Chemical stabilisation combined with phytostabilisation applied to mine waste contaminated soils

Viktória Feigl[1], Ágota Atkári[1], Nikolett Uzinger[2], Katalin Gruiz[1]

[1] Budapest University of Technology and Economics, Department of Agricultural Chemical Technology, Environmental Microbiology and Biotechnology

Address: 1111 Budapest, Szt. Gellért Sq. 4, Hungary; *Phone:* 0036 1 463 2347; *E-mail:* gruiz@mail.bme.hu, http://envirobiotech.mkt.bme.hu

[2] Research Institute for Soil Science and Agrochemistry of the Hungarian Academy of Sciences, *Address:* 1022 Budapest, Herman Ottó u. 15, *Phone:*0036 1 224 3648

Introduction

The Hungarian **model site of the Difpolmine project** is the **Toka Valley in Gyöngyösoroszi**, which is an area of a **former lead-zinc sulphide ore mine** situated in the Mátra Mountains, Northern Hungary. According to the **Difpolmine approach** applied at the La Combe du Saut site, the identified diffuse pollution sources and the residual pollution area that remain after removal of the point sources will be subjected to **combined chemical and phytostabilisation**.

The aim of the phytostabilisation is to **reduce the mobility of contaminants** in the soil. The plant cover hinders leaching of metals, dusting and erosion, therefore reduces metal transport on all possible transport pathways. The metal amount that get into the food chain are diminished by the application of plants which transport small quantity of metals from the roots to the shoots.

Phytostabilisation is usually combined with **chemical stabilisation**, therefore chemical stabilisers are added to the soil before settling of plants. Chemical stabilisers lower bioavailable toxic metal mobility in the soil, therefore enable settling of plants. Since less metal get into the plant it becomes healthier and produce a higher biomass. The addition of chemical additives to the soil reduce leaching of toxic metals from soils and as a final result lower the environmental risk of the polluted soil and plants grown on it.

Objectives

Before establishing a full-scale phytoremediation on the site of Gyöngyösoroszi, the type of vegetation and the stabilising additive that fits to the local parameters (soil type, slope, exposition, metal concentrations…etc.), has to be finalised. Laboratory and field experiments were done to choose the **suitable plants and additives**.

Before the field experiments preliminary modelling tests were done in **microcosm** at laboratory scale to select the most **suitable chemical stabilizer** for the Gyöngyösoroszi soil. The good immobilising additive should be able to **reduce the mobility and biological availability** of the toxic metals **on long term**.

The following chemical additives were tested: two types of alkaline **fly ash**, **alginite**, **hydrated lime**, **raw phosphate**, **lignite** and the mixture of the latter four. In another microcosm experiment two types of **Fe-Mn-hidroxid precipitate**, **red mud** and a not alkaline fly ash were also tested.

Experimental

Microcosm

The soil samples treated with different additives and the untreated control sample were placed in 2 kg pots each. They were incubated at 25 °C, were mixed and watered every two months. The duration of the experiments varied from 17 to 25 months and the third series of experiments are still going on.

The soil in Gyöngyösoroszi is mainly contaminated with As (170–300 ppm), Cd (6,5–11 ppm), Cu (240–330 ppm) Hg (2–6 ppm), Pb (960–1540 ppm) and Zn (1140–1740 ppm), but out of these metals Cd and Zn are the most mobile for which reason their availability was closer studied. According to the different extractions 26–34% of Cd and 23–24% of Zn is in mobile form (in acetate extract compared to total metal content) and 7–13% of Cd and 6–11% of Zn is water-soluble.

Integrated methodology

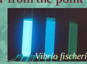
The stabilisation of toxic metals in the soil was monitored by an integrated methodology, which combined physico-chemical analysis with biological and ecotoxicity testing. The chemical analysis included the following measurements:

- dissolvable metal content in water extract,
- mobile metal content in ammonium-acetate (pH=4,5),
- metal content in ammonium-acetate + acetic acid + EDTA,
- total metal content after Aqua Regia digestion.

The metal content of these different extracts was determined by Atomic Emission Spectrometry.

