EXTRACTION OF VALUABLE COMPONENTS
FROM THE BOTTOM-ASH WASTE
AT THE KHABAROVSK THERMAL POWER
PLANT (RESULTS OF LABORATORY
AND PILOT TESTS)

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The results of laboratory and pilot studies of complex processing of the bottom-ash waste of a thermal power plant are presented. Special attention is paid to the extraction, from this waste, of precious metals being in particulate form. Different variants of the concentration plants were tested. The process flow schemes of waste processing with extraction of the valuable and especially valuable components have been developed.

KEY WORDS: bottom-ash waste, ash-disposal areas, brown coals, gold, platinum, concentration plants, thermal power plant (TPP), Khabarovsk City

1. INTRODUCTION

In the course of activities of electric power enterprises, a large amount of bottom-ash waste (BAW) is accumulated. The annual addition of the ash at the ash-disposal areas reaches from 2.5 to 3.0 million tons in Primorsky Krai and up to 1.0 million tons in the Khabarovsk one. More than 16 million tons of ash is stored only within the Khabarovsk City and more than 1.5 billion tons in the entire Russian Federation (Tselykovsky, 2000). The use of such wastes for economic purposes is by now limited and one of the reasons of this is the waste toxicity. The waste contains an appreciable quantity of hazardous elements. The ash-disposal areas fill continuously the air with dust, active forms of elements are actively washed by precipitation and pollute the air, waters, and soils. Disposal of such waste is one of the most pressing challenges.
The idea of the uselessness of BAW is attributed to the firm beliefs that ash is unusable waste. Moreover, the bottom-ash wastes from the ash-disposal areas are low processable. The intense formation of dust, dirt, and gases hinders the usage of ash. The bottom-ash wastes are also not used in construction due to the increased content of unburnt carbon and complex granulometric composition.

At the same time, the BAW can be a source of a number of metals and elements (Arbuzov et al., 1999; Bakulin and Cherepanov, 2002; Leonov et al., 1998; Persikov and Suslova, 1990; Cherepovskiy, 2004; Yudovich et al., 1985; Yudovich and Ketris, 2003). Burning coals, being natural sorbents, contain the impurities of many elements including rare earths and precious metals. In the course of burning, their content in the ash increases 5–6 times and can be of interest for the industry (Persikov and Suslova, 1990; Zharov et al., 1996). Brown coals containing a broad range of components, sometimes in increased quantities, are of special interest (Arbuzov et al., 1999; Yudovich et al., 1985; Kler et al., 1987; Krapiventseva, 2005; Seredin, 2004; Seredin and Shpirt, 1999; Stepanov, 2005).

The disposal of BAW attracts attention of many investigators. More than 300 technologies of their processing and using are known (Tselykovsky, 1998; Shpirt, 1986) but they are mainly devoted to the use of ash in construction and in the production of construction materials without holding a prejudice that toxic and harmful components are extracted from them. The extraction of useful and valuable components is impossible without studying their content and the forms of occurrence.

2. METHODS AND SUBJECTS OF RESEARCH

The BAWs of the buried and functional ash-disposal areas of thermal power plants (TPPs) in Khabarovsk City, Birobidzhan and, with lesser extent of details, in the Primorsky Krai as well as in other regions were studied.

During the field studies of BAWs, testing of the ash-disposal areas and coals burned at TPP, as well as analyzing the ash in the systems of transporting from the combustion furnaces (boilers) to the ash-disposal areas were made with an analysis of burning and transporting technologies. Testing of the ash-disposal itself was made by means of drifting the accessible places through a widely spaced grid of test pits and survey pits with taking samples in them by furrow or bulk method.

After the standard sample processing, all the routine samples were subjected to spectral semi-quantitative analysis and atomic absorption analysis for Au and Pt. In connection with the nonreproducibility of the analysis results, 2–3 determinations of Au and Pt were performed for each sample consisting of separate weights and, then, the average Au and Pt grades in samples were calculated.

The combined samples composed of the remains of routine samples were divided into three parts (weights). One part was subjected to spectral, atomic absorption, and chemical silicate analyses, the second part was used as a small technological sam-
ple with determination of commercial components in it using laboratory-technological studies, while the third weight was washed in the pan or processed in a laboratory concentrator. Its heavy fraction was subjected to a mineralogical analysis. This analysis was used for investigating the BAW composition, analyzing the concentrates produced, and determining the yield of precious metals and other washed products. The diagnostics of the platinum group of minerals (PGMs), native minerals and alloys was performed using the microprobe analysis at the Institute of Volcanology and Seismology of the Kamchatka Scientific Center, Far-Eastern Branch of the Russian Academy of Sciences (KSC FEB RAS) in Petropavlovsk-Kamchatsky. Individual samples were studied for the PGM at the United Institute of Geology, Geophysics and Mineralogy, Siberian Branch of RAS (SB RAS) in the City of Novosibirsk (analyst N. Tolstykh). With a view to monitoring the determination of the content of precious metals, the combined samples, part of routine samples and the products of the technological conversion were subjected to assay tests. The technological studies were carried out using small (up to 10–20 kg) and large (up to 18 t) samples. In order to extract precious metals and divide BAW into the components, we used the concentrators made by Russian Klondike, Itomak, and Knelson companies, as well as a multifunctional concentration unit (MFCU) devised by V. T. Kardash at the Far-Eastern Federal University for extracting fine-grain gold.

