# Extraction of Nonferrous Metals and Production of Building Materials from Copper-Nickel Smelting Slags


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*Abstract*

*Nowadays, mining and metallurgical enterprises are necessarily involved in recovering of technogenic deposits generated by their operations. By doing so, they obtain additional mineral resources and improve the environment situation. Studies of the processability of pelletized slag from copper-nickel process tailings (Kola MMC, JSC) have disclosed the possibility of extracting nonferrous metals via flotation. It has been shown that the flotation tailings of copper-nickel slag can be processed to obtain building ceramic materials with advanced physical-mechanical characteristics.*



*Keywords: granulated slag, non-ferrous metals, electric pulse destruction, flotation, ceramic building materials*


## Introduction

Technologies for slag recovery are being actively developed in the USA, Britain and Japan. Reportedly, grinding of 90% slag to the size of -0.063 mm provides a 70% increase in copper extraction, the most efficient method being leaching with ammonia solutions. At Mount Morgan factory, Australia, slag from reverberating furnaces has been processed to extraction copper and gold following a pattern including a two-stage crushing to the size of -8 mm, two-stage milling and flotation at a pH = 6.8–7.5. The cleaning flotation concentrate contains 20% copper; the level of copper extraction is 80% and gold extraction is 94% (Chainikov, Kryuchkova, 1994). In Russia, nonferrous metallurgy slag is recovered at "Sredneuralsky Copper Smelter" JSC. The slag is ground, classified and subjected to flotation. The resulting copper concentrate, containing 50–60% solids and copper concentrations of 10 to 26% is sent to burdening department of copper-smelting shop (Makarov, A., 2006).

In Murmansk region, Russia, an example of technogenic deposit is the copper-nickel smelting slag of "Pechenganickel" Combine ("Kola MMC" JSC) dumped since 1945 and accommodating over 45 mln t of raw materials (Makarov, D. et al., 2013).

The recoverability of copper-nickel slag (pelletized slag of the "Pechenganickel" Combine) has been examined in work (Kasikov et al., 2008). The amount of main components extracted to solution during leaching with hydrochloric acid varied, %: Fe – 81–93; Cu – 91–96; Ni – 89–94; Co – 91–99; Mg – 94–99, depending on leaching regimes.

Both from commercial and environmental viewpoints, it is desirable that the silicate part of the slag also be recovered. In a research dedicated to utilization of "Kola MMC" JSC slag in manufacture of building and technical materials it has been shown (Kasikov et al., 2008) that the waste of non-ferrous metal hydrochloric leaching can be used as components for binding materials. In work (Zosin and Pryimak, 1999) there have been developed geopolymeric slag-alkali materials based on "Pechenganickel" Combine slag utilizable as sorbents for effluent treatment from heavy metals.

In this work, we have justified methods and developed a slag process providing extraction of nonferrous metals and further processing to building materials.

## Objects of research

Impound current and old slags were analyzed for the extent of property alteration and environmental hazard. Old slags (15 years) differed from their current counterparts in increased contents of fraction -0.1 mm. Old slag was more heterogeneous in grain size, which characterized all grain

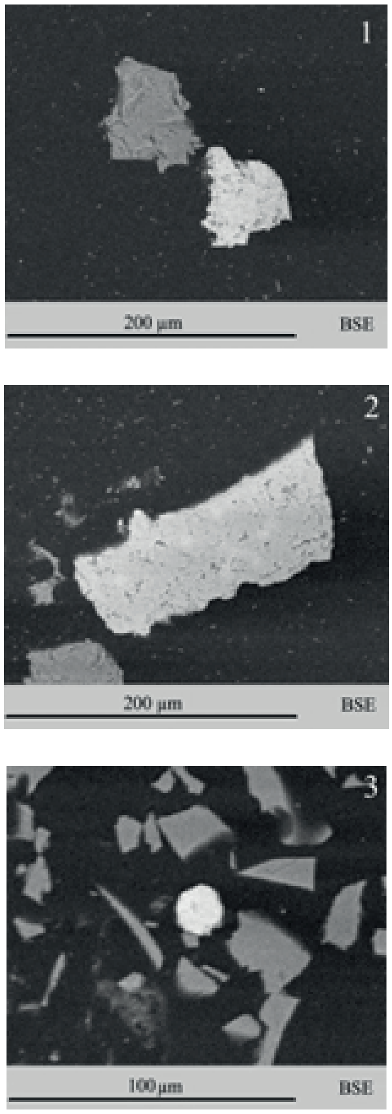


Fig. 1. Light with high reflectivity grain sulfide copper-nickel slag production after the procedure EPD presented pentlandite $(FeNi)_9S_8$

