Modelling of bioleaching in microcosms

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Introduction

Two site-specific processes were examined in laboratory soil microcosms to understand and quantify metal emission and transport as well as their consequences, with focus on a former base metal sulphide mining area in Hungary. The quantitative results of the microcosm tests are used as site specific parameters for the GIS based catchment scale transport model, enabling the creation of site specific target risk values and target concentrations. The complex leaching of metal sulphides containing waste rock and the secondary sorption of leached metals on soil were simulated.
1. Complex leaching: the complex process of weathering, chemical leaching coupled with the microbiological sulphide oxidation further to water input by precipitation were studied. The main scenarios were simulated and studied in successive time intervals: **a. the initial phase** of the complex leaching process, reproducing the average annual rain conditions, **b. dry weather conditions** phase with 1/3 of the average annual rain water input, **c. depletion phase** of the complex leaching process, reproducing average annual rain conditions, showing sulphide depletion of the leached mine waste.
2. Sorption of leached metals on soil: the leachate produced by complex chemical and biological leaching of mine waste material comes into contact on site with the surrounding environment. The natural metal-filtering ability of two types of local soils (clayee and forest soil) was investigated in a laboratory flow-through microcosm experiment to assess the partition of different metals between leachate and soil, and calculate the metal-filtering capacity of the soil in support of environmental risk assessment of toxic metals polluted mining sites.

Objectives

The objective of the experiments was to generate site specific quantitative parameters for risk assessment and planning of risk reduction, with the target to reduce metal containing emission from the point and diffuse sources. The aim of the bioleaching test was to check the leaching efficiency in case of various water input rates, and to predict the long term flow of the process. The metal-sorption experiments in flow-through laboratory microcosm aimed at determining the metal sorption capacity of the soil and the partition of the risk between leachate and surrounding soil.

Materials and Methods

The experiments simulated typical processes occurring within a former mining area. The mine waste and soil derived from the Gyöngyösoroszi zinc-lead sulphide mining area in Northern Hungary.
1. Complex leaching: two typical cases were modelled in four microcosms for more than 3 years: 1.1. bioleaching within a large waste dump in two replicate microcosms containing only mine waste (M1, M2) and 1.2. bioleaching in a mine waste dump in contact with surrounding soil in two other replicate microcosms, containing mine waste on top of a thin soil layer (T1, T2). The waste material and the soil were analysed for total (Aqua Regia extract) and mobile metal ($NH_4OAC+AcOH+EDTA$ extract) content at the start of the experiment. The quantity and quality (pH, As, Cd, Cu, Pb, Zn content) of the output leachates from each microcosm were measured at regular time intervals. The temperature within the microcosms was monitored. The microcosms (Figure 1) were 6 liter volume HDPE flasks filled with homogenised mine waste typical of sulphide ore from the Gyöngyösoroszi site. The amount of mine waste was 4,5 kg in each microcosm. The 1 kg of single layer soil was placed on top of 5 cm gravel layer and overlain with the mine waste in the T1, T2 microcosms. The irrigation rate was based on an annual rainfall rate of 756 mm/m²/year with allowance for evaporation. Monthly water input as per the average annual precipitation on the 154 cm² surface was 960 ml, and 320 ml in the dry period, simulating four slight intensity and one heavy intensity rain event/month. The microcosms are still operating. The results are provided for three phases of the leaching in three successive time intervals.
2. Metal sorption: two types of soil, homogenised forest soil and loamy soil, were washed through in 3:5 ratio in a flow through reactor with toxic metal containing leachate resulted from the „complex leaching" microcosm. The resulted secondary leachate was collected and analysed for As, Cd, Cu, Pb, Zn. The forest and loamy soils were analysed for As, Cd, Cu, Pb, Zn before and after contact with the heavy metal loaded leachant.

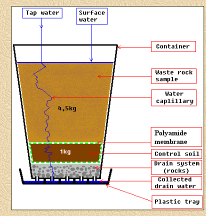

Figure 1 Leaching microcosm containing mine waste on top of a thin soil layer

Results and discussions

1. Complex leaching: the results of the leaching experiment were evaluated at **a.** the initial phase within which the stationary equilibrium of the process is reached and the water input is the equivalent of the average annual rain. **b**. dry conditions phase within which the water input is 1/3 of the average annual rain. **c.** the final phase of the process within which the microcosms are depleted of metal sulphides and the water input is equivalent of the average annual rain. To get comparable results, all data are given as a specific amount for 3 months period. Figure 2 shows the input leachant modelling precipitation and output leachate volumes for the 3 scenarios. The output leachate volume is ½ of the input precipitation during the average rain period but only 1/5 during the dry period.

