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# Elimination of Heavy Metals from the Material of Sludge Bed Slovinky

KOZÁKOVÁ Ľubica[1, a], ZELEŇÁK Miroslav[1,b], BAKALÁR Tomáš[1,c*] and ZELEŇÁK Fridrich[1,d]

[1]Technical University of Košice, Faculty of Mining, Ecology, Process Control and Geotechnologies, Institute of Earth Resources, Letná 9, 042 00 Košice, Slovakia

[a]lubica.kozakova@tuke.sk, [b]miroslav.zelenak@tuke.sk, [c]tomas.bakalar@tuke.sk, [d]fridrich.zelenak@tuke.sk

**Keywords:** environmental load, Slovinky, heavy metal, sludge bed.

**Abstract.** Old environmental loads are priority environmental problems in Slovakia. An old environmental load is an anthropogenic constituent in landscape which has its origin in past works (for example mining and mineral processing) but in present time it can also pose risk for the environment. One of environmental loads in Slovakia is sludge bed in Slovinky. Village Slovinky is well-known for mining activities during several centuries. From the beginning copper ore was mined there, later on iron ore which was processed in the metallurgical factory in Krompachy. The mining activity in Slovinky was stopped in 1993. Flotation slurry from ore treatment plant was deposited on the sludge bed which was operated from 1968 to 1999. More than 4.8 million cubic meters of slurry is deposited there. Locality of Slovinky is included in State Remediation Program of Environmental Loads (2010-2015). The paper summarizes the actual state of knowledge about environmental impact of mineral processing and theoretical analysis of problem of environmental impact of environmental load – sludge bed in Slovinky. Experimental part of the paper is focused on study of possibilities of elimination of heavy metals in sludge bed material with the aim of improvement of the environmental quality of surveyed locality.

## Introduction

Mining and mineral processing of primary raw materials had a long tradition in Slovakia. Old environmental loads – heaps and sludge beds were remained after these activities [1].

Sludge beds have been built on a disposal of waste, these waste had varying amounts of water [2]. Sludge bed Slovinky (Eastern Slovakia) contains flotation waste from mineral processing of sulphide ores and industrial slag from metallurgical processing in fine-grained form [3].

The constructive conditions of this sludge bed are bad, the stability of the embankment could be disrupted and it is danger of ecological disaster [4].

Several authors were studied this region from different views e.g. evaluation of impoundment sediments from ore processing [3], thermal analysis and mineralogical characterization of contaminated sediment [5], and leaching of selected potentially toxic elements [6], etc.

Our previous research was focused on the study of the selected physical-chemical properties of sludge bed material [7-9]. Experimental part of the paper is focused on study of possibilities of elimination of heavy metals in sludge bed material with the aim of improvement of the environmental quality of surveyed locality.

## Materials and Methods

The studied material is from the surface of the sludge bed Slovinky, dark gray, in a fine-grained composition.

**Leaching in distilled water.** The leachates in distilled water were prepared from 10 g of sludge bed material and distilled water in the amounts of 50 ml, 100 ml, and 200 ml. Three measurements, i.e. a total of nine measurements were performed for each sample of distilled water leachate. The samples were homogenized in an orbital shaker (Environmental Incubator Shaker ES - 20/60) in wide neck bottles for two hours at 25 °C and 200 rpm. After homogenization the samples were allowed to leach for 20 hours. After this time they were again placed in the orbital shaker for additional two hours (a total of 24 hours). Subsequently, the samples were filtered and the leachates were used to determine the concentrations of metals by Atomic adsorption spectrometer (AAS). This procedure was repeated with different leaching time of 68 hours (instead of 20 hours; i.e. a total of 72 hours).

**Leaching in $HNO_3$.** The leachates in HNO3 were prepared in the same way as the leachates in the distilled water using 2 mol.l-1 HNO3 instead of distilled water.

Three measurements were conducted, i.e. a total of nine measurements in distilled water and nine measurements in $HNO_3$. The values were recorded as average values of each set of three measurements.

**XRF analyses.** The qualitative and quantitative analysis of the samples of sludge bed material (in the fraction of below 100 mm) was done by X-ray - fluorescence spectroscopy (XRF) using SPECTRO iQ II (Ametek, Germany).

**XPS analyses.** X-ray - photoelectron spectroscopy (XPS) (SPECS, USA) was used for qualitative, quantitative, and structural analyses of all the samples of natural materials and the sludge bed material.

