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The Method of Aluminothermic Neutralization and Recycling of Copper Electroplating Sludge

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Abstract—The possibility of neutralization and partial transformation of a widespread and environmentally hazardous electroplating sludge waste into marketable product was demonstrated. The chemical composition of copper electroplating sludge is determined. The process of aluminothermic reduction of copper plating sludge to produce marketable products in the form of a bronze ingot and abrasive was studied.

Keywords: copper electroplating sludge, thermal treatment, sludge, ingot, aluminothermic reduction

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INTRODUCTION

Electroplating sludge is a precipitate formed by alkaline treatment of wastewaters from electroplating plants, mainly with solutions of $Ca(OH)_2$ and NaOH. Because in a majority of domestic plants the wastewaters from different electroplating procedures (copper, nickel, chromium-plating, etc.) are treated together, the released electroplating sludge commonly contains all heavy metals, as well as iron and other elements in ratios, dependent on the specificity of a plant. In appearance, electroplating sludge is pasty mass of complex and volatile composition. In addition to iron and calcium, it contains the compounds (hydroxides) of heavy metals (manganese, lead, chromium, nickel, copper, etc.), which are hazardous to the environment and human health.

The average concentration of metals in electroplating sludge is (%, in terms of dry weight): copper, from 3 to 5, nickel, from 1 to 2, zinc, from 8 to 10, chromium, from 8 to 10, and iron, from 8 to 10. Cadmium, tin, lead, manganese, and other metals may be present in lesser amounts. Electroplating sludges are mostly class I or II hazard. The sludge precipitated with $Ca(OH)_2$ contains about 50% gypsum (in terms of dry weight). The humidity of electroplating sludge is commonly 80–90%.

Heavy metals present in electroplating sludge, if enter the human body, can cause serious diseases. For example, cadmium leads to the formation of kidney stones, causes anemia, and decreases the oxygen content in the blood. Excess copper contributes to cancer. Chromium and nickel are highly carcinogenic metals.

Metal hydroxides are insoluble in normal water, whereas dissolve even when small amounts of the acid are present, for example during acid rain. Therefore, storage of electroplating sludge in open landfills is prohibited. According to the Domestic environmental documents, it must be packed in sealed plastic bags and stored “on demand” in the territory of plant or taken out in this package to special landfills. Both procedures are cost-consuming [1].

Currently, electroplating sludge is widely used as additive in the manufactory of construction materials and road surfaces is [2–5]. In a process, the toxic properties of the sludge are prevented owing to binding with inert substances or vitrification at high temperatures. However, in the authors’ opinion, dilution of a electroplating sludge in building materials is unacceptable, because the building blocks have the short live, from 10 to 50 years, and then are thrown in a landfill as debris. Under the action of acid rain, heavy metals gradually decompose with the formation of compounds with different solubility falling into water sources.

Fig. 1. Appearance of electroplating sludge.

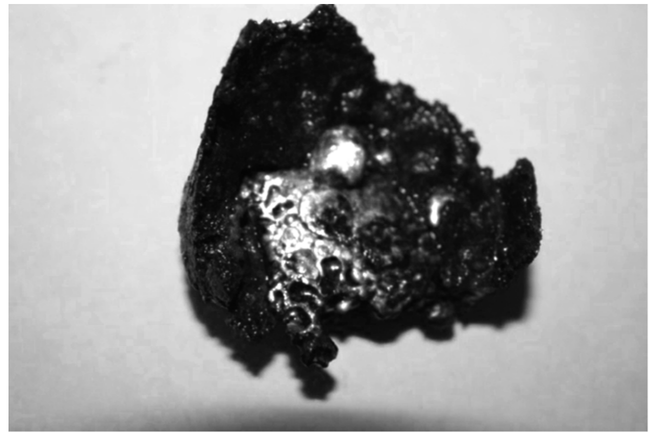

Fig. 2. Metal ingot (yellow) and slag after removal from the crucible.

In the search for ways to use electroplating sludge as technogenic raw materials, attempts were made to recycle electroplating sludge into free metals, or metal salts, oxides or hydroxides. For this purpose, the ammonia technology for producing hydroxides of individual metals was approbated at the Prioksky sludge recycling center in Nizhni Novgorod. However, this technology is environmentally hazardous and hydroxides obtained are expensive.

The special Design and Technology Bureau "ERG" (St. Petersburg) has developed the technology for recycling electroplating sludge into pigments and metal powders. However, this technology was also unprofitable [6].

Attempts to recycle electroplating sludge into pigments were also made in Yaroslavl, Novochebok-sarsk, and Nizhni Novgorod. However, the obtained pigments had low quality and were costly. Threrefore, this sludge recycling technology is not presently implemented in practice too.

