Chemical stabilisation combined with phytostabilisation applied to mine waste contaminated soils in Hungary

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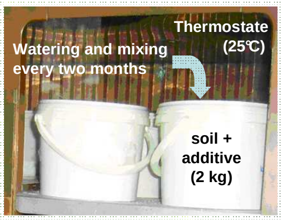
Abstract Gyöngyösoroszi is an abandoned lead-zinc sulphide ore mining area in Hungary. The diffuse pollution sources of mining origin identified in the area and the residual pollution after removal of the point sources will be subjected to combined chemical- and phytostabilisation. To select the best chemical stabiliser laboratory scale experiments were performed in microcosms. The following chemical additives were tested in various concentrations: three different fly ashes, lignite, alginite, hydrated lime, raw phosphate, iron hydroxide wastes from drinking-water treatment, red mud and the mixture of selected ones. The stabilisation of toxic metals in the soil was monitored by an integrated methodology, which combined physico-chemical analysis with toxicity testing. Based on the chemical analytical and the bacterial and plant toxicity test results, one of the tested fly ash types was the most effective: the mobile Cd and Zn concentration decreased by 50–99% in the fly ash treated contaminated soil, the bacterial and plant toxicity decreased by 30-70%, and the bioaccumulated metal amount by 70%. The combination of lignite, alginite, lime and phosphate was also efficient.

Microcosms



Soils and additives

Additives

♣Fly ashes:
- ♣ "A" and "B" from the power plant in Oroszlány, Hungary (added in 1, 2 and 5 w%),
- ♣ "T" from Tata, Hungary (2 and 5 w%) [No. 6]

♣ Alginite (1,5 w%),
♣ Hydrated lime (1 w%),
♣ Raw phosphate (1 w%),
♣ Lignite (10 w%),
♣ Fe-Mn-hydroxide precipitate („C" and „R") from drinking water cleaning in Budapest, Hungary (2 and 5 w%) [No. 3 and 5],
♣ Red mud (2 and 5 w%) from bauxite processing [No. 4].

Soils tested

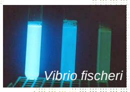
♦ Agricultural soil [No. 1] and spoil material [No. 2] – total metal contents: As 60–333 mg/kg, Cd 4–23 mg/kg, Cu 170–479 mg/kg, Pb 956–1660 mg/kg, Zn 861–4420 mg/kg,
♦ According to the different extractions 26–34% of Cd and 23–24% of Zn are in mobile form (in acetate extract compared to total metal content) and 7–13% of Cd and 6–11% of Zn are water-soluble.

Monitoring by integrated methodology

The complex processes going on in the microcosms were monitored on long term (1 to 2 years), by combined physico-chemical analysis with biological and ecotoxicity testing.

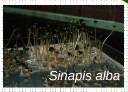
Chemical analysis

♠ Metal-analyses in water-, ammonium-acetate- (pH=4,5) and ammonium-acetate + acetic acid + EDTA-extract.
♠ Total metal content in Aqua Regia extract.
The metal content of these different extracts was determined by IPC-AES.



Toxicity testing and bioaccumulation

In order to assess the actual risk of the treated soils toxicity measurements are also needed. Therefore the stabilisation processes were followed by ecotoxicity and bioaccumulation testing:
♥ *Vibrio fisheri* luminescence inhibition test,
♥ *Azotobacter agile* dehydrogenase enzyme-activity inhibition test,
♥ *Sinapis alba* (white mustard) root and shoot growth inhibition test,
♥ Self-developed five days bioaccumulation test with *Sinapis alba*.