**AAS analysis.** The determination of concentrations of selected heavy metal ions was done using atomic absorption spectrometer iCE 3300.

**Results**

**XRF and XPS analyses.** The results of the analyses of the natural materials and the sludge bed material are shown in Table 1 (by XRF method), and Fig. 1 (by XPS method).

Table 1. Chemical composition of sludge bed material [$mg.kg^{-1}$].

| Na | Mg | Al | Si | K | Ca | Cu | Cd | Fe | Ni | Sb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4.410 | 23.560 | 21.118 | 116.700 | 4.159 | 56.720 | 8.528 | 27.1 | 278.7 | 478.2 | 6.764 | 43.520 |

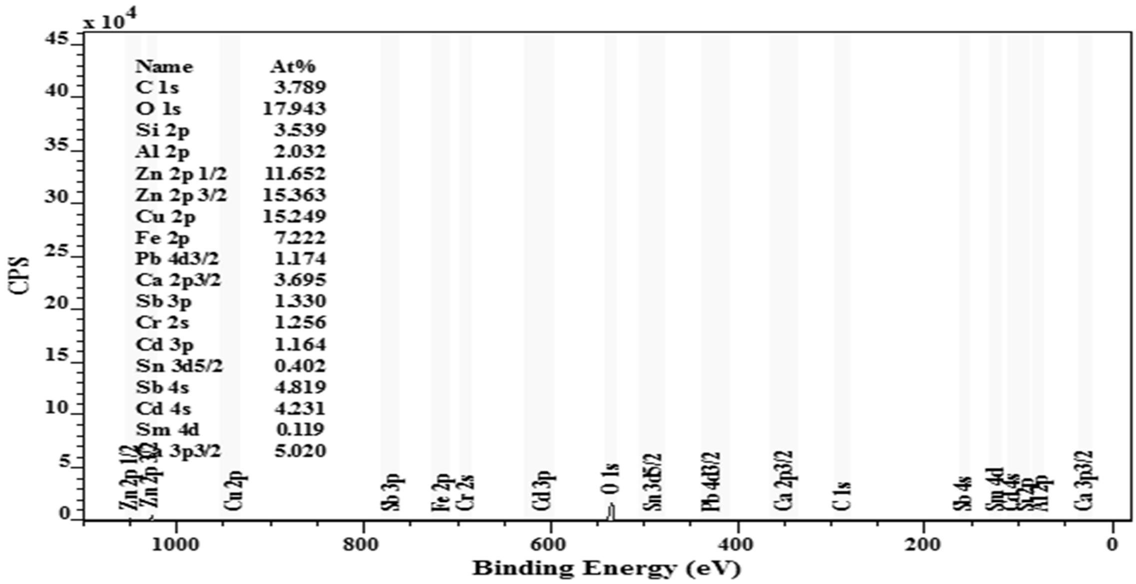


Fig. 1. Chemical composition of sludge bed material.

Both methods (XRF and XPS) confirmed high levels of Cu, Fe and Zn in the sludge bed material.

**Leaching.** Results of heavy metal concentrations analyses in the leachates in distilled water after 24 and 72 hours are presented in Figs. 2 and 3.

The results of the measured heavy metal concentrations in leachates in distilled water after 24 hours demonstrated low efficiency of the leaching. Most nickel, iron, copper, and zinc were leached in 200 ml, 100 ml, 200 ml, and 200 ml, respetively, of distilled water. No cadmium and antimony was detected in leachates.

The results of the measured heavy metal concentrations in leachates in distilled water after 72 hours showed similar values for nickel in 200 ml. Most copper and iron was leached in 200 ml and most zinc in 100 ml of distilled water. The concentrations of Cd and Sb were zero, too.

The comparison of heavy metal concentrations after 24 and 72 hours of leaching showed that the time factor only affected the increase in concentration of nickel.

