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Micro-Mineral Composition of Ash and Slag Waste of CHP-2 in the City of Vladivostok and the Prospects for Their Use

[1]Evgeniy Ivanovich Shamray, [2]Andrei Vasilyevich Taskin, [3]Sergei Ivanovich Ivannikov, [4]Vladimir Viktorovich Ivanov and [5]Aleksandr Alekseevich Yudakov
[1]Engineering and Technological Centre, Institute of Chemistry of FEBRAS, Prospect of the 100th Anniversary of Vladivostok, 159, 690022 Vladivostok, Russian Federation
[2]Department of a Separate Division of DIR, Far Eastern Federal University, Address. Sukhanova ul.,8, 690091 Vladivostok, Russian Federation
[3]Department of Chemistry, Laboratory of Sorption Processes, Institute of Chemistry of FEBRAS, Prospect of the 100th Anniversary of Vladivostok, 159, 690022 Vladivostok, Russian Federation
[4]Department of Geology and Mineralogy, Leading Research Scientist, Geological Institute of FEBRAS, Prospect of the 100th anniversary of Vladivostok, 159, 690022 Vladivostok, Russian Federation
[5]Department of Engineering, Deputy Director for Research and Innovation, Engineering and Technological Centre, Institute of Chemistry of FEBRAS, Prospect of the 100th anniversary of Vladivostok, 159, 690022 Vladivostok, Russian Federation

Abstract: An extensive study of chemical and mineralogical composition of the ash and slag waste of power production enterprises, sampled from landfills of CHP-2 in Vladivostok was carried out. The data on the content and forms of finding gold and silver in the ash and slag waste of CHP-2 in Vladivostok are given. The elemental and mineral composition of studied samples selected from dumps of power production enterprises is given. Difference in the mineral composition of heavy and light fractions of ash and slag waste concentrate is shown. The data on the mineral composition of the micro-spheres contained in the ash and slag waste of CHP-2 in Vladivostok are shown.

Key words: Technogenic deposits, wastes of power production industry enterprises, ash and slag waste, finely, dispersed gold, mineralogical analysis

INTRODUCTION

In the course of the activity of enterprises burning coals, a lot of ash and slag waste is produced. For example, the annual entry of ash in ash dumps of primorsky terrritory in certain years reached 3.0 million tons. The result of such technogenic activity is the accumulation of huge ash stocks so according to the literature data, the amount of ash and slag waste accumulated in Russia is approaching 2 billion tons placed within territories of >22,000 ha.

At the same time it is known that ash and slag waste contain commercial amounts of valuable components. Chemical and mineralogical composition of Ash and Slag Waste (ASW) indicates that it is more correctly to consider them as enriched raw materials for various industries (construction, road, cement, metallurgical, chemical). ASW can be a source of As, Be, Bi, Co, Ge, Hf, Nb, Se, Sr, Te, Tl, Y, Al, Cd, Ga, Fe, Mo, Ti, V, Zn, gold, platinum group metals and rare earth elements (Leonov *et al*., 1998; Allegrini *et al*., 2014; Karagiannidis and Logothetis, 2013; Kursun and Terzi, 2015).

A complicating factor in the technology of extraction and subsequent use of metals which are present in ash and slag waste can be the fact that metals in coals and ashes are simultaneously in several mineral phases (in the native state and in the form of intermetallic compounds, in the form of oxides, sulphides, carbonates, phosphates silicates, etc.) and in a fine dispersed dimensions (preferably up to 10 um). Such a state of substance note many researchers of metal content in coals (Seredin, 2004; Ilyenok, 2013; Sorokin *et al*., 2012). The morphology of grains of all micro-mineral formations is very diverse: microspheres, clusters of microspheres, sponge and plate formations, lumpy and crystalline

Corresponding Author: Evgeniy Ivanovich Shamray, Engineering and Technological Centre, Institute of Chemistry of FEBRAS, Prospect of the 100th Anniversary of Vladivostok, 159, 690022 Vladivostok, Russian Federation

segregations. In this regard, the study of the mineral composition of ash and slag waste of power production enterprises and metal occurrence forms, particularly gold in such waste is the important task in order to achieve the ultimate goal-development of high-effective integrated utilization mechanisms of power production enterprise's waste.