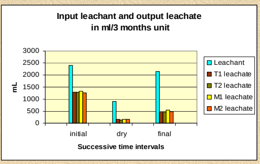

Figure 2 Input leachant and output leachate volumes in successive time intervals in ml/3 months unit

The biological oxidation and chemical degradation of sulphidic ore resulted a continuous low pH in the microcosm leachates and temperature increase in the microcosms. The pH is function of the input leachant amount and the cell concentration of the sulphide-oxidizing bacteria (*Acidithiobacillus ferrooxidans*: $1{,}1*10^3$ cell/g waste). The pH during the dry period is significantly lower (1,5 and 2,5), than during the normal 2,0 and 3,2). The leachate pH profiles are shown in Figures 3, 4 and 5 for the two mine waste+soil containing (T1, T2) and the two, only mine waste containing microcosms (M1, M2). The pH of the mine waste containing microcosms in the initial and in the dry period of the process is one (1) unit below the mine waste+soil containing microcosms. The buffering capacity of the soil is obvious (Figure 3 and 4). A gradual pH increase occurs in the final phase of the process (Figure 5). The pH of both microcosms increased to 3,5–4 at the end of the studied final phase.

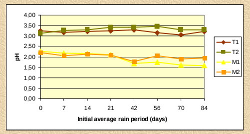

Figure 3 T1, T2, M1, M2 microcosm leachate pH as function of time during the initial average rain period

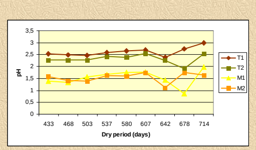

Figure 4 T1, T2, M1, M2 microcosm leachate pH as function of time during the dry period

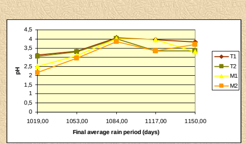

Figure 5 T1, T2, M1, M2 microcosm leachate pH as function of time during the final average rain period

The metal concentration of the leachates at an average period is: As: 0.741 mg/l; Cd: 1.20 mg/l; Cu: 4.71 mg/l; Pb: 3.58; Zn: 163.53 mg/l; where the As is 30 times, Cd is 240 times, Cu is 24 times, Pb is 350 times, Zn is 800 times the Hungarian quality criteria for underground waters.
The metal amount leached out from the waste rock in the microcosms was calculated for the three successive time spans of the study. To compare leached metal amounts and leaching efficiencies all data were given in mg leached metal/kg waste/3 month unit. Table 1–3 show this specific metal amount for the initial average rain, the following dry and the final average rain periods. The leached metal amount is not always proportional with the volume of the rain: the Zn, Cd and As amount leached in the 1/3 rain period from the M microcosm decreased only to the half as compared to the initial average rain period, although the leachate was more concentrated. The metal amount leached from the T microcosms was lower than from the M and almost constant during the three years of experiment. Therefore, the metal retention capacity of the soil is high. This assumption will be validated after completion of the experiment and analysing of the soil layer in the microcosm.

Table 1 Average metal amount leached in the initial phase from M and T microcosms in mg metal/kg waste/3 months

Element	Initial average rain period	
	M	T
	leached metal mg/kg/3months	leached metal mg/kg/3months
As	0.22	0.02
Cd	0.35	0.10
Cu	1.4	0.13
Pb	1.0	0.49
Zn	47.0	11.0

Table 2 Average metal amount leached in the dry phase from the M and T microcosms in mg metal/kg waste/3 months

Element	Dry period	
	M	T
	leached metal mg/kg/3months	leached metal mg/kg/3months
As	0.11	0.01
Cd	0.11	0.07
Cu	0.66	0.14
Pb	0.17	0.10
Zn	19.7	10.1

Table 3 Average metal amount leached in the final phase from the M and T microcosms in mg meta/kg waste/3 months

Element	Final average rain period	
	M	T
	leached metal mg/kg/3months	leached metal mg/kg/3months
As	0.01	0.01
Cd	0.04	0.07
Cu	0.05	0.08
Pb	0.33	0.59
Zn	3.6	8.8