Testing of toxicity and bioaccumulation

In order to assess the risk of the treated soils, toxicity measurements are also needed. Therefore the soils of the microcosms were sampled and tested by bacterial and plant ecotoxicity and bioaccumulation tests. The bacterial tests for predicting the ecotoxicity of the soil included *Vibrio fisheri* luminescence inhibition test and *Azotobacter agile* dehydrogenase enzyme-activity inhibition test. The *Sinapis alba* (white mustard) root and shoot growth inhibition test and the five days plant accumulation test was used for getting direct information on the suitability of the chemical stabiliser from the point of view of the following phytostabilisation process.



Results and discussion

Fly ash treatment:

In the first microcosm experiment two types of fly ash from the power plant in Oroszlány were tested as possible stabilizers for Gyöngyösoroszi soil. Both chemical analytical and bacterial and plant ecotoxicity test results showed that the fly ash is the most effective immobilizing agent for the toxic metal pollution in the Gyöngyösoroszi soil.

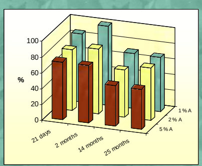


Fig. 1: Acetate extractable zinc in fly ash stabilised soil compared to the non-treated control = 100%

Table 1: Decrease in acetate extractable metal concentrations in soils treated with fly ash „A" compared to the non-treated control = 0%

	As	Cd	Cu	Hg	Pb	Zn
1% fly ash A	<DL	25%	29%	<DL	58%	32%
2% fly ash A	<DL	29%	31%	<DL	56%	33%
5% fly ash A	<DL	45%	30%	<DL	68%	49%

Table 2: Decrease in water soluble metal concentrations in soils treated with fly ash „A" compared to the non-treated control = 0%

	As	Cd	Cu	Hg	Pb	Zn
1% fly ash A	<DL	90%	<DL	<DL	<DL	74%
2% fly ash A	<DL	94%	<DL	<DL	<DL	94%
5% fly ash A	<DL	99%	<DL	<DL	<DL	99%

Decrease in the acetate soluble metal content was observed already 21 days after fly ash addition and the stabilising effect of a single treatment **remained unchanged after 2 years** (Fig. 1). Due to the addition of 5 w% fly ash to the soil the **acetate soluble Zn and Cd decreased by 45–49%,** while the **water soluble** Zn and Cd concentration decreased by **99%** (Table 1 and 2).

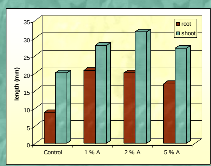


Fig. 2: Root and shoot lengths of *Sinapis alba* test plants on 5 g soil (25 months after treatment)

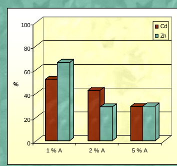


Fig. 3: Decrease in zinc and cadmium uptake of *Sinapis alba* (after 25 months, non-treated control = 100%)

The results of the **toxicity tests** confirmed the results of the chemical analysis, that **the toxicity of the soil was reduced**. The **bacterial** *Vibrio fisheri* and *Azotobacter agile* **test** showed that the **toxicity decreased with ~40%** particularly after 2 and 5 w% of fly ash treatment and the *Sinapis alba* **plant growth** test showed **30–50% reduction in toxicity** even after 1 % fly ash treatment (Fig. 2). The **rapid bioaccumulation test** showed that addition of 5 w% fly ash to the soil **diminished the Cd and Zn uptake** of the test plant **by 58–74%** (Fig. 3).

Lime, phosphate, alginite, lignite:

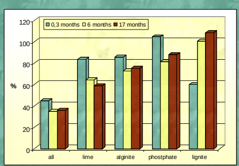


Fig. 4: Acetate extractable cadmium in stabilised soils compared to the non-treated control = 100%

In the second series of microcosm experiments four other additives were tested. These were: hydrated lime (added in 1 w%), alginite (1.5 w%), raw phosphate (1 w%) and lignite (10 w%). Comparing the additives **17 months** after the treatment (Fig. 4, Table 3 and 4) the **mixture** of lignite, alginite, hydrated lime and raw phosphate was the **most advantageous (64–68% reduction in metal mobility)**, since it contained all stabilizers. The second best was **hydrated lime**, which **reduced the metal mobility** with **41–53%**. It also **reduced the toxicity of the soil for bacteria** (Table 5), but it **was not effective** in reducing the toxicity of contaminated soil **for plants**, which would be very important from the point of view of the following phytostabilisation application. **Alginite** reduced the mobile metal solubility with 25–31% and was **effective in reducing bioavailability and toxicity for plants**. **Raw phosphate** was **slightly effective** in reducing metal mobility, but had a stimulating effect for bacteria and plants. **Lignite increased both metal mobilitiy, toxicity** and metal accumulation.