The basic part of the technological and laboratory-analytical investigations was performed at the Far-East Institute of Mineral Raw Materials of the Russian Ministry of Natural Resources (Arbuzov et al., 1999; Cherepanov, 1999) and completed at the Institute of Tectonics and Geophysics of FEB RAS. The studies concerning the possibility of BAW to be used for production of construction materials and road building materials were carried out under the contract terms by the members of the departments "Construction Materials" of the Far-Eastern State Transport University and Pacific State University in Khabarovsky City.

Individual samples and concentrates were reprocessed into metal using an original technology of the Research and Production Enterprise "GEOTEP" in Moscow. This technology is based on combining the plasma-arc melting and electrolysis in a single process. The technology is without parallel in the world. There are no publications to which the references could be made. However, the author, who worked with the developers of technology of examining the bottom-ash wastes, had the opportunity to use their results but without the right to describe and divulge the technology.

In Khabarovsky City, samples were taken in the ash-disposal areas of the TPP-1 and TPP-3. The area of TPP-2 was not included due to the results of preliminary evaluation analysis. In the ash-disposal areas, the test pits and survey pits were drifted through the grids of 100 × 200 m and 100 × 100 m (depending on sizes) and samples were taken by furrow and tear methods. These are routine samples with weights of 3–5 to 15–16 kg which were afterwards used to compose combined samples.
The TPP-1 was put into operation in 1954. It consumes 2.0–2.2 million tons of coal per year. The plant was designed for firing coals of the Raichikhinsk coal deposit. Subsequently, coals from the Kharanor, Urgal, and other deposits were delivered. The plant has three ash-disposal areas, two of which are closed now and one area is functioning.

The ash-disposal area No. 1 has an area of \(1200 \times 200\) m\(^2\) and a depth of 8–10 m. It was used in 1954–1986. Until 1979, the coals of the Raichikhinsk coal deposit were supplied and thereupon the coals of the Kharanor, Neryungri, Gusino-Ozersk and, in small amounts, Pavlovsk (Primorsky Krai) and Darkhan (Mongolia) coal deposits. The ash-disposal area is characterized by 39 routine and 9 combined samples.

The ash-disposal area No. 2 having an area of \(450 \times 1200\) m\(^2\) and a depth of 8–10 m was filled in 1987–1996. In this period, the coals of not less than 10 coal deposits were delivered to the TPP but the coals of the Kharanor, Gusino-Ozersk, and Pavlovsk deposits predominated. The ash-disposal area is characterized by 31 routine, 8 combined, and one 16-t technological samples.

The ash-disposal area No. 3 with an area of \(800 \times 400\) m\(^2\) is situated in the natural hollow. The thickness of BAW reaches in places 20 m and more. It is filled from 1995. The coals from different deposits were burned but the coals of the Kharanor, Gusino-Ozersk, Urgal, and Azeisk deposits predominated. It is characterized by 61 routine and three enlarged samples weighting 50 kg, 350 kg, and 12 t. Apart from the BAW, the samples of the circulated water used from the BAW transporting and foam from the surface of the clarification reservoir consisting largely of the aluminosilicate hollow microspheres were taken. At the TPP itself, the samples of ashes, slags, and pulp with BAW immediately near the boilers as well as samples of coals burned at the time of sampling and depositions in the pipes of the BAW hydrotransportation were taken.

The TPP-3 uses mainly the coals of the Neryungri coal deposit. Over the last years, the coals of the Urgal deposit and coals from China (deposit in the Heilongjiang province) became to be used. In 1998–2000, the samples were taken in the ash-disposal area No. 1 used at that time. Its dimensions are \(500 \times 800\) m\(^2\), maximum depth is 35–40 m and average one is 18–25 m; 67 routine, 15 combined, and two small technological samples with weights of 50 and 150 kg were taken. At the TPP itself, the samples of the circulated water, depositions in pipes, varieties of BAW, transporting pulp and coals burned at the time of sampling were taken.

The Birobidzhan TPP, the ash-disposal area No. 1 with an area of \(359 \times 400\) m\(^2\) and filling depth of 8–10 m was studied. The ash-disposal area was characterized by 27 routine samples, 4 combined, and three small technological samples of 30–50 kg in weight. At the TPP, the samples of BAW varieties, transporting pulp, coals burned at the time of sampling and coals from the neighboring and surveyed Ushumun coal deposit were taken.