In [7], the electrolysis method was proposed for the individual separation of non-ferrous metals (for example, only copper and only zinc). However, cost of metals produced by this method was much higher than their market value.

Along with the excessive dearness, the above-mentioned technologies are not environmentally perfect: solving one problem, they give rise to other problems, such as formation of large amounts of contaminated wastewater, although less dangerous.

The possibility of using electroplating sludge from the OJS Company KnAAPO (Association Open Joint-Stock Company at Komsomolsk-on-Amur), as a substitute for barytes in paints, filler of primers, thixotropic additives, and coloring pigments for paving and building structures was determined at the Institute of Chemistry, Russian Academy of Sciences, Far East Branch [3]. At the above institute, the aluminothermic extraction of heavy metals was also studied. The product is a metal ingot containing iron as base metal and chromium and nickel as impurities [8–10], slag, and gaseous reaction products.

In the study, the method of aluminothermic reduction was tested to extract copper and iron from the electroplating sludge formed in etching of copper plates at the "Radiopribor" OJC, Vladivostok, Russia. Because the sludge contain more than 50% copper and no less than 15 iron, the resulting product is a copper base alloy containing aluminum and iron, similar in composition to the high-quality bronze.

Aluminothermic reduction using simple apparatus and involving exothermic reactions is the efficient and fast method, ensuring reliable separation of metal and slag, suitable for obtaining bronze from a copper-containing electroplating sludge. The forming slag with high content of Al_2O_3 may be used in the manufacture of abrasive.

EXPERIMENTAL

We used in the study a copper electroplating sludge taken from the storage locations of the "Radiopribor" plant, Vladivostok (Fig. 1). Reducing agent was the PA-1 aluminum powder containing no less than 99% aluminum with a bulk density of 0.96 g/cm^3. The sludge was dried in a ShSP-0.5-200 desiccator at 200°C to remove water.

The dry and finely-divided sludge was mixed with aluminum powder and entered the aluminothermic reaction:

$$3CuO + 2Al = Al_2O_3 + 3Cu.$$

The reaction proceeded in a graphite crucible. A mixture of the composition a copper plating sludge 88% + aluminum 12% was placed in the crucible in an amount of 0.8 of its volume and compacted. For the utilization we used an apparatus for the metallothermic reduction of electroplating sludge [9].

The prepared graphite crucible was placed in the apparatus and the lid of the apparatus was sealed. Then, the hatch was open to initiate aluminothermic reaction. After initiating the reaction, the hatch was sealed. The gaseous reaction products were discharged through special pipeline supplied to the apparatus and passed through a neutralizing solution, where most of the harmful reaction products was delayed. The end of the aluminothermic reduction was monitored visually at the end of bubbling. After that, the volume of the apparatus was subjected to forced ventilation with an air compressor for 3 min in order to maximize removal and neutralization of gaseous reaction products. To cool a part of the crucible, the reaction product was kept in the crucible for another 3–5 min. Then, the upper lid was depressurized, the crucible together with the reaction products was withdrawn and the reaction products were removed from the crucible by pushing caked clay inside the crucible.

The reaction product was a metal ingot, in which copper was base metal and iron and aluminum were impurities (Fig. 2).

The thermic products were separated onto the metal and slag and their properties were determined.

Apparatus and measurement. Samples of electroplating sludge were taken from the storing tanks with a soil auger in accordance with GOST (State Standard) 17.4.3.01-83 “Nature Protection. Soil. General requirements for sampling.”

RESULTS AND DISCUSSION

Elemental composition of sludge was determined by the atomic absorption method (AA-780 spectrometer).

Chemical composition of the initial samples and products formed in aluminothermic reduction was determined by the X-ray fluorescence analysis on a TXRF instrument (FEI Company, Germany).

Table 1. Loss of mass by the electroplating sludge during the heat treatment

Heating temperature, °C	Heating time, min	Mass loss, %
200	120	15
500	120	35

The X-ray diffraction patterns were recorded on a D8 ADVANCE diffractometer in CuK_α radiation and analyzed using the EVA search program with the PDF-2 powder data bank.

Elemental composition of the metal ingot was determined on an energy dispersive micro analyzer based on a JXA 8100 electron microprobe (Japan) and an INCA energy dispersive spectrometer (England).

The slag was ground on a Pulverisette 4 vario planetary mill for 5 min. The container and grinding balls of the mill were made of the hard-alloy steel.

Heat treatment was carried out in a SNOL 7.2/11muffle furnace.

The temperature of the sample during the heating was monitored with a Raytek Raynger ST25 laser pyrometer.

The sample weight was determined on an SCL-300 laboratory scale.

Experience in heat treatment of electroplating sludge showed that the process should be carried out in two stages (Fig. 3).

