ABSTRACT

The dissertation titled: " Research of the extraction process on heavy metals from zinc and lead metallurgical wastes" presents the problem of metal separation from metallurgical wastes, and the main objective of the dissertation was to indicate the possibility of leaching such metals as Pb, Zn, Cu, Fe, and Cd from wastes come from "Miasteczko Śląskie" zinc smelter by using hydrometallurgical methods. The study aimed to investigate the influence of varying parameters of the process control on extraction efficiency. The materials tested were slag from the Short Rotary Furnace of the Lead Refining Department (KPO), slag taken from the Hazardous Waste Landfill (KPO SON), as well as a sample of post-neutralization sludge taken from the Company's Wastewater Treatment Plant. In addition, the obtained post-extraction solutions were further treated using pressure-driven membrane process (nanofiltration) to determine the potential for effective metal retention and concentration of metals. The research was supplemented with column leaching tests to present an alternative method to static extraction for metal leaching. The tested materials were also subjected to a broad analysis, including qualitative, quantitative, or phase composition assessment. Then, selected physicochemical parameters were determined, and the topography of the tested samples was evaluated.

The first stage of the study involved performing a general characterization of the studied wastes. The process of crushing, drying, and grinding, as well as selecting a suitable method of digestion of the analyzed samples was carried out. Microwave-assisted aqua regia digestion was selected. Qualitative, quantitative, and phase analysis of the metals present in the materials was carried out using analytical methods (such as BCR sequential extraction), as well as instrumental methods (such as ASA, SEM with EDS, and XRD). The basic physicochemical properties (such as moisture content, pH, and loss on ignition) were also determined for the materials tested and varied considerably between samples. Analysis of the slag and sludge samples revealed the presence of many metals, in varying forms of occurrence such as Fe, Pb, Zn, Cu, Cd, Na, Ca, K, Ni, Mn, Cr, with the metals present in the samples in the highest amounts (above $5\%_{wt.}$) being Fe, Pb, Zn, Cu in the slag samples and Pb, Zn and Cd in the sludge sample. X-ray microanalysis with EDS revealed a high variability of metal concentrations in different micro-areas of the sample. SEM images of the studied materials showed a relatively smooth and non-porous structure of the slag samples and a low-porous structure of the sludge sample. The variety of forms of metal occurrence in the materials studied is mainly attributed to the type of bonds formed during the primary and processing processes, variability of conditions during the storage process, and indicates the considerable heterogeneity of the samples in terms of chemical composition.

The second step was to perform leaching tests of Pb, Zn, Cu, and Fe from the slag samples, and Pb, Zn, and Cd from the sludge sample. The type, concentration, and pH of the leaching agent used, the size of the slag grain fraction, the solid/liquid S/L ratio, temperature, time, and the multiplicity of the process were investigated in terms of the extraction process efficiency.

The results obtained in this stage of the study confirmed that with appropriate adjustment of process parameters, it is possible to control the process yields, as well as its selectivity. The most effective leaching agents included HCl at 2 mol/dm^3 (in leaching of slag metals), 1.5 mol/dm^3 HNO_3 (for sludge extraction), as well as Na_2EDTA (at 0.15 mol/dm^3 (pH=4) for KPO extraction and 0.075 mol/dm^3 (pH=4) for KPO SON and sludge samples), and NaOH (2 mol/dm^3 for KPO and KPO SON leaching, and 0.5 mol/dm^3 for sludge). The optimal process parameters were an S/L ratio of 1/100, leaching of an unfractionated slag sample, single-stage extraction, a temperature of 25°C, extraction running time of at least 360 minutes, which determined that equilibrium was reached in all cases studied.

The next issue analyzed was the nanofiltration process of selected post-extraction solutions. This stage of the work was aimed at presenting the possibility of further processing of the obtained post-extraction solutions. The evaluation was also intended to indicate the variability of the process efficiency depending on the applied pH of the feed and the type of solution. Based on the results obtained, it was determined that nanofiltration is a highly effective method for the final concentration of heavy metals in post-extraction solutions, and with the use of appropriate process parameters, it is possible to achieve both high efficiency and relative selectivity of metal separation. Using appropriate process parameters (high pH values ~8-10), it was possible to obtain the highest values of metal retention factors for most cases.

The metal leaching using column extraction was intended to indicate the possibility of using an alternative leaching method while reducing costs, as well as increasing effectiveness. The effects of process parameters such as leaching agent flow rate, column bed weight, and fraction size on the extraction efficiency of metals such as Pb, Zn, Cu, and Fe from the KPO sample in the column were investigated. The results of column leaching were most favorable for a higher value of leaching agent flow rate, a lower value of bed mass (thus a higher S/L value), and the smelter of the two grain size fractions tested. Compared to the static method, in which the maximum leaching was reached just after 6 hours, the yield obtained after the same time for column samples was much lower, and therefore the use of this method appears to be inefficient and uneconomical.