Besides the ash-disposal areas listed above, the BAWs of the ash-disposal areas of the Luchegorsk state district power station (SDPS) (8 samples), Vladivostok TPP

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No. 2 (12 samples), TPPs of Artyom and Partizansk towns (two samples in each) as well as individual samples of ash from the Moscow region and Siberia TPPs were investigated.

2.1 Brief Characteristic of the Bottom-Ash Waste

At the TPPs surveyed, the coal is burned at temperatures of $1100-1600^\circ\text{C}$. When burning the organic part of coals, the volatile compounds in the form of smoke and vapor are produced while the incombustible mineral part of the fuel is released as the solid combustion residues forming the dust-like mass (ash) as well as caked slags. The quantity of solid residues for the black and brown coals varies from 15 to 40%. The coal is disintegrated before burning and the mazout (fuel oil) is added in it in small quantities (0.1–2%) for better burning.

When burning disintegrated fuel, the fine and light particles of the ash are swept away by the smoke fumes and they are referred to as the fly ash. The size of the fly ash particles varies from 3–5 to 100–150 μm. The amount of the bigger particles does not amount usually to 10–15%. The fly ash is caught by the ash collectors. At the Khabarovsk TPP No. 1 and Birobidzhan TPP, the ash catching is wet and is made by scrubbers with Venturi pipes, while it is dry and performed using electrofilters at the Vladivostok TPP No. 2.

The heavier particles of ash settle on the bottom of the furnace and agglomerate into caked slags consisting of aggregated and fusing particles of ash with sizes of 0.15 to 30 mm. The slags are disintegrated and removed by water. The fly ash and disintegrated slag are removed separately and then are mixed to form the bottom-ash mixture.

In the composition of the bottom-ash mixture, the particles of unburned fuel (underburning) in the amount of 10–25% are permanently present in addition to ash and slag. Depending on the types of boilers, type of fuel, and the condition of its burning, the amounts of fly ash and slag can reach 70–85% and 10–20% of the mixture mass, respectively. The bottom-ash pulp is transported to the ash-disposal area through pipelines (Fig. 1).

The ash and slag in the course of hydrotransport and in the ash-disposal area interact with water and the carbon dioxide of air. In them, the processes similar to diagenesis and lithification occur. They are quickly amenable to weathering and begin to fill the air with dust in the course of drying at a wind speed of 3 m/s. The color of the BAW is dark grey and stratified in section which is caused by the interchange of anisometric laminas as well as by depositing of white foam consisting of the aluminosilicate hollow microspheres.

The ashes of the TPPs using black coal, as compared to the ashes of the TPPs using brown coals, differ in the increased content of $\text{SO}_3$ and other impurities, reduced concentrations of silicon, titanium, iron, magnesium, and sodium oxides. The slags are characterized by the increased contents of silicon, iron, magnesium and sodium...
oxides and reduced contents of sulfur and phosphorus oxides, other impurities. Generally, the ashes are highly-siliceous with a sufficiently high content of aluminates.

The average chemical composition of the BAW at the surveyed TPPs is given in Table 1.

According to data of the spectral semi-quantitative analysis of the routine and combined samples the contents of impurity elements in the BAW are listed in Table 2.

According to (Zharov et al., 1996), gold and platinum are of commercial value and Yb and Li approach to them by maximum values. The content of harmful and toxic elements does not exceed the acceptable values though the maximum contents of Mn, Ni, V, and Cr approach the toxicity "threshold."

**TABLE 1:** The average limits of basic BAW components content

<table>
<thead>
<tr>
<th>Component</th>
<th>Average Contents, %</th>
<th>Component</th>
<th>Average Contents, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>51–60</td>
<td>CaO</td>
<td>3.0–7.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.5–0.9</td>
<td>Na₂O</td>
<td>0.2–0.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16–22</td>
<td>K₂O</td>
<td>0.7–2.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5–8</td>
<td>SO₃</td>
<td>0.09–0.2</td>
</tr>
<tr>
<td>MnO</td>
<td>0.1–0.3</td>
<td>P₂O₅</td>
<td>0.1–0.4</td>
</tr>
<tr>
<td>MgO</td>
<td>1.1–2.1</td>
<td>other impurities</td>
<td>5.8–18.8</td>
</tr>
</tbody>
</table>

