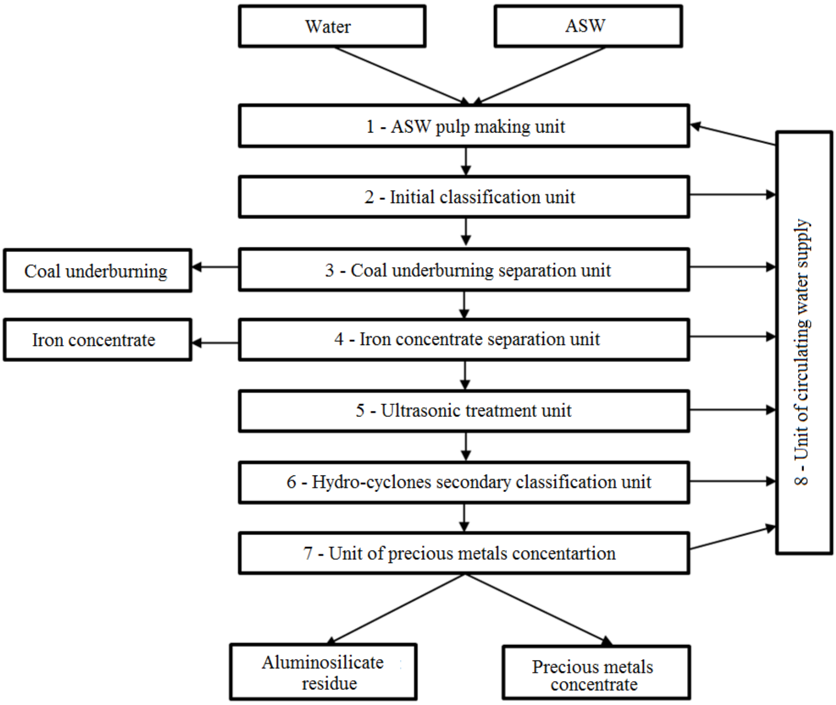

Fig. 4. Block diagram of comprehensive processing plant from ash and slag wastes of enterprises of energy sector of Primorsky Krai

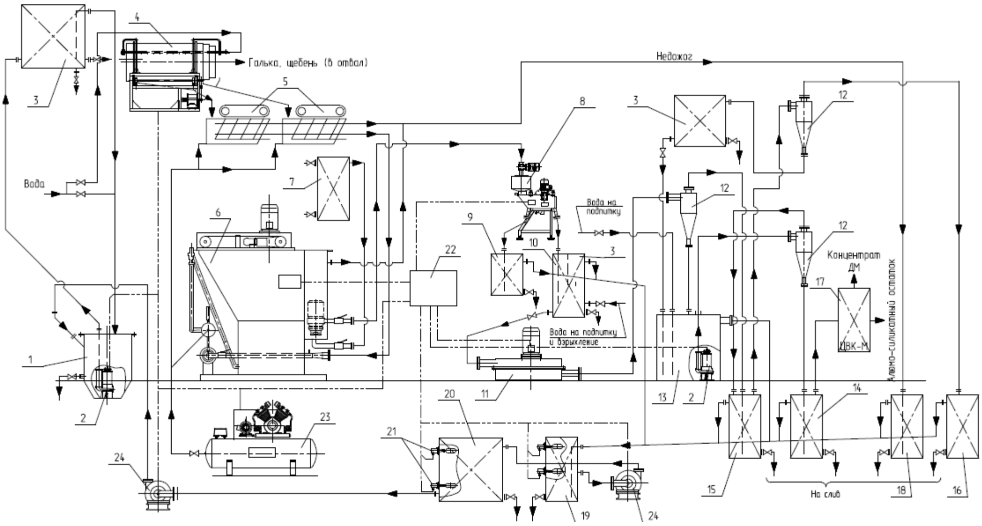

Fig. 5. Technological scheme of comprehensive processing plant from ash and slag wastes of enterprises of energy sector of Primorsky Krai: 1 - mixing container, V = 0.5 m^3; 2 - slurry submersible pump GSZ-4; 3 – recycling container, V = 0.5 m^3; 4 - hydro-grate; 5 – container for coil underburning of the first stage; 6 - flotation unit of the second stage of flotation FML-02; 7 – container of the flotation reagent V = 0.1 m^3; 8 - magnetic separator PBM-P-25-10; 9 - container for magnetic fraction V = 0.3 m^3; 10 - container for non-magnetic fraction V = 0.5 m^3; 11 - dispersant of ultrasonic I100-6 / 9M; 12 - hydrocyclone GPC-75; 13 - container for heavy non-magnetic fraction of stage I, V = 0.5 m^3; 14 - container for heavy non-magnetic fraction of stage II, V = 0.5 m^3; 15 - container for the finely divided fraction of stage I, V = 0.5 m^3; 16 - container for the fine fraction of stage II, V = 0.5 m^3; 17 - modernized centrifugal vibroconcentrator (CVC-M); 18 - container for coal underburning after flotation, V = 1.0 m^3; 19 - a tank-settler of return water, V = 2.0 m^3; 20 - capacity of cleaned recycled water, V = 2.0 m^3; 21 - level sensors; 22 - control panel; 23 - electro compressor B5900V / 270; 24 - centrifugal pump for circulating water.

The main difference of the developed technological scheme from the existing ones, in the comprehensive approach to the processing of ash and slag wastes, the most effective separation of the initial material into separate mineral fractions and the fullness of the recovery of the concentrate of valuable components from ASW. ASW integrated processing technologies provide a good basis for further research. This requires the development of new technological solutions aimed at the extraction of other valuable components besides gold, in particular silver, platinum group metals, REE, silicon oxides, aluminum and iron, and the use of new non-traditional energy methods for the disintegration of mineral complexes, to improve the efficiency of the process extraction of valuable components.

4 Conclusions

The chemical composition of ASW is highly dependent on the type of fuel burned from various fields, but for the site of a separate CHP plant, the chemical composition can be considered stable for practical use, being guided by the median value.

ASW enterprises of the power sector of the Primorsky Krai have a rich trace element composition, which is related to the specific composition of the burned coals and the enrichment of certain trace elements that occur when the organic part of the fuel burns out during combustion. Under the content of coal underburning - up to 20%, ASW of Primorsky Krai refer to raw materials with an average content of combustible substances (5-20%).

The conducted studies show the possibility of efficient separation of ash and slag wastes into separate mineral fractions and separation of the preliminary concentrate of valuable minerals in which most of the gold, BM and REE will be collected. At the same time, the remaining mineral fractions: coal underburning, magnetic fraction containing iron and titanium oxides, microdispersion fraction containing aluminosilicate microspheres and light aluminosilicate fraction can be used as raw stock for the making of commercial products with stable liquidity.

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