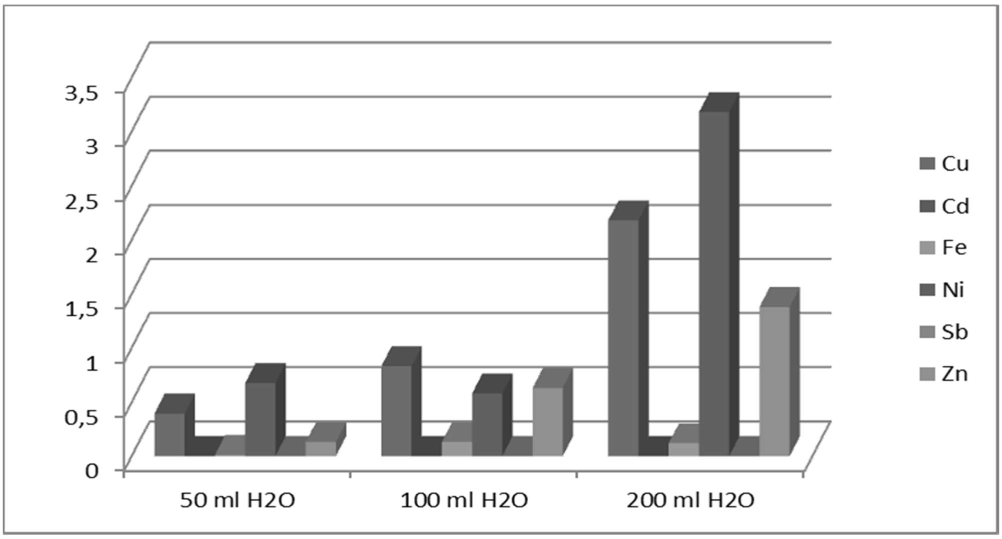


Fig. 2. Heavy metal concentrations in leachates in distilled water after 24 hours [$mg.kg^{-1}$].

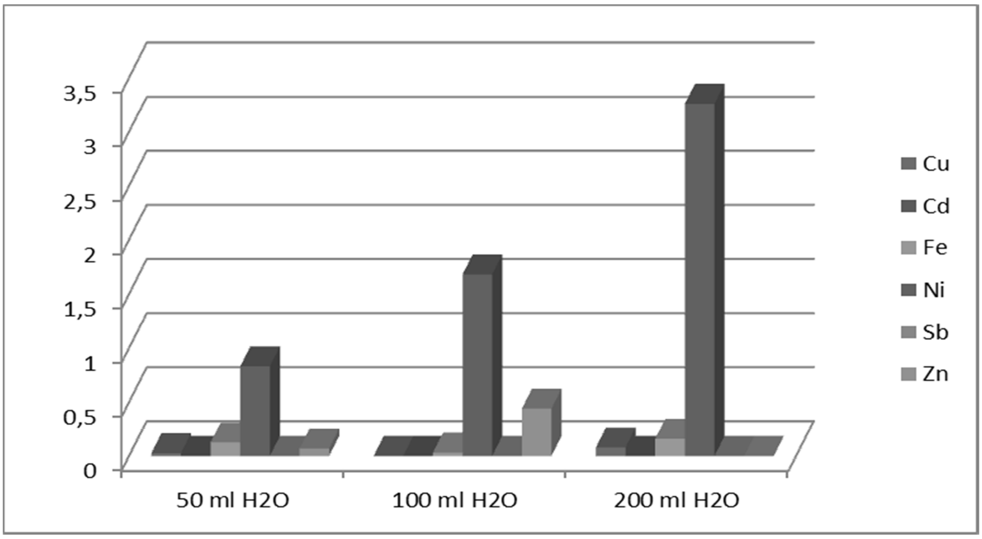


Fig. 3. Heavy metal concentrations in leachates in distilled water after 72 hours [$mg.kg^{-1}$].

Comparison of heavy metal concentrations in leachates in distilled water after 24 and 72 hours, and in the sludge bed material is shown in Fig. 4.