5.8–18.8 | 10.6
<table>
<thead>
<tr>
<th>Element</th>
<th>TPP-1 Maximum</th>
<th>TPP-3 Maximum</th>
<th>Average</th>
<th>Maximum</th>
<th>Average</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>40–80</td>
<td>100</td>
<td>30</td>
<td>60–80</td>
<td>Ba</td>
<td>1000</td>
</tr>
<tr>
<td>Co</td>
<td>2–8</td>
<td>60–100</td>
<td>3–8</td>
<td>10</td>
<td>Be</td>
<td>2–6</td>
</tr>
<tr>
<td>Ti</td>
<td>3000</td>
<td>6000</td>
<td>3000</td>
<td>6000</td>
<td>Y</td>
<td>10–80</td>
</tr>
<tr>
<td>V</td>
<td>60–100</td>
<td>200</td>
<td>80</td>
<td>100</td>
<td>Yb</td>
<td>1–8</td>
</tr>
<tr>
<td>Cr</td>
<td>80</td>
<td>300</td>
<td>40–80</td>
<td>100–600</td>
<td>La</td>
<td>–</td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
<td>8</td>
<td>1</td>
<td>–</td>
<td>Sr</td>
<td>200</td>
</tr>
<tr>
<td>W</td>
<td>–</td>
<td>40</td>
<td>–</td>
<td>–</td>
<td>Ce</td>
<td>–</td>
</tr>
<tr>
<td>Nb</td>
<td>8</td>
<td>20</td>
<td>10</td>
<td>20</td>
<td>Sc</td>
<td>10</td>
</tr>
<tr>
<td>Zr</td>
<td>100–300</td>
<td>400–600</td>
<td>400</td>
<td>600–800</td>
<td>Li</td>
<td>60</td>
</tr>
<tr>
<td>Cu</td>
<td>30–80</td>
<td>100</td>
<td>30</td>
<td>80–100</td>
<td>B</td>
<td>200</td>
</tr>
<tr>
<td>Pb</td>
<td>10–30</td>
<td>60–100</td>
<td>30–60</td>
<td>80</td>
<td>K</td>
<td>8000</td>
</tr>
<tr>
<td>Zn</td>
<td>60</td>
<td>80–200</td>
<td>40</td>
<td>100</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sn</td>
<td>1</td>
<td>3–40</td>
<td>1–2</td>
<td>1–8</td>
<td>Au</td>
<td>0.07</td>
</tr>
<tr>
<td>Ga</td>
<td>10–20</td>
<td>30</td>
<td>20</td>
<td>30</td>
<td>Pt, mg/t</td>
<td>10–50</td>
</tr>
</tbody>
</table>
In the BAW composition, the crystalline, glassy, and organic components are distinguished. The crystalline substance is presented by both primary minerals of the mineral substance of the fuel and new formations obtained in the course of burning and also during hydration and weathering in the ash-disposal area. In all, up to 150 minerals are determined in the crystalline component of the BAW. The predominant minerals include meta- and ortho-silicates as well as aluminates, ferrites, aluminoferrites, spinels, dendrite-shaped clay minerals, oxides: quartz, tridymites, christobalite, corundum, \(\gamma\)-alumina, oxides of calcium, magnesium, etc. Often, but in small amounts, there are ore minerals (cassiterite, tungstenite, tin pyrites, etc.), sulfides (pyrite, pyrrhotine, arsenopyrite etc.), sulfates, chlorides, while the fluorides are very seldom observed. As a result of hydrochemical processes and weathering in the ash-disposal areas, the secondary minerals (calcite, portlandite, hydrous ferric oxides, zeolites, etc.) appear.

The native elements and intermetallides which include lead, silver, gold, platinum, aluminum, copper, mercury, iron, plessite, chrome-ferrides, copper gold, different alloys of copper, nickel, chrome with silicon, etc. are of utmost interest. Their sizes vary from microns to dozens of microns. In the fresh ashes, they bear the traces of heat treating (fritting, melting with other minerals and congeries). In the old ashes, their self-cleaning is often observed.

Despite the high temperature of coal burning, the presence of the dropping-liquid mercury is a fairly often phenomenon, especially, within a heavy fraction of washed products. Likely, this explains the mercurial infection of soil when the BAWs are used as a fertilizer without special cleaning.

The vitrification is a product of suspended transformations in the course of burning and presents the essential part of ashes. It is presented by differently colored, predominantly, black glass with metallic luster, various spherical glassy, pearly-like microspheres (balls) and their aggregates. They compose the basic mass of the slaggy component of the BAW. In composition, they are aluminum, potassium, sodium and, to a lesser degree, calcium oxides. To them, some products of heat treatment of the clay minerals belong too. The microspheres are often hollow and create the foamy formations on the surface of the ash-disposal area and sludge settling ponds.

The organic matter is presented by slugs (underburning). The organic matter transformed in the furnace is greatly different from the initial one and is in the form of coke and semi-coke with very low hygroscopicity and volatile-matter yield. The amount of unburned carbon in the investigated BAWs was 10–15%.