Rys. 1. Ziarna jasne o wysokiej refleksyjności siarczków miedziowo-niklowych z żużla po procedurze EPD występuje w postaci pentlandytu $(FeNi)_9S_8$

sizes classes. Apparently, this is due to substance differentiation and, possibly, hypergenic processes occurring in dumps (Makarov, D. et al., 2013; Potapov, D., Potapov, S., 2013). Higher contents of nonferrous metals in slag of current production are due to higher richness of initial concentrates and leaching out in dumps. In pelletized slag of current production, sulfides impregnations are distributed nonuniformly and not in all grains of the slag matrix consisting of olivine and glass. The chemical composition of sulpfides in both old and current slag can be satisfactorily described by the formula of pentlandite (FeNi)9S8. As revealed by dynamic experiments, leaching of both nonferrous metals and iron is fairly intensive both from mature and fresh slag (Makarov, D. et al., 2013).

**Results and discussion**

***Slag flotation***

Flotation experiments were carried out on fresh slag. The slag was finely ground (to -40 µm of about 100%). Samples 50 g each were subjected to flotation in a cell of 150 $cm^3$ (a laboratory flotation unit FM2M manufactured by "Mekhanobr" JSC). A sample was wetted with distilled water and transferred to the flotation cell. The bath was agitated for one minute at an impeller velocity of 1500 $min^{-1}$. Agitation with potassium butyl xanthate (BX) lasted 3 minutes; with methyl isobutyl carbinol (MIBC) – 1 minute. The reagent consumption was: with BX – 200 g/t, with MIBC – 30 g/t. Flotation proceeded under moderate aeration, at the impeller velocity of 3000 $min^{-1}$. Foam was removed during 4 minutes. Then, slowing

Tab. 1. The results of microprobe analyses of sulphide grains – pentlandite $(Fe, Ni)_9S_8$ in slag after EPD

Tab. 1. Analiza mikroskoowa ziarn siarczków – petlantyd $(Fe, Ni)_9S_8$ w żużlu po EPD

| Content element, wt. % | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Grain № | Number of analycity points | Fe | Cu | S | Ni | Co | As | Zn | Bi | Sum |
| 1 | Average of 5 analyses | 32.92 | 5.69 | 33.33 | 26.67 | 0.78 | 0.12 | 0.01 | 0.01 | 99.53 |
| 2 | Average of 3 analyses | 36.14 | 3.49 | 33.35 | 25.76 | 0.62 | 0.05 | 0.04 | – | 99.45 |
| 3 | Average of 3 analyses | 32.18 | 5.15 | 33.29 | 27.46 | 1.00 | 0.27 | 0.02 | – | 99.37 |
| Crystallochemical formulas | | | | | | | | | | |
| 1 | $(Fe_{4,56}Ni_{3,52}Cu_{0,72}Co_{0,08}As_{0,01})_{8,89}S_8$ | | | | | | | | | |
| 2 | $(Fe_{4,96}Ni_{3,36}Cu_{0,40}Co_{0,08})_{8,88}S_8$ | | | | | | | | | |
| 3 | $(Fe_{4,48}Ni_{3,60}Cu_{0,64}Co_{0,16}As_{0,03})_{8,83}S_8$ | | | | | | | | | |

