OLD METALLURGICAL SLAG NEAR SMOLNÍK VILLAGE (SLOVAKIA) AND ITS IMPACT ON ENVIRONMENT

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Abstract

The old metallurgical slag is northeast of village Smolník by the stream Smolník. Composition of the slag was studied by optical microscopy, X-ray diffraction, chemical analyses and by electron microprobe analyser. Laboratory leaching experiments were done to find out behaviour of elements in the weatherig process. In the expriment were leached fractions 0,8 - 4 mm in diameter in different solutions: distilled water, HNO_3 solution and citrate solution. The ratio solid/solution was 1/10 and the chemical analysis were performed in periods 1, 5, 10, 15, 20, 25 and 30 days. The slag is composed mainly from olivines and spinels. Citrate solution reached most metal contents leached from slag material. Water is able to leach only small concentrations of metals from slag. Generally Fe, Cu and Zn are most leachable in to the solution, Mn and Pb only slightly. Cu and As content in plants growing on the slag are exceeding the normal values in all analysed samples. Pb in all samples was below the normal concentration. Zn acceptable values were exceeded only in alder and grass.

Introduction

Old mining town Smolník (eastern Slovakia) (Fig. 1) and surrounding countryside is well known with its mining wastes and acid water accident in 1994 (1). Pyrite-chalcopyrite mines were mined for centuries till 1991. There is also an old metallurgical slag northeast of village Smolník. The slag come from old smelter in Smolnícka Huta village. This slag is next to the stream Smolník and it can have potentially harmful impact on the environment because this material contain high concentrations of heavy metals (Cu, Sn, Pb, Mn, Co, Zn, As). Metallurgical slag was often used for road constructions. It´s easy to find it in many road material in environ of Smolník and Smolnícka Huta villages. It´s important to determine the stability of heavy metals in slag material and possible release of contaminants in weathering conditions (2, 3). Specific plants with adaptibility to heavy metals are growing on the slag and on the mine heaps also.

Methods

The mineralogical composition of slag was studied in thin and polished sections by transmitted and reflected light microscopy, X-ray diffraction (diffractometer Philips PW 1710), scanning electron microscopy, and by electron microprobe analyser (Cameca SX100).

Fig. 1 – Localisation of Smolník village.

By the leaching experiment were used 5g of sieved crushed slag material (grain size 0,8 – 4 mm) leached by different solutions for periods 1, 5, 10, 15, 20, 25 and 30 days. Used solutions were: distilled water (initial pH 5,8), HNO_3 solution (initial pH 1,6) was prepared from 1 ml of concentrated HNO_3 and 500 ml of distilled water, citrate solution was prepared from 46,5 ml of citrate acid (0,1 M) with 3,5 ml of citrate sodium (0,1 M) diluted with 100 ml of distilled water (initial pH 2,7). For each sample (5 g of slag) were added 50 ml of solution. The samples were shaken by table shaker, by ambient temperature, without acces of light. Measurements of conductivity, Eh and pH (in periods 1, 5, 10, 15, 20, 25 and 30 days) were performed with MC 126 conductivity meter Mettler Toledo, Redox potential and pH meter Mettler Toledo 1120. The glass electrode was calibrated at 25^{o}C using Mettler-Toledo pH buffer solutions at pH of 4.01 and 7.00 and Mettler Toledo redox buffer solution. Leachates were filtered through 0,45 µm Millipore filter and stored in refrigerator until analyses. Leachate from each sample was analysed for Fe, Mn, Cu, Pb, Zn by atomic absorbtion spectrophotometry (AAS) and inductively coupled plasma atomic emission spectroscopy (AES-ICP). Consequential data were calculated to quantity of leached elements from 1 kg of slag material.

The slag material, ochres and soil from slag were digested with nitric acid at 95 ºC for 2 h and Fe, Mn, Al, Cu, Pb, Zn, As, Co concentrations were analysed using ICP-AES.

The plants - spruce (needles), alder (leaves), grass (above-ground part), heather (above-ground part)) and moss (above-ground part) found on slag were dried and analysed by AAS.