3. VALUABLE AND USEFUL COMPONENTS OF BAWs

Among the components of BAW, of practical interest are the precious metals, rare and trace elements, iron-bearing magnetic concentrate, secondary coal, aluminosilicate hollow microspheres, and inert mass of aluminosilicate composition.
3.1 Gold

As a result of performing the works on sampling and investigating the material composition of the BAW, the gold was determined practically in all samples. The content of Au in the routine samples varied from traces to 25 g/t. The average data for the ash-disposal areas of the Khabarovsk TPPs is presented in Table 3.

The gold in BAW is basically fine-grain dust and is presented by grains and, more rarely, by cloddy aggregates with grade of 5–40 μm and more. According to the data of screen assay, an increase in the mass fraction of gold in the finest classes was noted. In a number of samples, the content increased also in the largest classes (at the expense of intergrowths). Maximum sizes of the gold nuggets of 0.5 × 1.0 mm were found in individual samples in the form of intergrowths with quartz. In fresh ashes, the amount of relatively large, extracted gold is least while it is largest in the "old," dried ash-disposal areas. In other words, the growth in sizes of gold grains takes place with time. In the "old" ash-disposal areas, the gold grains are cleaner, while in new areas, especially in the fresh ash, the gold grains bear traces of melting, are coated with different deposits, and they are often in the form of intergrowths and alloys with other minerals and ash particles. This is opened predominantly in the class of 0.071 mm.

The shapes of gold grains (nuggets) are irregular, whimsical, dendrite-shaped, plate-like with roundish and rugged contours, curve-plate, cloddy, wavy, hooked, spherical, and drop-shaped (Fig. 2). The roundish plates are frequent. In the higher fraction, the crystalline forms — octahedron in combination with hexahedron with the smoothed facets — are found. Some grains are fritted, the interfused aggregates of grains are also noted and intergrowths with quartz and alloys of gold with copper are frequent. The crusts of the fine-grain gold on the plates and wires of copper and iron were observed. Some grains are coated with thin brown and black deposits. The color of gold is golden-yellow with greenish cast, while in dust-like releases gold acquires a brassy-black color.

TABLE 3: Average data of Au content in the ash-disposal areas of the Khabarovsk TPPs

<table>
<thead>
<tr>
<th>TPP</th>
<th>Ash-Disposal Area</th>
<th>Content of Au, g/t</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>According to the Data of Analysis of Combined and Technological Samples</td>
<td>from</td>
</tr>
<tr>
<td>TPP-1</td>
<td>No. 1</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>No. 2</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>No. 3</td>
<td>0.13</td>
</tr>
<tr>
<td>TPP-3</td>
<td>No. 1</td>
<td>0.2</td>
</tr>
</tbody>
</table>
The major part of gold is related to the slag component. The average content of Au in slag samples taken immediately at the Khabarovsk TPPs was 1.93 g/t (18 samples) while it reached 15 g/t in some samples. The content of Au in fly ash is 0.152 g/t (12 samples). These results coincide with the data of S. B. Leonov et al. (1998) for ash of the Reftinsk state district power station (SDPS) suggesting that the major gold (85%) is related to slag the yield of which is 20–25% while that of ash is 75–80%. At the same time, in the course of hydraulic transportation of BAW, the redistribution of gold takes place due to the sorption of its ash component.

Except for the free, visible gold, the gold is noted in the alloys with other metals, most often with copper, or it is captured by segregations of glass in the slag. A part of gold remains in unburned carbon is, most likely, in the form of complex organo-metal compounds.

According to the data of the plasma-metallurgical processing of the BAW concentrates and BAWs themselves, the quantitative values of Au content are higher by 0.3–1.5 g/t than in accordance with the data of technological and chemical-analytic determinations.

### 3.2 Platinum Group Metals (PGM)

Ashes and slags are difficult to be analyzed due to the presence of free carbon (Varshal et al., 1994; Kursky et al., 1995). The basis of the studies was formed by the results of the mineralogical analyses of the routine and technological samples. The mineralogical analysis allowed us to discover the grains similar to the platinoids (platinum-group metals). Their check with the use of microprobe analysis made at the
Institute of Volcanology and Seismology of KSC FEB RAS showed that one third of 105 samples containing 1–3 grains proved to be platinum and platinoids. Two thirds of grains were alloys with composition of Fe–Cr–Mn, Cr–Fe–Ni, Cu–Zn–Sn–Fe–Si, Fe–Mn. Exteriory, they are very similar to platinoids and it was difficult to distinguish them under the microscope, especially, in ashes and coals (Fig. 3).