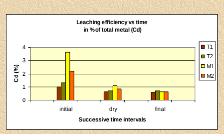

Figure 6 Leaching efficiency of Cd vs time in % of total Cd

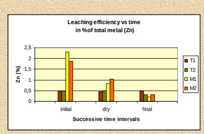

Figure 7 Leaching efficiency of Zn vs time in % of total Zn

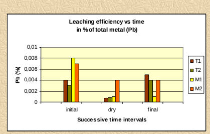

Figure 8 Leaching efficiency of Pb vs time in % of total Pb

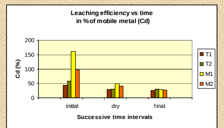

Figure 9 Leaching efficiency of Cd vs time in % of mobile Cd

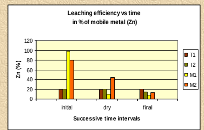

Figure 10 Leaching efficiency of Zn vs time in % of mobile Zn

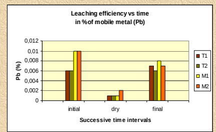

Figure 11 Leaching efficiency of Pb vs time in % of mobile Pb

Leaching efficiency (%) versus time of As, Cd, Cu, Pb, Zn was calculated for every individual microcosm as compared both to the total (Figures 6-8) and mobile metal contents (Figure 9-11) of the original mine waste. Leaching efficiency is given in % leached metal/3 months unit. Cd and Zn exhibit the highest leaching efficiency during the initial average rain phase. In the dry period leaching efficiency decreased to ½ of the initial phase. Leaching of Cd and Zn decreased drastically in the depletion phase, while Pb shows almost 3 fold increase from the dry to the final phase. The buffering capacity of the soil observed in the mine waste+soil containing microcosms substantiated further study on the metal sorption capacity of the soil in contact with the leachate.
The leaching microcosm data provided the parameters for estimation of the long term emission from the sources, the decrease of their contamination, as well as the increase of the concentration and the risk in the surrounding environment.

2. Metal sorption: to simulate the process, that usually occurs in the surrounding area of a mine waste dump in contact with the soil, a short term flow-through microcosm experiment was run. The metal concentration of the soil was measured before and after the flowing through of the metal loaded leachant. The metal concentration of the recovered leachate from the forest and loamy soils was also determined. To give the partition between the polluted soil and the output leachate (Table 5) the metal concentration of the input and output leachates was calculated. As a result of a single flow through of the metal loaded leachate the loamy soil adsorbed 3 times more Cd and 2 times more Zn than the forest soil. The loamy soil hasdthe highest metal sorption capacity for all metals. The extent to which the metal concentration of the soil increased after flow through contact with the metal loaded leachant is given Table 6. The parameters are likely to be used to estimate quantitative risk and plan the necessary risk reduction.

Table 5 Partition between the polluted soil and output leachate

Metals	Leachant metal conc. (µg/ 50ml)	F. soil leachate (µg/l)	L. soil leachate (µg/l)	F. soil leachate % metal	L. soil leachate % metal	F. soil metal sorption % metal	L. soil metal sorption % metal
As	27.5	0.6	0.4	2.2	1.5	97.8	98.6
Cd	31.5	19	1.3	60.3	4.1	39.7	95.9
Cu	195	50	3	25.6	1.5	74.4	98.5
Pb	144	14	5	9.7	3.5	90.3	96.5
Zn	6 200	3 230	319	52.1	5.2	47.9	94.9

Table 6 Metal concentration increase of the soil after addition of metal loaded leachant

Metals	Input Leachant	Forest soil initial conc.	Forest soil final conc.	Loamy soil initial conc.	Loamy soil final conc.
	µg/ 50ml	mg/kg	mg/kg	mg/kg	mg/kg
As	27.5	37	nd	17	18
Cd	31.5	0.2	0.8	0.6	1.7
Cu	195	24	29	33	38
Pb	144	31	25	30	36
Zn	6 200	90	209	100	303

Conclusions

The flow through soil microcosms can be successfully used for the simulation of on site hardly measurable natural processes. The complex processes and parameters can be followed and various scenarios can be modelled. The characteristic parameters of the complex leaching can be used for the long term estimation of the quantity, the nature and fate of the emission from mine waste deposits. The transport pathways, including partition between soil phases can be modelled by the sorption tests, which characterise the most frequent risk-situation at waste disposal sites: the secondary pollution of the surrounding and underlying soil. These two experimental tools allow us to measure transport parameters used in models and to characterise the often debated process, the natural attenuation in case of toxic metal polluted sites.
The above experiments concluded that mobile metals, like Zn and Cd can be completely leached out in a few years from mine wastes exposed to average precipitation : half-time for Cd leaching is about 3 years, for Zn about 6 years, but in case of Pb only 0,1 % will be leached out in 3 years. The increased risk posed on the target environmental elements can be also estimated: a single flow through of contaminated leachate resulted 3-4 fold increase of the Cd-content and 2-3 fold increase of the Zn content in the surrounding soil.

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