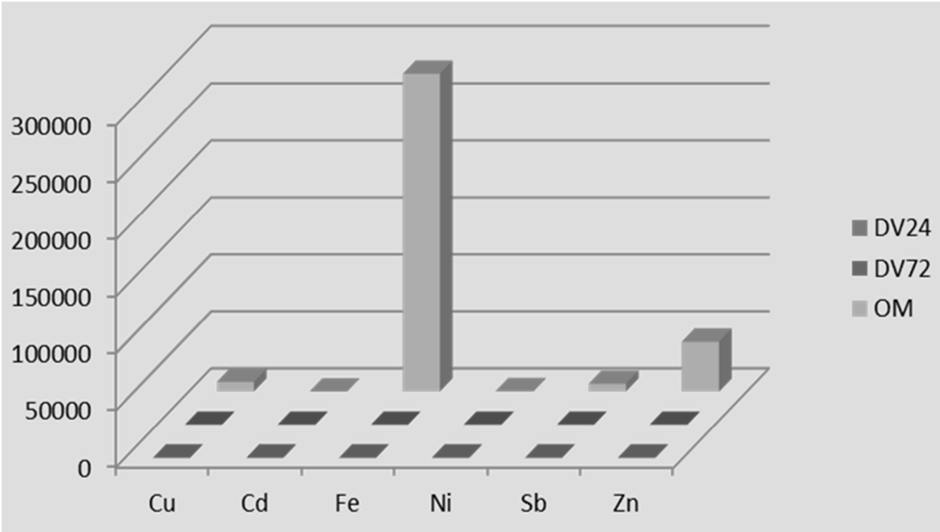


Fig. 4. Comparison of heavy metal concentrations in leachates in distilled water after 24 (DV24) and 72 hours (DV72), and in the sludge bed material (OM) [$mg.kg^{-1}$].

Results of heavy metal concentrations analyses in the leachates in $HNO_3$ after 24 and 72 hours are presented in Figs. 5 and 6.

Comparing the results obtained by leaching of the sludge bed material for different times (24 and 72 hours) it was found that the time factor had no influence on the concentrations of copper, iron, nickel, antimony and zinc. The longer leaching time positively impacted the concentration of cadmium.

The comparison of heavy metal concentrations after leaching in $HNO_3$ and the concentration of heavy metals in the initial material showed that the efficiency of leaching reached the highest value for copper and zinc (68% to 94% and 58% to 78%, respectively). The effectiveness of nickel, iron, and antimony leaching of ranged from 24% to 36%, 30% to 53%, and 16% to 36%, respectively. The time factor affected the effectiveness of Cd leaching, which was in the range of 19% to 68%.

These results indicate that the 2 $mol.l^{-1}$ $HNO_3$ is a suitable leaching agent for the reduction or elimination of heavy metals from sludge bed material.

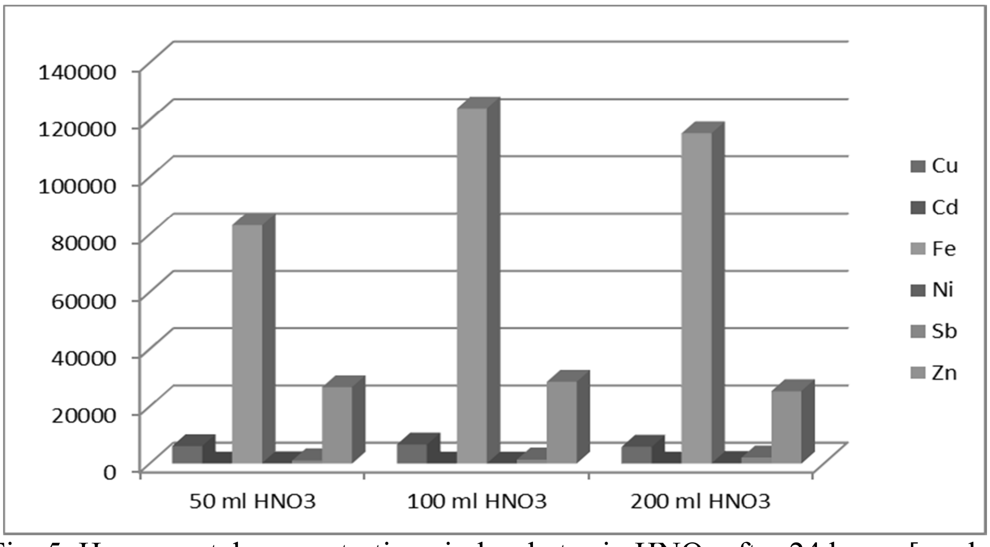


Fig. 5. Heavy metal concentrations in leachates in $HNO_3$ after 24 hours [$mg.kg^{-1}$].