Table 3: Decrease in acetate and water extractable metal concentrations in stabilised soils compared to the non-treated control = 0%

	Acetate extract				Water extract			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
all together	64%	84%	77%	68%	99%	30%	99%	99%
lime	41%	43%	59%	53%	99%	-39%	99%	99%
alginite	24%	41%	49%	31%	84%	33%	71%	92%
phosphate	12%	31%	54%	21%	45%	32%	99%	97%
lignite	-9%	40%	-89%	-31%	-142%	-179%	0%	-199%

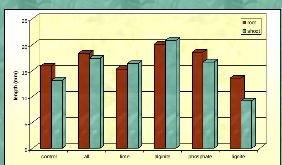


Fig. 5: Root and shoot lengths of *Sinapis alba* test plants on 5 g soil (17 months after treatment)

Red mud, Fe-Mn precipitates and not alkaline fly ash:

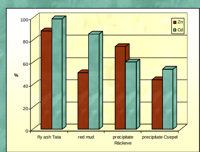


Fig. 5: Acetate extractable cadmium and zinc in stabilised agricultural soils compared to the non-treated control = 100%

Table 4: Decrease in acetate extractable metal concentrations in stabilised soils compared to the non-treated control = 0% (1.5 months after treatment)

	As	Cd	Cu	Hg	Pb	Zn
2 % fly ash Tata	<DL	~0%	-15%	<DL	25%	11%
5 % fly ash Tata	<DL	1%	-16%	<DL	21%	12%
2 % red mud	<DL	3%	-8%	<DL	26%	30%
5 % red mud	<DL	15%	15%	<DL	62%	49%
2 % prec. Ráckeve	<DL	20%	3%	<DL	24%	16%
5 % prec. Ráckeve	<DL	40%	19%	<DL	49%	26%
2 % prec. Csepel	<DL	22%	27%	<DL	84%	27%
5 % prec. Csepel	<DL	46%	99%	<DL	99%	56%

In the third experiment red mud and two types of Fe-Mn precipitates (from the drinking water plants in Ráckeve and Csepel) was added to the soils in 2 and 5 w%. Since the availability of fly ash "A" is limited, a third type of not alkaline fly ash from the power plant in Tata was also tested in soil microcosms. These experiment are **still going on**, they were evaluated in the first **1.5 months**. According to the results of the acetate extractions **5 w% of additive** to the soil was more effective than 2 w%. 1.5 months after the treatment 5 w% **red mud** and the **two Fe-Mn precipitates** from water treatment seems **promising**, since they showed **15–56% decrease in** acetate extractable **Cd and Zn** concentrations. The toxicity measurements show **increasing toxicity** with time in all treated samples, within the examined period of 1.5 months, therefore **the stabilization process has to be followed on a longer term**, to prove the efficiency of the additives.

Ranking of the additives

Table 5: Ranking of the stabilisers according to their effectiveness (+++: most effective, –: not effective)

Additive:	Alkaline fly ashes	Not alkaline fly ash	Lime	Alginite	Raw phosphate	Lignite	Red mud	Fe-Mn precipitates
Water extractability	+++	+/–	+++	+++	++	–	++	++
Acetate extractability	+++	+/–	+++	++	+	–	++	+++
Bacterial toxicity test	+++	++	++	+	++	–	+/–	+
Plant toxicity test	+++	+	+	+++	++	–	++	+/–
Bioaccumulation test	+++	+/–	+++	+++	++	–	+	+/–

Conclusions

The **aim of the experiments** performed **in microcosms** was to **select the best chemical stabilizer**, which could be used combined with pytostabilisation on the metal polluted site, Gyöngyösoroszi in Hungary. Of the additives tested the alkaline **"A" fly ash** showed the **best immobilizing effect on long term** (25 months). The **mixture** of hydrated lime, alginite, raw phosphate and lignite resulted a decrease in the extractability of Zn and Cd, but it was not followed by lower toxicity. Short term treatment (1.5 months) with **red mud and Fe-Mn precipitates** caused a decrease in extractability, but the toxicity has not changed yet. According to the results of the microcosm experiments the promising stabilizers, like fly ash and lime containing mixtures will be tested **in field experiments** in Gyöngyösoroszi.

Acknowledgement

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