

Development of geochemical barriers for a natural demobilization of heavy metals from mine waters

Theofanis Zoumis, Wolfgang Calmano

Dept. of Environmental Science and Technology, Technical University of Hamburg-Harburg,
Eissendorfer Str.40, D-21073 Hamburg, Germany, theofanis@tu-harburg.de

ABSTRACT

The shut-down of ore mines always causes problems with polluted mine waters. The objective of this study is to solve that problem by the development of geochemical barriers which can be filled into shafts to stop a dispersion of heavy metals. The barriers have the purpose to sorb and / or to precipitate heavy metals from mine waters. To have low capital costs the decision is to concentrate on waste material from nature and industry. First results on the use of bark as a barrier are presented. Oak and pine bark seem to be suitable for a retention of zinc, iron, manganese, lead, nickel and cadmium. The sorption rate could be enhanced by an appropriate buffer system.

INTRODUCTION

The *Erzgebirge* is one of the largest ore deposits in Europe and one of the most important mining areas is the *Freiberger Revier*. Ore mining activities were stopped in 1969, and it was decided to discontinue the ground-water lowering. That was the cause for the flooding of the mines. In 1971 the mine water reached the *Reiche Zeche* shaft mouth, which is the main shaft in the *Freiberger Revier*, and caused a discharge through the so called *Rothschönberger* day level (Kluge et al. 1994). From that level the mine water finds its way to the river *Triebisch* which flows into the *Elbe* river.

The drawdown of the groundwater table led to an oxidation of ores in the mine, and consequently they were mobilized by the flooding. This led to a high contamination of surface waters with heavy metals. Year by year the heavy metal content decreased, and reached a relatively high „equilibrium level“ today. The shut-down of the last metalliferous mines in the *Erzgebirge* and consequently their flooding has already started in 1990.

The objective of this research project is to decrease the dispersion of heavy metals by an in-situ remediation. It should be developed an economic system, which is able to hold heavy metals back in the shaft. Since an engineering system has except of high capital costs, also high running costs,

barrier materials are going to be tested, which can be filled into shafts and can remediate mine waters by sorbing or precipitating heavy metals.

Barrier materials are selected under the following criteria:

- * sorption capacity and / or precipitation ability for heavy metals
- * costs
- * availability
- * long-term stability

Costs are very important. Therefore, the decision is to concentrate on waste material from nature and industry. Some possible materials are bark and red mud (sorption barrier), fly ash (sorption and precipitation barrier) and gypsum (precipitation barrier). These materials are characterized (surface area (BET), buffer capacity, sorption capacity). In this paper the tests on bark are presented.

Metals are bound by ion exchange onto the bark surface (Gaballah et al. 1994, Randall et al. 1974). The pH decreases because of the release of hydrogen ions. This decrease could be inhibited by a pretreatment of the bark (Gloaguen and Morvan 1997, Gaballah et al. 1997, Gaballah et al. 1994). Firstly, the sorption capacity without any bark pretreatment is investigated, because it is time consuming and expensive.

MATERIALS AND METHODS

As material for the active barrier bark from a forest south of Hamburg is investigated. It is oak and pine bark, which can be found in high amounts in Central Europe (Benkert et al. 1996, Schönfelder und Bresinsky 1990). The bark is ground, dried and classified into three grain-size ranges ($x < 125 \mu\text{m}$, $125 \mu\text{m} < x < 200 \mu\text{m}$, $200 \mu\text{m} < x < 500 \mu\text{m}$). The preloading with zinc, iron, manganese, cadmium, lead and nickel is determined by digestion and atomic absorption spectrometry (Perkin Elmer PE 1100, Perkin Elmer PE Zeeman/3030 with HGA - 300). The buffer capacity is determined by the acid neutralization capacity (Calmano et al. 1993) and the surface area after BET (NOVA-1200 BET Surface Area Analyzer).