MATERIALS AND METHODS

As a control method of fine gold content in the waste of power production enterprises, the method of Instrumental Neutron Activation Analysis (INAA) at compact set-up with a radionuclide source of excitations based on 252Cf developed at the institute of Chemistry FEB RAS. Determination of gold content was performed according to the RCAM procedure. Detection limit for Au by 198Au isotope for INAA from 50-100 g sub-samples was 0.05-0.10 g ton^{-1}.

X-ray Fluorescence Analysis method (XFA) was used to determine the chemical composition of ash and slag technogenic waste. Measurements were carried out on the energy-dispersive X-ray fluorescence spectrometer EDX-800HS (Shimadzu, Japan). The sensitivity for elements from Na-U was up to 1 ppm; mean-square deviation in the range from 1 ppm to 1% did not exceed 5% in the range over 1%-not >1%.

When carrying out mineralogical studies, the Scanning Electron Microscope (SEM) JSM-6490LV (JEOL, Japan) was used which was equipped with the Energy-Dispersive Spectrometer (EDS) INCA energy and system of microanalysis for Wave Dispersion Spectrometer (WDS) INCA Wave. This X-ray micro-analyser with the electron probe allows carrying out the quantitative concentration determination analysis of a wide range of chemical elements (from B-U) in the range of 0.001-100 % by weight. Lateral locality of 2-5 um.

Photographing grains with the help of EDS was carried out in the mode of Secondary Electrons (SE-detector). Microanalysis with the help of WDS was performed in the Backward Scattered Electron mode (BSE-detector) at the accelerating voltage of 20 kV. Microanalysis results were processed using INCA Point and ID program.

Powder material samples of concentrates which were previously viewed under the stereo microscope were subjected to EDS-study. Unpolished particles (grains) of a concentrate were attached to a substrate of a conductive carbon adhesive tape adhered to cylindrical aluminium bars with diameter of 10 mm (Fig. 1). Metallization for charge drain under electron beam effect on a sample surface was not performed. Samples were sprayed with carbon. Morphometric and analytical study of mineral grains was carried out in series-steps "from one site with one or another grain or grains to another site". Each of sites was studied successively with increase of magnifications and elemental analysis of these particles (micro-grains). In this way >350 grains were tested some of which were subjected to elemental microanalysis.

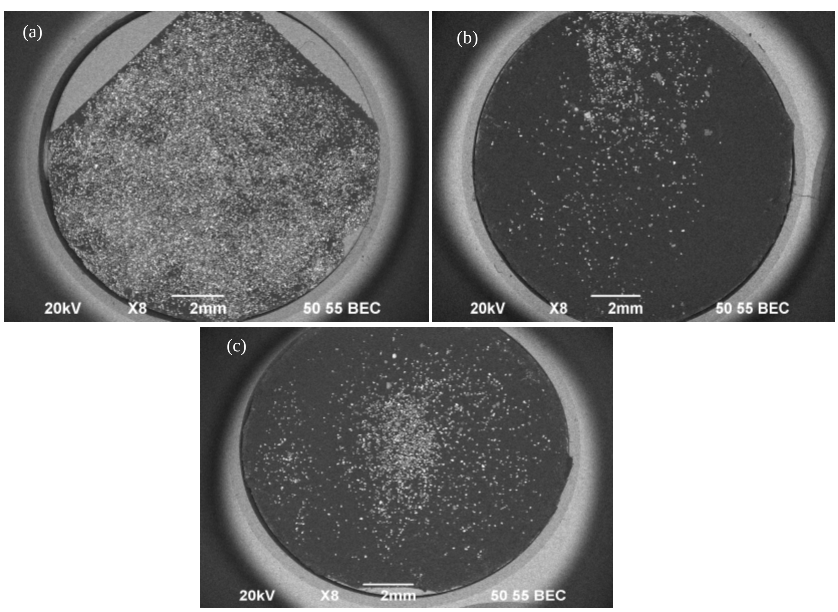

Fig. 1: EDS-image (top view) of bars with powder material attached to carbon conductive adhesive tape