Results

The main detected minerals in slag material are olivines and spinels (Fig. 2).

Leaching Experiment: H_2O (Fig. 3): The water leached most Cu, Fe and Zn. Volume of Cu and Zn in the water raised only slowly. Fe and Mn precipitated and dissolved again. Pb is not leached by the water.

HNO_3 (Fig. 4): The highest concentrations leached by HNO_3 solution has Fe. The diagram of Fe concentration copy essentially pH values (intense increase and afterwards slowly decrease). Cu achieve also high concentrations. The concentration of Cu raised with time and afterwards Cu partly precipitated. Zn as well

but slower. Pb and Mn in HNO_3 solution have relatively low concentrations but stable.
Citrate solution (Fig. 5): Volume of leached Fe achieve very high concentrations with highest increase in first days of experiment, whatever this exactly matching the pH values. Cu is leached slowly in first days and after 10 days the concentration raised fast and after 25 days partly precipitated. Zn after fast release into the solution slowly precipitated. Pb and Mn after slowly increase of concentration were stable in solution.

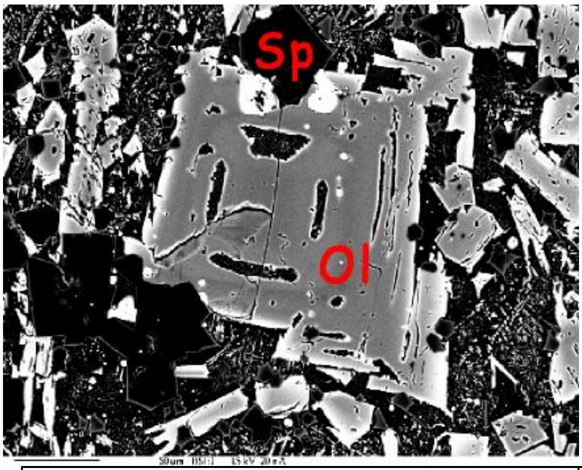


Fig. 2. Olivines (Ol) and Spinels (Sp) are the main minerals of slag.

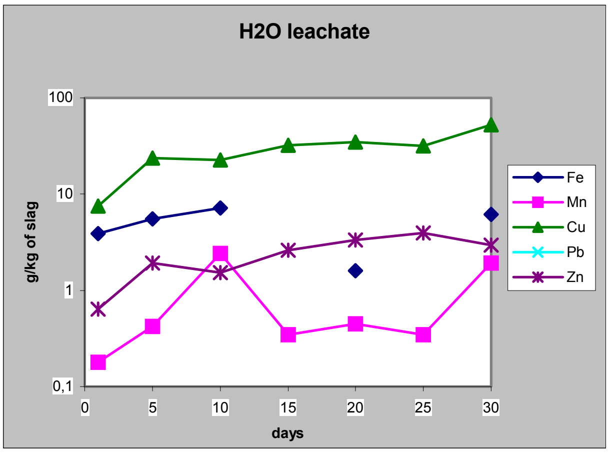


Fig. 3. Concentrations of metals leached by H_2O.

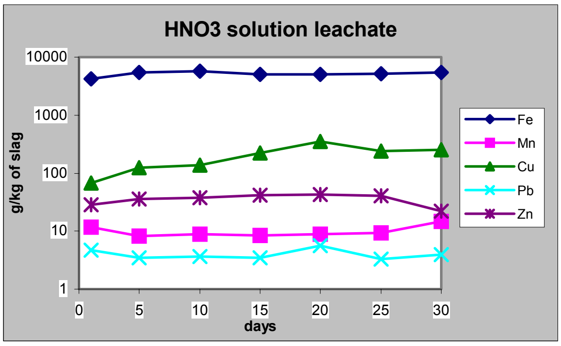


Fig. 4. Concentrations of metals leached by HNO_3 solution.