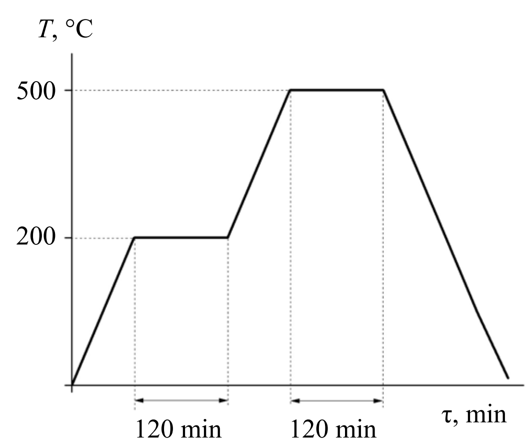

Fig. 3. Temperature vs. the time graph for the thermal treatment of electroplating sludge.

Table 2. Mass fraction of movable forms of elements (% in terms of dry weight)

Sample	Ca	Si	Al	Pb	Cd	Sn	Ni	Cr	Zn	Cu	Fe
Electroplating sludge	0.11	0.036	Not determined	0.45	Not determined	0.011	0.0025	0.0096	0.026	60.67	0.32

Table 3. Results of the analysis of the ingot

Chemical composition of ingot, %						
Fe	Cu	Mn	Cr	Al	Si	P
2.73±0.14	87.00±0.89	Not determined	Not determined	8.99±0.83	0.28±0.14	0.34±0.10

The first stage is the evaporation of free moisture and the second stage, removal of a bound moisture. Raising the temperature to values that ensure the evaporation of bound moisture without preincubation at lower temperatures leads to excessively intense evaporation of free moisture and causes sludge to spread within a muffle furnace. The heat treatment of the electroplating sludge is accompanied by a loss of mass (Table 1).

The loss of mass by the sludge heat-treated at 200 and 500°C, respectively, is 15 and 35%. Therefore, the heat treatment of the sludge is the required stage and should be performed at 500 °C to maximize dehydration.

According to the X-ray analysis, in the sludge generated by the technological process at the JSC Radiopribor plant the initial concentration of complex copper-containing compounds is large (60-70%). Heating the sludge to 600°C causes all copper-containing compounds to convert virtually completely into copper oxide during the first 10 min. The same process occurs on heating to 500°C, whereas in this case, the heating time should be increased to 2 h (Fig. 4).

Results of the atomic-absorption analysis of copper-containing electroplating sludge are given in Table 2.

As seen, the content of movable forms of heavy metals in the sludge studied is high. The total content of the movable forms of heavy metals in copper electroplating sludge from the Radiopribor plant is 61.5%.

Results of the X-ray fluorescent analysis of the ingot obtained after the alumino-thermic reaction in the composition constituted by a copper plating sludge and aluminum powder are given in Table 3.

As seen, product of the aluminothermic reaction is a copper base alloy containing aluminum and iron, i.e., in fact, it is the BrAZh9-3 bronze (Table 3).

The X-ray analysis of the slag produced during the aluminothermic reaction revealed corundum, Al_2O_3 as major phase, a certain amount of copper oxides (CuO and Cu_2O), and a double oxide $CuAlO_2$. Consequently, the conditions of the aluminothermic reduction of a copper plating sludge require further optimization in order to minimize the content of copper-containing compounds in the slag.

CONCLUSIONS

(1) The method of aluminothermic reduction for the utilization of electroplating sludge with high content of copper was tested.

(2) The reaction product is a copper base metal ingot, similar in composition to the copper alloy no C95400.

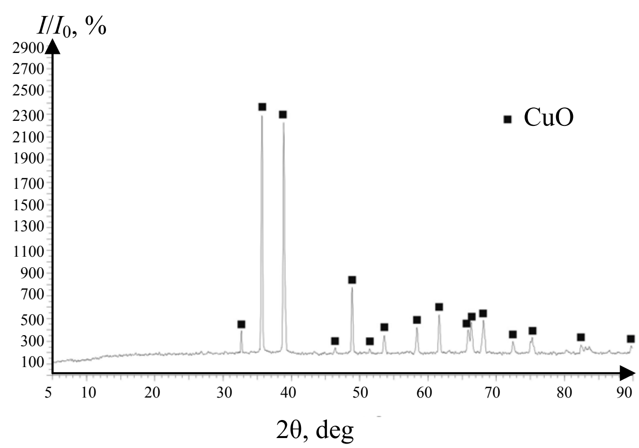

Fig. 4. Phase composition of the electroplating sludge heat-treated at 500°C for 2 h.

(3) Slag obtained from the aluminothermic reduction is mainly composed of Al_2O_3 and may be used in industry as abrasive.

(4) The method of aluminothermic reduction and extraction of metals from copper electroplating sludge may serve as basis for the development of technology suitable for the utilization of a technogenic waste and re-use of the utilization products in industry.

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