According to the analysis results, the following compounds were identified among the grains of platinoids: ferrous platinum containing 85–95% of Pt, 9–12% of Fe, and trace impurities of and, more rarely, Ni and Si; ferrous platinum with iridium (75–90% of Pt; 1–1.5% of Ir; up to 1% of Cu; 9–12% of Fe and impurities of Rh and Ru); platinum–iridous osmium (80–90% of Os; 0.5–15% of Pt; 10–12% of Ir with impurity of Fe (up to 0.5%); iron–platinum–osmiridium (50% of Ir; 15–25% of Pt; 1–3% of Fe; 20–25% of Os). Sporadically, the impurities of Rh and Ru (0.2–1.0%) are found in insignificant amounts (up to 0.6). In this case, Pd was not recorded but its presence was noted. Subsequently, the diagnostics of platinoids and doubtful grains was performed using the spectral analysis which showed "base" or "exist" when analyzing the grains of platinum minerals. The control checks at the United Institute of Geology, Geophysics and Mineralogy SB RAS confirmed the presence of isoferroplatinum and other minerals of platinum group.

When concentrating the BAWs, the platinoids being in them pass into concentrate accumulating in both magnetic and nonmagnetic fractions. So, in the concentrate of first washing from the ash-disposal area No. 1 of the Khabarovsk TPPs, the contents of Au (126 g/t), Pt (80 g/t), and Pd (28 g/t) were determined by assaying method with

**FIG. 3:** Shapes and sizes of platinum grains and metal alloys from the ashes of the TPP-1, Khabarovsk City
atomic absorption analysis. This and other data show that the total concentration of platinoids in the BAW is close to that of gold.

The new methods of analyzing and determining the contents of precious metals in the refractory ores (method of inductively-coupled plasma in atomic emission spectrometry — ICP AES, pyrometallurgical method with the use of plasmatron and others) developed over the last years allowed us to reveal the real contents of precious metals in the bottom-ash waste. So, the average contents of Au (1.5 g/t) and Pt (2.5 g/t) were earlier determined in the ash of the Vladivostok TPP No. 2. By applying the pyrometallurgical method and thermal ionization, the repeatedly averaged results were obtained for Au (1.5 g/t) and Pt (2.5 g/t).

The presence of platinoids in the TPP ashes is confirmed by our findings of platinum grains in coals of a number of coal deposits in the Far East (Arbuzov et al., 1999) as well as discoveries of native platinum by the scientists of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (Leonov et al., 1998).

3.3 Rare Earth Elements

We did not perform the special studies on determining the contents of rare-earth elements (REE) in the BAW. Their possible presence is confirmed by the studies carried out in other regions (Arbuzov et al., 1999; Seredin and Shpirt, 1999; Yudovich and Ketris, 2003) and our findings of such minerals as monazite, xenotime, etc. in the composition of BAW. In addition, Seredin and Shpirt (1999) have demonstrated a relationship of REE with humic substances of coals for the metal-bearing coals where their content is 2.5–4 times higher than in the coals themselves. When such coals are burned, the REE in the BAW can be in dispersed state. In the process of concentration, the REEs accumulate in the nonmagnetic part of heavy fraction.

3.4 Iron-Containing Magnetic Concentrate

Products from the bottom-ash waste include 70–95% of spherical magnetic aggregates and fire scale. The rest minerals (pyrrhotine, limonite, hematite, pyroxenes, chlorite, epidote) are present in amounts of sporadic grains to 1–5% of the concentrate weight. In addition, the rare grains of platinoids as well as iron–nickel–chromium alloys are sporadically recorded in the concentrate.

In appearance, these are the fine-grain powder mixture of the black and dark-grey color with predominant particle size of 0.1–0.5 mm. The quantity of particles with sizes larger than 1 mm is not more than 10–15%.

The content of iron in the concentrate varies from 50 to 58%. The composition of the magnetic concentrate from the bottom-ash waste of the TPP ash-disposal area No. 1 is as follows: 53.34% of Fe, 0.96% of Mn, 0.32% of Ti, 0.23% of S, and 0.16% of P.
According to the data of spectral analysis, up to 1% of Mn, first tenths of % of Ni, up to 0.01–0.1% of Co, 0.3–0.4% of Ti, 0.005–0.01% of V, 0.005–0.1% (up to 1% more rarely) of Cr, and traces to 0.1% of W are present in the concentrate. As for the composition, it is a good iron ore with dope additives.

According to the data of the magnetic separation, the yield of magnetic fraction varies under laboratory conditions from 0.3 to 2–4% of the ash mass. According to literature data (Shpirt, 1986; Kizilshein et al., 1995), the yield of magnetic concentrate under production conditions of the bottom-ash waste processing by way of magnetic separation reached 10–20% of the ash mass, and, in this case, 80–88% of Fe₂O₃ are extracted and iron content is 40–46%.

The magnetic concentrate from the bottom-ash waste can be used for production of ferrosilicium, cast-iron, and steel. It can also serve as the initial stock for the powder metallurgy.