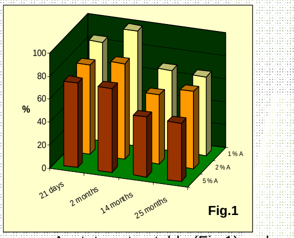


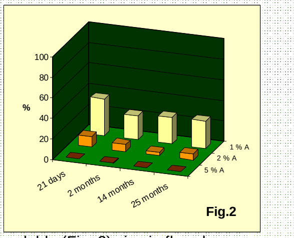
Results

According to the different extractions, one type of fly ash, hydrated lime, and the mixture of hydrated lime, alginite, raw phosphate and lignite showed the best results in immobilising the toxic metals in Gyöngyösoroszi soils (Table 1). The higher the amount of fly ash added (1, 2, 5 w%), the greater was the decrease in the metal mobility (Figure 1 and 2). The results of the toxicity tests proved the results of the chemical analysis, that is the toxicity of the soil was reduced by the addition of fly ashes "A" and "B" (Table 2). The mixture of hydrated lime, alginite, raw phosphate and lignite and hydrated lime alone were nearly as effective as fly ash "B" relative to bioaccumulation, but they did not reduce the toxicity of contaminated soil for plants, which would be very important from the point of view of phytostabilisation.

Table 1. Decrease in acetate extractable and water soluble metal contents in treated soils (decrease in the non-treated control = 0%); selected best results for each amendment

	Fly ash "A"	Fly ash "B"	Fly ash "T"	Lime	Algi-nite	Raw phosph	Lignite	Mixt. of 4	Prec. "R"	Prec. "C"	Red mud
Acetate extractable Cd	**45%**	**30%**	2%	**41%**	24%	12%	-9%	**64%**	53%	64%	42%
Acetate extractable Zn	**49%**	**34%**	12%	**53%**	31%	21%	-31%	**68%**	26%	63%	62%
Water soluble Cd	**99%**	**94%**	53%	**99%**	84%	45%	-142%	**99%**	71%	79%	71%
Water soluble Zn	**99%**	**98%**	83%	**99%**	92%	97%	-199%	**99%**	27%	51%	83%





Acetate extractable (Fig.1) and water soluble (Fig. 2) zinc in fly ash stabilised soil compared to the non-treated control = 100%

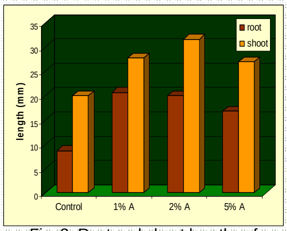


Fig. 3: Root and shoot lengths of *Sinapis alba* test plants on 5 g soil (25 months after treatment)

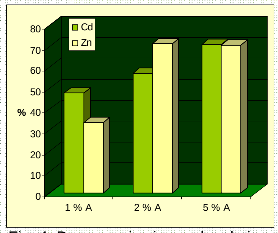


Fig. 4: Decrease in zinc and cadmium uptake of *Sinapis alba* (after 25 months, non-treated control = 0%)

Table 2. Highest decrease in toxicity and metal bioaccumulation in treated soils (decrease in the non-treated control = 0%); selected best results for each amendment

	Fly ash "A"	Fly ash "B"	Fly ash "T"	Lime	Algi-nite	Raw phosph.	Lignite	Mixt. of 4	Prec. "R"	Prec. "C"	Red mud
Bacterial toxicity	**30%**	**30%**	~0%	**80%**	~0%	~100%	~0%	**60%**	0%	0%	0%
Plant toxicity	**70%**	**60%**	62%	**20%**	31%	20%	-15%	**30%**	60%	56%	~0%
Bioaccumulation	**70%**	**74%**	~0%	**70%**	70%	48%	-33%	**70%**	~0%	~0%	~0%

Conclusions

The aim of the experiments performed in microcosms was to select the best chemical stabilizer, which could be used in combination with pytostabilisation on the metal polluted site, Gyöngyösoroszi. Out of the additives tested the "A" fly ash from Oroszlány showed the best immobilizing effect on long term (2 years). One single treatment with 5 w% "A" fly ash reduced the acetate extractable metal amount by 45–49% and the water soluble part by more than 99%. It also reduced soil toxicity for both bacteria and plants and decreased the bioavailable metal amount by 70%. Amongst the other additives some caused decrease in metal extractability, but were not able to reduce the toxicity of soil. According to the results of the microcosm experiments the promising stabilizers will be tested in field experiments in Gyöngyösoroszi.

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