Tab. 2. The results of slag flotation

Tab. 2. Wyniki flotacji żużla

| Experiment № | Product | Yield, % | Content, % | | Recovery, % | |
|---|---|---|---|---|---|---|
| | | | Ni | Cu | Ni | Cu |
| 1 | Concentrate | 16.8 | 0.40 | 0.24 | 43.5 | 34.3 |
| | Tailings | 83.2 | 0.10 | 0.09 | 56.5 | 65.7 |
| | Slag | 100.00 | 0.155 | 0.115 | 100.00 | 100.00 |
| 2* | Concentrate | 35.7 | 0.30 | 0.19 | 67.8 | 56.7 |
| | Tailings | 64.3 | 0.08 | 0.08 | 32.2 | 43.3 |
| | Slag | 100.00 | 0.155 | 0.115 | 100.00 | 100.00 |
| 3* | Concentrate | 31.9 | 0.32 | 0.19 | 64.9 | 53.0 |
| | Tailings | 68.1 | 0.08 | 0.08 | 35.1 | 47.0 |
| | Cleaning stage concentrate | 12.5 | 0.49 | 0.29 | 39.5 | 31.5 |
| | Cleaning stage tailings | 19.4 | 0.21 | 0.13 | 60.5 | 68.5 |
| | Slag | 100.00 | 0.155 | 0.115 | 100.00 | 100.00 |

down the impeller velocity to 1500 $min^{-1}$, we added MIBC (20 g/t) and agitated for 1 minute. Next, air was blown in and foam was removed during 6 minutes.

To improve the flotation performance, some of the experiments were preceded by electric pulse destruction (EPD) of slag pellets. The EPD technologies offer new possibilities for tackling the environmental issues due to deeper recovery of process waste (Usov and Potokin, 2014).

Slag from the grinding unit was placed into a tank with manufacturing water and exposed to 900 high-voltage pulses of 180 kV each and total power of 640 Joules. Crushing was performed until a size of -1 mm was achieved.

Sulfides found microprobe analyzer only in the preparation ShT-1EPD. The microphotographs of sulfides obtained on the photo-attachment to microprobe analyzer Cameca SX 100 and presented in Fig. 1.

It can be seen that the shape of pentlandite grains is either isometric and prismatic, having either complicated interfaces (grains 1 and 2) or plain and smooth, like a sphere or a drop of sulfide melt (grain 3). Similar morphological peculiarities were observed in sulfide grains in initial slag samples, unaffected by EPD [2]. The size of sulfide grains varies over a wide range, from the first tens of microns to the first hundreds of microns. Thus, grains 1, 2, 3 had the sizes of 45 × 65 µm, 80 × 180 µm, and 16–17 µm, respectively. The grains had no cracks or shears. Apparently, EPD generates intergrain cracking along the sulfide – silicate matrix boundary, facilitating the liberation

Tab. 3. Chemical composition of the slag

Tab. 3. Skład chemiczny żużla

| Content, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $TiO_2$ | $K_2O$ | $Fe_2O_3$ | FeO | CaO | MgO | $Na_2O$ | $A1_2O_3$ | MnO | $SiO_2$ |
| 0.71 | 0.53 | 12.00 | 23.51 | 2.09 | 13.31 | 1.04 | 6.03 | 0.11 | 40.61 |

Tab. 4. Characteristics of ceramic materials produced from the slag

Tab. 4. Charakterystyka materiału ceramicznego z żużla

| Sintering temperature, °C | Compacting pressure, MPa | Density, g/cm$^3$ | Shrinkage, % | Ultimate strength, MPa | | Water absorption, % | Thermal conduction, Wt/m K |
|---|---|---|---|---|---|---|---|
| | | | | Compressive | Bending | | |
| 900 | 20 | 1.87 | 0 | 11.10 | 1.66 | 20.1 | – |
| | 50 | 1.95 | 0 | 14.53 | 2.18 | 18.4 | – |
| | 100 | 2.06 | 0 | 17.73 | 2.83 | 16.2 | – |
| 950 | 20 | 1.89 | 0 | 13.32 | 3.58 | 20.0 | 0.38 |
| | 50 | 2.00 | 0 | 17.46 | 5.34 | 15.6 | – |
| | 100 | 2.06 | 0 | 19.80 | 4.76 | 15.3 | 0.35 |
| 1000 | 20 | 1.87 | 0 | 19.71 | 4.16 | 20.0 | – |
| | 50 | 1.93 | 0 | 23.97 | 6.35 | 17.6 | – |
| | 100 | 2.03 | 0 | 39.47 | 13.35 | 14.8 | 0.32 |
| 1050 | 20 | 2.2 | 4.1 | 80.00 | 11.12 | 13.2 | – |
| | 50 | – | 6.6 | 140.00 | 12.83 | 6.7 | – |
| | 100 | – | 5.9 | 135.00 | 15.70 | 6.3 | – |
| 1100 | 20 | 2.64 | 9.9 | 130.40 | 34.00 | 0.2 | – |
| | 50 | 2.62 | 8.5 | 177.10 | 39.60 | 0 | – |
| | 100 | 2.62 | 7.0 | 218.70 | 47.70 | 0 | – |

of sulfides and, consequently, better concentration during flotation.