### 3.5 Secondary Coal

In the course of technological study by the flotation method, the coal concentrate called the secondary coal was obtained. It consists of the particles of unburnt coal and products of its thermal treatment — coke and semi-coke and is characterized by increased calorific value (>5600 kcal) and ash content (up to 50–65%). After adding of mazout, the secondary coal can be burned at the TPP, and sold in the form of fuel briquettes to people. This coal is extracted from the BAW by the flotation method. Its yield reaches 10–15% of mass of processed BAW. The sizes of coal particles are 0–2 mm and, less frequently, up to 10 mm.

The increased gold mineralization is one of the features of the secondary coal. In the produced concentrates of the secondary coal, the content of Au was in the range of 0.6–4.4 g/t. Most likely, the gold existed in the form of organo-metallic compounds or sorbed particles. Such coals should be burned in special furnaces with the aim of complete extraction of gold.

Aluminosilicate hollow microspheres present the dispersed material formed by hollow microspheres of size from 10 to 500 μm. The poured density of material is 350–500 kg/m³ while the specific one is 500–600 kg/m³. The basic components of the phase-mineral composition of microspheres are aluminosilicate glass phase, mullite, and quartz. Hematite, feldspar, magnetite, hydromica, and calcium oxide are present in the form of impurities. The predominant components in their chemical composition are silicon, aluminum, and iron (Table 4). The trace impurities of different components in amounts lower than toxicity or commercial significance thresholds are possible. The content of natural radionuclides does not exceed the permissible limits. The maximum specific effective activity is 350–450 Bq/kg and conform with II class construction materials (up to 740 Bq/kg).

Due to the regular spherical shape and low density, the microspheres possess the properties of an excellent filler in different products. The promising directions of in-
Industrial application of aluminosilicate microspheres include the production of spheroplastics, road-marking thermoplastics, grouting and drilling fluids, heat-insulating, radiolucent and reduced-weight building ceramics, heat-insulating nonfired materials and fire-proof concretes (Kizilshtein et al., 1995).

In the world, the microspheres are widely applied in different branches of industry. In Russia, the use of hollow microspheres is extremely limited and they, together with ash, are thrown to the ash-disposal dumps. The microspheres are the "adverse material" for the TPPs because they choke the pipes of recirculated water supply. For this reason, it is necessary to replace all the pipes once every 3–4 years or to perform complex and expensive works on their cleaning.

3.6 Inert Mass

The aluminosilicate composition comprising 60–70% of the BAW mass is obtained after extraction, from ash, of all the above-listed concentrates and useful components and the heavy fraction. In composition, it is close to the overall composition of ash but will contain one order less iron and harmful and toxic elements. Its composition is mainly aluminosilicate. In contrast to the ash, it will have a finer uniform granulometric composition (due to regrinding when extracting the heavy fraction). According to ecological and physicochemical properties, it can be widely used in production of construction materials, construction and as the fertilizer — substitute of the limestone flour (ameliorant).

4. RESULTS OF TECHNOLOGICAL STUDIES

When performing technological studies, emphasis was given to the extraction of valuable components, first of all, gold, the analytic determination of which in the BAW
and products produced from these was developed. This allowed us to calculate the balance of metal and to determine the metal extraction.

The extraction of precious metals from BAW was investigated with the use of the concentrators made by Knelson, Itomak, and Russian Klondike companies, multifunctional concentrating unit and artisan trammel.

When washed with the use of a trammel, the mat meshes became obstructed with quickly consolidating ash and washed material flowed away over the meshes. The yield of washings was 0.7 kg/m³. The content of gold in the washing increased slightly as compared with that in the ash.

When processing the ash without BAW regrinding in the centrifugal Knelson separator (laboratory variant with productivity of 30 kg/h of the solid), the concentrates with Au content of 10–50 g/t (100–150 g/t rarely) and extraction of 20–35% of gold were obtained. As for the "fresh" ashes and ashes containing the impurity of mazout, the gold extraction did not exceed 10%. In case of double processing of BAW and preliminary regrinding, the gold extraction increased to 40–50%.

When using the "Itomak" concentrator with the design productivity of 1 t/h of the solid, the industrial product with Au content of 4–6 g/t and yield of 1.5 to 4% of the processed mass was obtained. The gold recovery is low. When working, it was impossible to create the necessary relation between the solid-to-liquid ratio.

The TsKL-8 centrifugal concentrator (the manufacturer and owner is JSC "Russian Klondike") was used to extract precious metals immediately from the pulp of the TPP pipeline. The ratio between the solid and liquid phases in pulp was 1:15–30 instead of required 1:1–3. As a result, the industrial product with Au content of 1.92 g/t and impurities of platinoid grains was obtained. The size of 60% of gold grains was less than 0.02 mm. The additional concentrating of the industrial product in the Knelson concentrator made it possible to release 54% of gold into the concentrate with Au content of 20 g/t.