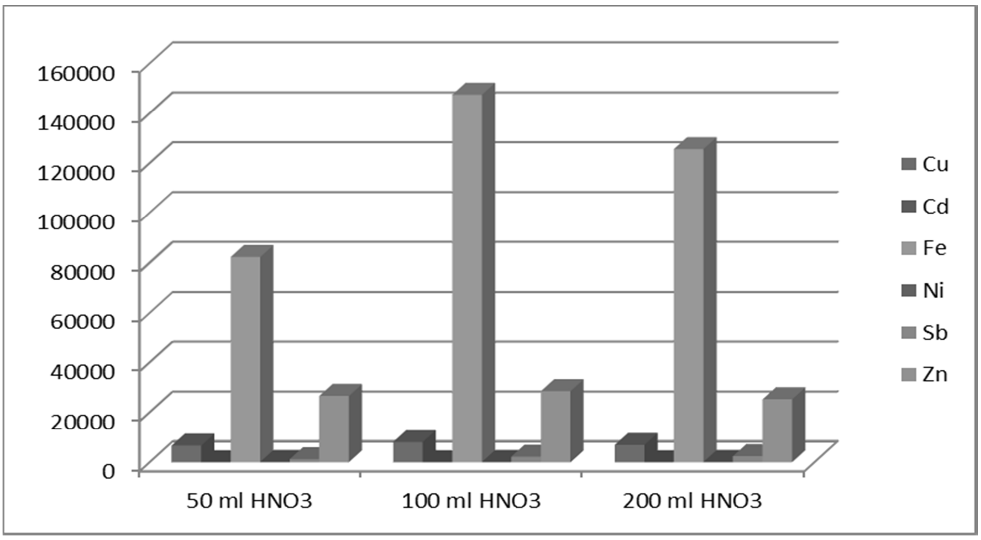


Fig. 6. Heavy metal concentrations in leachates in $HNO_3$ after 72 hours [$mg.kg^{-1}$].

Comparison of heavy metal concentrations in leachates in $HNO_3$ after 24 and 72 hours, and in the sludge bed material is shown in Fig. 7.

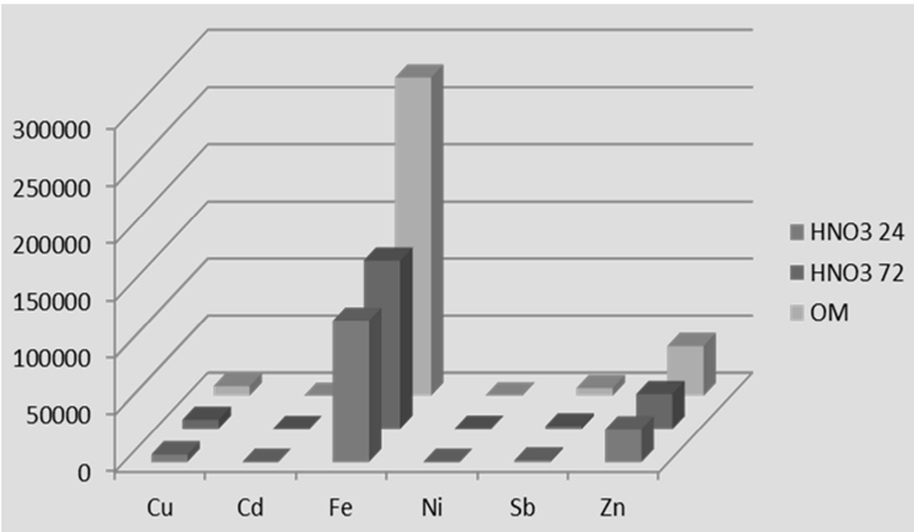


Fig. 7. Comparison of heavy metal concentrations in leachates in $HNO_3$ after 24 (HNO3 24) and 72 hours (HNO3 72), and in the sludge bed material (OM) [$mg.kg^{-1}$].

**Summary**

The location of Slovinky is included in the list of environmental loads with the high priority of monitoring to the created register of contaminated sites. In the locality increased concentrations of heavy metals can be found in the soil even two decades after the end of mining and mineral processing activities. In addition to mining and mineral processing activities it can also be a result of natural geochemical anomalies in the region. This is also one of the reasons for studying the leachability of heavy metals from the sludge bed material.

Considerable amount of authors studied sludge bed materials from different views. Their results and our results both confirmed increased concentrations of some metals.

2 $mol.l^{-1}$ $HNO_3$ was proved to be suitable leaching reducing agent for elimination of heavy metals from the material of sludge bed Slovinky. The possibility of obtaining some metals (Cu, Fe, Zn) from the material of sludge bed was indicated by partial results of monitoring the concentrations of heavy metals in leachate of $HNO_3$ and it was confirmed by several authors [6, 10].

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