RESULTS AND DISCUSSION

Researches of waste of power industry enterprises were carried out with samples taken from CHP-2 landfills in Vladivostok. Samples were taken in the amount of 10 kg, after which the taken material was ground with the disk attrition grinder of "Fritsch" company to a particle size of 0.1 mm. Ground sample was poured into the container in which water was supplied. The sample was mixed well, settled. A foam was collected from the surface, consisting of pumice and carbon black. To remove the clay and carbon black the water was supplied into the container with the moistened sample at a low pressure wherein washout of silt, clay, ground coal from the sample proceeded. The water overflowed the container edge and run into the clarifying tank where suspended particles settled and accumulated. After removal of silt, clay, coal from the sample the residue was obtained in the form of fine-grained sand. The heavy fraction was got from the obtained sand using artisan hutch-a concentrate consisting of magnetic and non-magnetic minerals and a light fraction. The resulting material was subjected to drying in an drying oven. Further researches were carried out with obtained samples in the form of 2 concentrates:

- Concentrate No.1; Dark grey fine-grained material (heavy fraction)
- Concentrate No. 2; Light grey fine-grained material (light fraction)

According to XFA, the bulk of all ash and slag samples form aluminium silicates, oxides of iron and titanium, in addition to them, macro-contents of barium, calcium, potassium, magnesium and sulphur are present in tested samples. Besides, the micro-content of chromium, copper, manganese, rubidium, strontium, vanadium, yttrium, zinc and zirconium were noted in a number of tested samples. Presence in all the tested samples of titanium and iron oxide macro-contents anticipates the possibility of magnetic separation of samples and isolation of magnetic minerals in a separate fraction.

According to NAA, the gold content in samples representing a light fraction (Concentrate No. 2) exceeded the gold content in the original samples on average by 50% while the gold content in the concentrate of heavy fraction almost 2-4 fold exceeded content in original samples.

As a result of performed mineralogical studies of 350 grains of heavy fraction concentrate, minerals of different classes (Table 1) were detected.

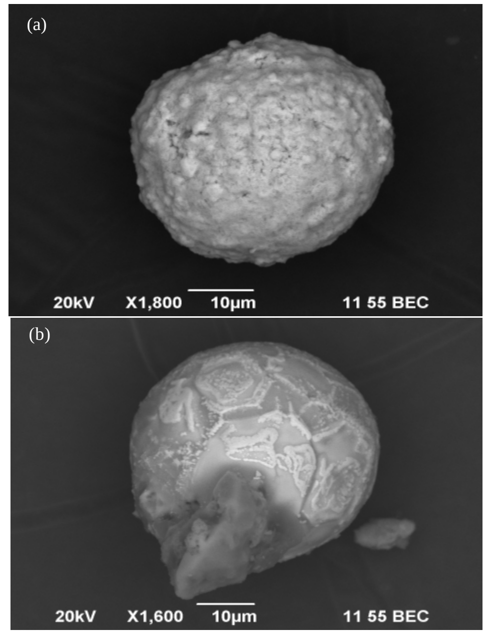

Fig. 2: a, b) Fe-O spherules photographed under a scanning electron microscope

Table 1: Minerals of heavy fraction concentrate from CHP-2 landfill in vladivostok

Mineral name	Mineral name
Oxides of iron and titanium	Silicon oxide (silica)
Iron oxides	Zr-Si-O (zircon)
Oxides of iron and chromium	Mn-Al-Si-O
Oxides of iron and titanium	Phases of nickel and copper, nickel and chromium
Titanium oxide (rutile)	Barium oxide
Tungsten oxide	Iron sulphides (pyrites, etc.)
Tin oxide	Silver-containing phase
Oxides and silicates of REE	Gold

As showed EDS studies, some of detected minerals represent spherules characteristic for coal combustion products, among which formations of 2 systems discern: Fe-O (Fig. 2) Ca-Si-Al-O with different content of Ti, Mn, Mg, Na, K and Fe (Fig. 3).