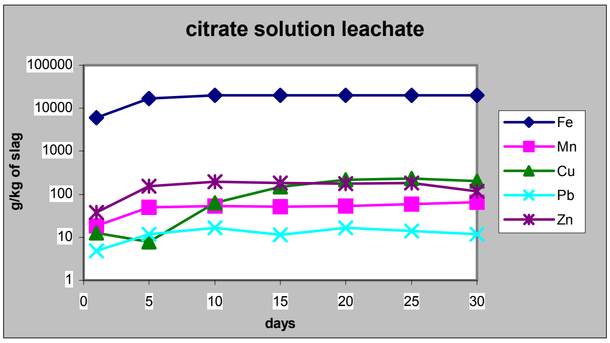
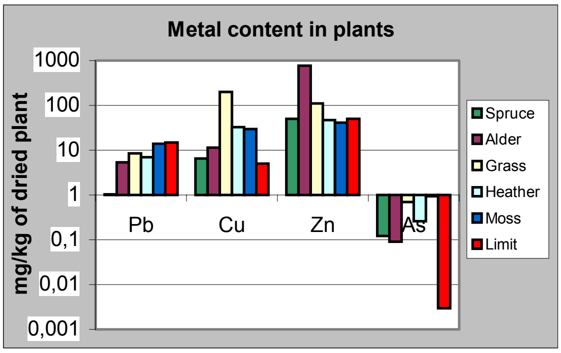


Fig. 5. Concentrations of metals leached by citrate solution.

Nitric acid digestion: In ochres on slag material are higher concentrations of Al, Cu, Mn, Co and As mobilised to the solution by nitric acid compared to slag material. It means that heavy metals are concentrated in ochres. In soil on slag are highly concentrated Pb and As (Fig. 6).

Plants: Cu and As content in plants growing on the slag are exceeding the normal values in all analysed samples. The moss have the most extreme As, Al and Fe contents. Zn is accumulating in leaves the most – alder exceeds the normal limit 15 times. Grass has extremely high content of Cu – the limit is 40 times exceeded. In generally the trees have lover content of metals together compared with moss, heather and grass (Fig. 7).



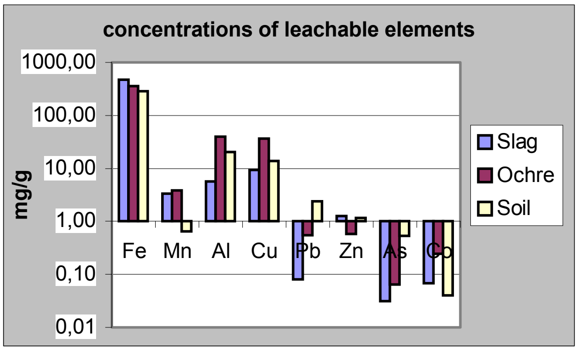


Fig. 6. Concentrations of metals in plants growing on slag compared with limit concentrations.	Fig. 7. Concentrations of metals released from slag, ochre and soil by nitric acid digestion.

Discussion

The goal of this experiment was to simulate weathering process on slag and first to compare effect of different solutions on slag material. As we expected distilled water leached the lowest concentrations of metals from slag material and citrate solution which correspond to organic acids naturally present in the soil leached the higest concentrations of metals. This let us to say that high concentrations of metals released by acide solutions from slag aren´t from sulphates leachable by water. (Because the slag was before experiment washed by distilled water to focus only to pure slag material.)

The concentrations of metals in leachate depends on stability fields of metals and the fall of Fe, Cu, Zn and Mn in the leachate is controlled by precipitation and absorption processes. The metals remain on filters if there were precipitated aggregates bigger than 0,45 µm.

The metals (mainly Fe, Cu and Zn) are leached from slag material in to the solution. Part of this solutions integrate with stream waters poluted with acid mine drainage (4) and part of it concentrating in soil or ochres.

Conclusions

Citrate solution leached most metals from slag material. Water is able to leach only small concentrations of metals from slag. Generally Fe, Cu and Zn are most leachable in to the solution, Mn and Pb only slightly.
This results do not represent really natural processes because the experiment was done as “batch experiment” and the natural system is open.

Acknowledgments

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