RESOURCE POTENTIAL OF WASTE MATERIALS FROM POLISH COPPER ORE PROCESSING CHAIN

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Introduction

Industrial development provides improvement of life quality for humans. On the other hand, it leads to increased demand for many raw materials, such as metals. Some of metals are of greater importance than the others due to their specific applications in high-tech industry, where they cannot be replaced. These metals (for example Co, Mo, rare earth elements - REE, V) are referred to as critical metals. Their importance comes also from the fact that their resources are limited and they are mostly provided by politically unstable countries. This fact triggered the exploration of critical metals resources worldwide. Conversely, some of metals are not 100% recovered (e.g. Cu, Pb, Zn). It is well known that these elements occur in the Polish Kupferschiefer Cu deposits; however, they are not recovered by currently applied industrial process and finish their life cycle in processing wastes. In this work we aimed at recognition of waste materials that concentrate critical metals and we made evaluation of their resource potential.

Materials and methods

The samples of wastes from copper ore processing in Poland have been taken from different part of the production chain to seek for potential concentration of valuable elements. Four samples of fresh residues from copper flotation were provided by three different flotation units. In addition, three types of slags have been sampled from different parts of smelting process: 1) shaft furnace slag, which is a primary residue from copper concentrate smelting; 2) granulated slag, which is a residue from the electric furnace where the primary Cu-rich slag is processed; 3) Dörschl slag, which is a residue from Pb recovery in reverberatory furnace (from dusts and slimes generated at smelting facilities). Additional samples have been collected from places where environmental protection activities take place: 4) residues from flue gas desulfurization; 5) residues from air pollution control instruments; 6) spent catalyst used to oxidize SO_2 from the flue gas; 7) contaminated sulfuric acid from H_2SO_4 production unit.

The collected samples were subjected to basic research methods in order to establish concentrations of critical elements and host phases of these elements. The chemical composition was measured using lithium tetraborate fusion performed at Bureau Veritas Minerals (former ACME) laboratories, Vancouver, Canada. Supplemental analyzes were carried out using X-Ray fluorescence at AGH-UST. The composition of waste sulfuric acid was measured using ICP-MS at AGH-UST certified laboratory. Phase analyzes were performed using X-Ray diffraction at AGH-UST. Polished sections of waste materials were subjected to microscopic observations using reflected light microscopy, SEM-EDS and electron microprobe (EPMA) at AGH-UST. Some results have already been described elsewhere (Mikoda et al., 2018, 2019).

Results

The fresh copper flotation wastes are composed mainly from the same mineral phases as found in the orebodies, namely quartz, carbonates (calcite, dolomite) clay minerals, unrecovered sulfides and other phases (e.g. barite, kaolinite etc); the proportion of mentioned phases is variable, depending on the main lithological ore type processed in given flotation plant. The content of metals of interest is given in Tab.1. The amounts of metals in the flotation wastes are considerably lower than in slags described by Mikoda et al. (2018), also shown in Tab.1. However, considering the annual amounts of waste generated - 28 Mt/year of flotation waste, 1 Mt/year of slags - one can come to conclusion that flotation waste exhibit greater resource potential when looking at the annual fluxes of metals (e.g. 1848-5236 t/year V from flotation waste vs 598-1228 t/year from slags; Tab.1). The calculated fluxes of metals show that if recovered, the metals present in waste materials could be economically viable addition to the company's budget. The results of SEM-EDS and EPMA measurements revealed that in case of both described waste types there are no specific phases which concentrate greater amounts of critical metals. In case of flotation wastes, Cu, Pb and Zn occur as sulfides which were either overmilled or were intergrown or encapsulated by rock-forming minerals and have not been picked by flotation. In slags, Cu, Pb and Zn are present in the form of sulfides and metallic inclusions (only Cu and Pb).

Table 1. *Metal concentrations in waste materials from copper processing in Poland and their annual fluxes (considering 28 million tons of CFW and 1 million tons of SR generated per annum)*

Concentrations of metals (g t^{-1})									
Waste type	Co	Mo	REE	Y	V	Cu	Pb	Zn	Ag
CFW	9.4-84.7	7.8-28.5	56.3-84.2	10.2-14.9	66-187	1267-1551	280-919	31-126	4.3-12.7
SR	187-1446	164-773	94-308	13-39	598-1228	2795-7415	2950-8959	5046-46020	1.8-8.9
Annual fluxes (t y^{-1})									
Waste type	Co	Mo	REE	Y	V	Cu	Pb	Zn	Ag
CFW	263-2371	218-798	1576-2357	285-417	1848-5236	35476-43428	7840-25732	868-3528	120-355
SR	187-1446	164-773	94-308	13-39	598-1228	2795-7415	2950-8959	5046-46020	1.8-8.9

CFW - copper flotation waste; SR - slag residue

Other wastes also exhibit interesting metal concentrations, but not necessarily for critical metals; the exception is the spent catalyst, that contains ca. 3% of V in the form of potassium salt doped on the porous SiO_2 matrix. Initial leaching attempts showed that 93-95% of V can be recovered from the spent catalyst by means of citric acid or bioleaching with *Acidithiobacillus thiooxidans*. Waste materials from air pollution control instruments and flue gas desulfurization unit exhibit high content of Cu, Pb and Zn (1364-1450 ppm Cu, 1714-4141 ppm Pb and 1590-9728 ppm Zn).

Conclusions

This research has shown that the wastes from Polish copper processing facilities exhibit a good resource potential in the case of critical elements, but also elements commonly recovered during processing, such as Cu, Pb and Zn. Preliminary tests of possibilities for recovery of other metals from wastes (e.g. with bacteria or organic acids) gave promising results. The obtained metal-free residues can be subsequently utilized in economic ways when environmental standards are met.

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