Silver in the concentrate of heavy fraction was detected as a thin film segregation of complex structure Ag-Ti-Cu-O with silver content of 8%. Since the size of phase with fuzzy edges is very small, of the order of 2 um (Fig. 4) a portion of these components (Ti, Cu, O) can reflect the composition of a substrate whereon the silver phase developed, due to inevitable its excitation by EDS electron probe. Gold in the concentrate of heavy fraction was detected in the amount of 4 fine grains. Their size varies from 0.7-117 um. Morphologically gold grains with size >30 um refer to xenomorphic (Fig. 6) and wrong (Fig. 7) and dedritoid (Fig. 8) cloddy types. Among 4 detected gold grains using WDS-analysis

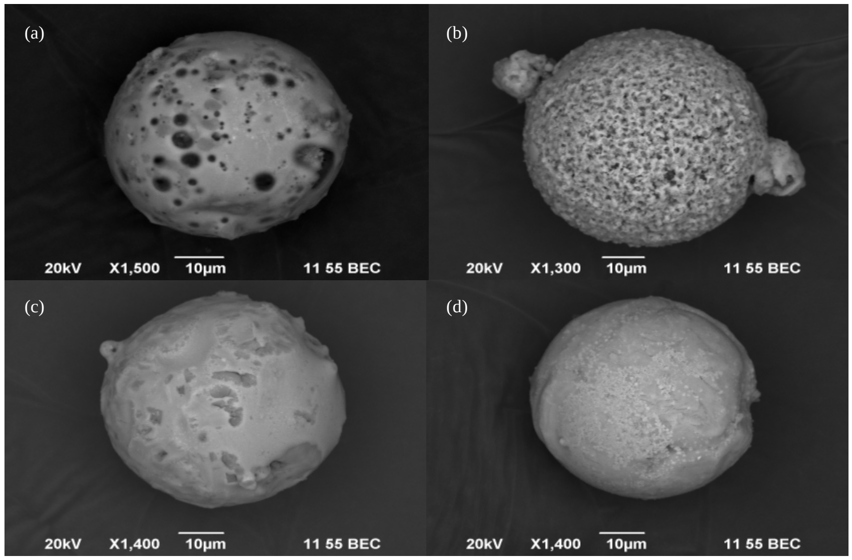

Fig. 3: Ca-Si-Al-O spherules photographed under a scanning electron microscope

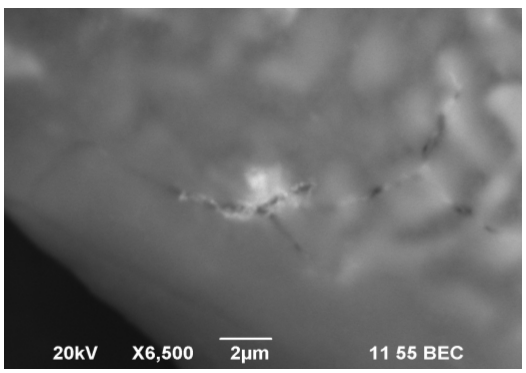

Fig. 4: The fine-dispersed silver-containing phase on inhomogeneous silicate spherule of complex composition, photographed under scanning electron microscope

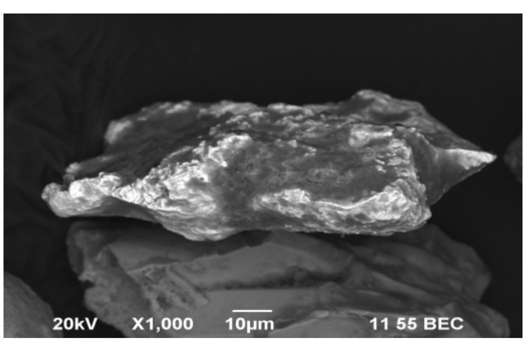

Fig. 5: Thin grain (0.7 and 1.0 um) of gold on Cr-Fe-O grain, photographed under scanning electron microscope