The chemical composition of the sulfides was determined using microprobe analyzer Cameca SX 100 (Table 1). In terms of crystallochemical formulas, the sulfides were represented by cupreous pentlandite with fairly high copper contents. In other words, this slag can be attractive for commercial extraction of both nickel and copper.

The results of slag flotation of pellets, either exposed or unexposed to EPD, are given in Table 2. It is evident that flotation is much inferior with unprocessed slag. Treatment with EPD allows to increase the concentrate yield 2-fold. In experiment No 3, the EPD procedure was followed by cleaning of the concentrate (Table 2). The reagent consumption was, g/t: BX – 127, MIBC – 64.

As a result of flotation of the slag preliminarily processed using EPD the nickel yield increased by 21–24%, that of copper – by 18–22%. The concentrate after cleaning flotation can be processed using bacterial leaching.

As demonstrated by flotation results, preliminary EPD quite effectively improves the slag floatability.

***Obtaining of building ceramic from slag***

The waste of slag flotation has been tested for the possibility of converting it into building ceramic. The chemical composition of the slag is presented in Table 3.

Other components added to the ceramic compounds were apatite-nepheline ore dressing tailings and quartz. The components ratio was as follows, %: slag – 40, nepheline tailings – 40; quartz – 20.

The feed components were ground down to a specific surface of 3000 cm$^2$/g. The mixture was blended, wetted to the optimum moisture content and molded by compressing at a specific pressure of 20–100 MPa. As a temporary binding agent, we used sulphite waste liquor in quantity of 0.5 wt. %. After drying at 105°C, the samples were burned at 900, 950, 1000, 1050 and 1100°C with an isothermal exposure during 1 hour. Then the temperature was decreased to 500°C at a rate of 2–3.5°C/min.

After cooling in a furnace for 8 hours, the samples were tested for compressive and bending strengths, average density, porosity, shrinkage, water absorption and frost resistance (Table 4). As the table shows, these compounds can be satisfactorily used in production of solid and cellular bricks with advanced mechanical performance. By increasing the temperature up to 1050–1100°C we obtained ceramics with physical-chemical properties similar to faience and semiporcelain.

In order to enhance the frost resistance, we treated the samples with water-repellent agents based on organomodified siloxanes. The frost resistance of samples burnt at 950–1000°C met the requirements of brand F 35, of those burnt at 1050–1100°C – F 100.

**Conclusions**

1. Studies of the reprocessability of pelletized slag from copper-nickel process tailings (Kola MMC, JSC) have disclosed the possibility of extracting nonferrous metals via flotation aftertreatment. By using electropulse pre-grinding EPD of slag pellets, it is possible to increase the nonferrous metal yield to concentrate by 18–24%. Further efforts will be aimed at improving the flotation procedures and optimizing the reagent regimes.

2. It has been shown that the tailings after copper-nickel slag flotation can be processed to obtain building ceramic materials with advanced physical-mechanical characteristics.

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*Odzysk metali nieżelaznych i produkcja materiałów budowlanych z żużli miedziowo-niklowych*

*Kopalnie i zakłady metalurgiczne podejmują tematyke odzysku metali ze złóż antropogenicznych (składowisk odpadów). Uzyskuje się w ten sposów dodatkowe surowce mineralne i poprawę stanu środowiska. Badania nad możliwością przeróbki żużla granulowanego z odpadów z miedzano-niklowych (z zakładów Kola MMC, JSC) pokazały możliwość odzysku metali nieżelaznych w procesie flotacji. Wykazano, że odpady flotacyjne z żużla miedziano-niklowego można poddać przeróbce i dzięki temu uzyskać m.in. ceramiczne materiały budowlane z zaawansowanymi właściwościami fizyczno-mechanicznymi.*



*Słowa kluczowe: żużel granulowany, metale nieżelazne, rozdrabnianie impulsem elektrycznym, flotacja, ceramiczne materiały budowlane*