The best results were obtained with the use of the MFCU (multifunctional concentrating unit). The laboratory variant of the concentrator designed for investigating geological samples of 10–100 L in volume was used. The basis of the MFCU is formed by the forced method of catchment of the fine and dust-like as well as small and sheet-like gold. The sizes of the caught gold particles are 0.15–0.005 mm. The principle of catching and the unit itself were patented as inventions in Russia and Ukraine (Alkov and Kardash, 1998).

When concentrating ash samples in the MFCU, the total yield of the concentrate varied from 3.6 to 20% of the ash volume with average value of 13.43%. The additional washing of the industrial product and tailings increased the yield of concentrate by 10–20%. The content of Au in the initial concentrate was 30–80 g/t. When panning the concentrate, the content of Au increased to 50–100 g/t. The gold recovery varied from 30% for fresh ashes and ashes contaminated with mazout to 95–96% in the "old" ashes, ashes with removed unburned carbon and preliminarily reground ashes.
The MFCU allowed us to provide the higher extraction of the precious metals into the concentrate without regard to ratio between the solid and liquid components of ash. In addition, the major part of the heavy fraction of ash including the magnetic concentrate and other metals passed into the concentrate (industrial product). The concentrate is susceptible to different methods of upgrading including cyanide leaching.

When using the MFCU for primary processing BAW, the chemical and other reagents are not used and dust is not formed. The unit can be combined with other mineral-processing equipment (magnetic separator, flotation machine, etc.).

4.1 More Extensive Technological Studies

More extensive technological studies were carried out on order to choose the industrial technology of extracting the precious metals and comprehensive utilization of the BAW. A series of the laboratory technological tests was carried out using the samples of 5–200 kg in weight. The tests for catching fine gold and other methods of concentrating including the chemical techniques of leaching were performed with applying different concentrators.

The BAW in the natural state is hardly suitable for processing with the use of the leaching methods including heap one. The fundamental reasons include the decomposition of the particles of aluminosilicate containing minerals, accumulation of clay component in the ash and low permeability for solutions. The removal of the clay component with inert mass or washout results in simple permeability of ash for solution.

When upgrading the gravitational and magnetic concentrations with the use of cyanide leaching, the gold recovery reached 98%. The reagent consumption is low.

The basic mass of the recovered gold in the concentrates produced from BAW is fine and dust-like. It is a cause of poor gold recovery in the flow concentrating machines. The high turbulence of the carrying flows leads to the situation when the particles of fine gold are suspended and do not settle to the catching surfaces. Owing to this, the immediate gold recovery from BAW by different concentrators does not exceed 20–30% except for the MFCU providing 40–59%. If the same concentrators are used for upgrading, then the loss of gold with the discharge reaching 50% of gold extracted to the concentrate takes place. The gold recovery and quality of concentrate improve if the unburned carbon and magnetic fraction hindering the process are preliminarily removed and regrinding of ash to –1.0 mm is performed. In the extensive technological studies, the concentrates with Au content of 2.8–700 kg/t were produced when upgrading the initial concentrates with Au content of 20–40 g/t.

5. RECOMMENDED TECHNOLOGY OF COMPLEX PROCESSING OF BAW

The fundamental variants of the diagrams of BAW complex processing are shown in Figs. 4 and 5.
In the first case, the release of coal fraction with subsequent separation of magnetic and heavy fractions is provided at the beginning of the processing line. The inert mass with the aluminosilicate composition is suitable for production of construction materials and using as the filler in construction and ameliorant in agriculture. The commercial concentrate of precious metals obtained from heavy fraction by way of upgrading and different concentrating methods including techniques of leaching and
hydrometallurgy is sent to the precious metals refinery. The other useful components (nonferrous and rare metals, probably, scandium and rare earths) are recovered from the remainder of heavy fraction as it accumulates.

In the second case, the magnetic separation with extraction of magnetic fraction, flotation of coal and gravity separation of heavy fraction are provided at the beginning of technological process after regrinding for the technical parameters improvement (Fig. 5). For obtaining the heavy fraction from BAW, the MFCU works best.

Depending on the particular conditions, the different variants of the equipment batching including the simplified schemes of BAW processing are possible.

Based on the recommended schemes of complex processing of BAW, the technical and economic calculations of profitability were performed. In the calculations, the

FIG. 5: Second variant of the principal diagram of the bottom-ash waste processing
variants with processing of 200 to 400 tons of BAW per shift, recovery of 30% of gold and realization of magnetic concentrate at the price of iron ore, gold and inert mass at the price of 80% from the cost of the river sand were used. All the calculations showed the high profitability of the complex processing of BAW with payback of capital investments for 1.5–2.5 years.

The bottom-ash waste should be referred to the technogenic mineral raw materials, which, in contrast to natural ones, are accumulated rather than exhausted with time which increases the perspective utility of their study and involvement into usage. The recovery of useful components and total utilization of the bottom-ash waste at the expense of their useful properties using and production of construction materials will allow to free areas occupied by dumps and to drop the negative impact on the environment.

REFERENCES