For the investigation of the maximum possible bark load with metal cations, batch tests with an artificial water are conducted. The water is very similar to the mine water from the *Reiche Zeche* shaft (sampling: february 1997). The values for zinc, iron and manganese are intentional higher than the measured ones. They are taken from an analysis after the flooding of the *Reiche Zeche* shaft (Kluge et al. 1994). pH, redox potential, conductivity, oxygen concentration, and important anions and cations are taken into consideration. Exact concentrations of the most important heavy metals can be found in table 1.

Table 1: Concentrations of some heavy metals in the artificial mine water

Element	Concentration (mg/L)
Zn	111
Fe	53,7
Mn	15
Cd	0,1
Pb	0,04
Ni	0,1

Altogether three experiments with each grain-size range are carried out. The mass concentration of bark in the suspension is varied (2,5 mg/L; 5 mg/L; 10 mg/L).

The bark is given into a cleaned plastic vial. After the addition of the artificial mine water, the container is shaken. Samples are taken after different periods of time, and analyzed with AAS to get the sorption kinetics for zinc, iron, manganese, cadmium, lead and nickel.

At the end of each experiment the suspension is filtered and the bark is analyzed concerning sorbed metals to examine the mass balance.

RESULTS AND DISCUSSION

The preloading of the bark is very low but has to be considered in the evaluation of the sorption capacity (table 2).

Table 2: Preloading of the bark with heavy metals

Element	oak bark load ($\mu\text{g/g}$)	pine bark load ($\mu\text{g/g}$)
Zn	22	20
Fe	190	150
Mn	118	60
Pb	-	11
Ni	1	1
Cd	-	2

The acid neutralization capacities lies between 0,05 and 0,1 mmol/g , i.e. the buffer capacity is negligible.

The specific surface areas for pine bark and oak bark are 1,0857 m^2/g and 1,3388 m^2/g respectively. These values are grain-size dependent, but should be taken into consideration in comparison to other materials.

Sorption capacity

The results of all experiments follow the theory elucidated before. The pH sinks rapidly at the beginning of the experiment (during the first minute) from 6,2 to a value around 4 and after that slowly to $3,6 \pm 0,2$. Slight pH deviations refer to different bark surface areas. The bigger the mass and the specific surface area, the stronger the ion exchange between hydrogen ions and metal cations. A pH decrease during the batch tests leads to a lower heavy metal retention, but this pH-change is, because of the mine water buffer capacity (carbonate) in nature, very unlikely. However, the following illustrations show that all considered metals were sorbed.

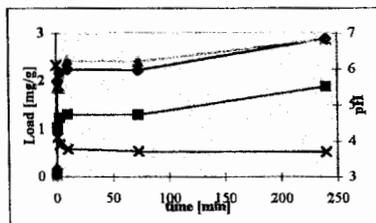


Figure 1: Sorption capacity (10 g/L pine bark) for zinc (x), iron (o), manganese (m)

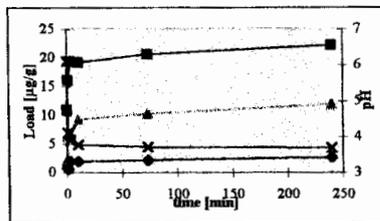


Figure 2: Sorption capacity (10 g/L pine bark) for cadmium (o), lead (m), nickel (x)

Both diagrams show exemplary the sorption capacity of pine bark for several heavy metals. It is an experiment with the grain-size range of $500\mu\text{m} < x < 1000\mu\text{m}$ and a bark concentration of 10 g/L. It is visible that there is a sorption of heavy metals parallel to the pH decrease. As a relatively constant pH value is reached, the sorption increases. Possible reasons could be surface complexation processes and / or coprecipitation (Fe-oxide / -hydroxide).

Further results are similar to the above curves. Oak bark achieved for the same experiment as above for zinc 9 mg/g, for iron 6 mg/g, for manganese 1 mg/g, for lead 24 µg/g, for nickel 25 µg/g and for cadmium 20 µg/g. Sorption capacity could be enhanced by a suitable buffer, e.g. fly ash or lime, which guarantees a neutral pH. After examinations with other materials column tests with active barrier systems will be carried out. By means of more realistic conditions, a better estimation of heavy metal retention is possible.

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