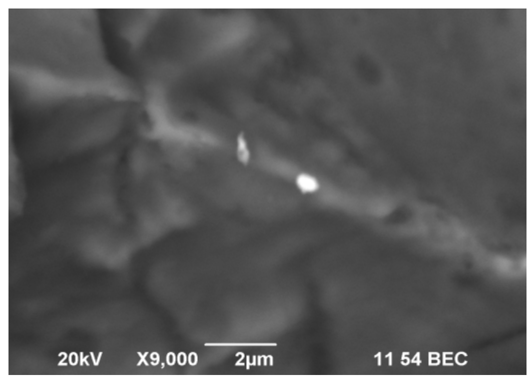

Fig. 6: Xenomorphic grain (117×37 um) of gold doped with mercury and silver, photographed under scanning electron microscope

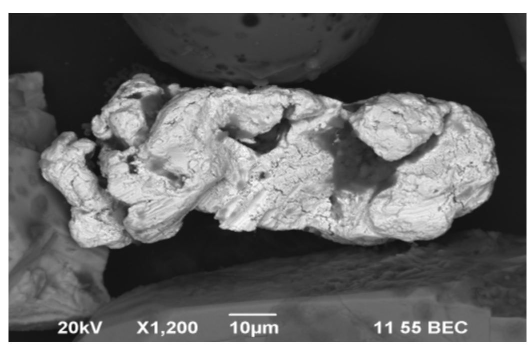

Fig. 7: Cloddy grain (117×37 um) of gold doped with mercury and silver photographed under scanning electron microscope

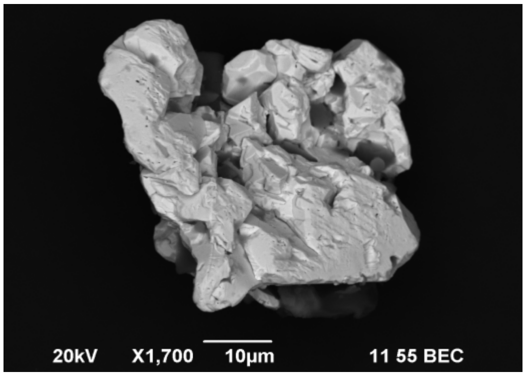

Fig. 8: Dedritoid cloddy grain (54×43 um) of unalloyed gold, photographed under scanning electron microscope

Table 2: Minerals of light fraction concentrate from CHP-2 landfill in Vladivostok

Mineral name	Content (%)
Silica	30
Feldspars	15
Coal particles	15
Ash particles	35
Spherules	5
Pyrites	Individualgrains
Zircon	Individualgrains
Biotite	Individualgrains
Chrysolite	Individualgrains

under scanning electron microscope the pure gold is fixed (Fig. 5 and 8) and gold (Fig. 6 and 7) doped with both mercury (21.6-27.9%) and silver (12.2-9.2%) (Table 2).

CONCLUSION

For the ash, selected from CHP-2 landfill in Vladivostok, coals are characterized by the presence of metals in simultaneously several micro-mineral phases of: oxides, sulphides, silicates, pyrites, in native form.

Carried out mineralogical and microscopic studies showed that particles of a free gold and other precious metals which are present in the waste of power production enterprises are represented mainly by fine and superfine class of particle size. Very diverse morphology of detected gold grains (xenomorphic, cloddy, dedritoid-cloddy shapes of grains) and fine-dispersed state of gold micro-particles (from fractions to tens of microns) are characteristic. Part of gold is associated closely with surrounding minerals. Gold and PM in ash and slag waste refer to the category of hard-to-recover and require using special procedures for concentration and additional uncovering. The small size of detected gold micro particles is indicative of the need in attracting methods of hydro-metallurgy for efficient extraction of gold from ash and slag waste, since as a number of studies shows, the effectiveness of pure gold extraction by gravity methods is inversely proportional to the size of the gold grains and at the size of <10 um is essentially zero (Usmanova and Bragin, 2007).

Micro-spheres, detected as a part of ash and slag waste can be used as a feedstock for production of high-strength concretes (Korolev and Inozemtcev, 2013). Complex and diverse micro-mineral composition of ash and slag waste of power production enterprises indicates the need for careful study of ASW landfills to determine the optimal approach to a complete waste processing of power production enterprises.

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