Combined chemical and phytostabilisation of metal polluted soils – From microcosms to field experiments

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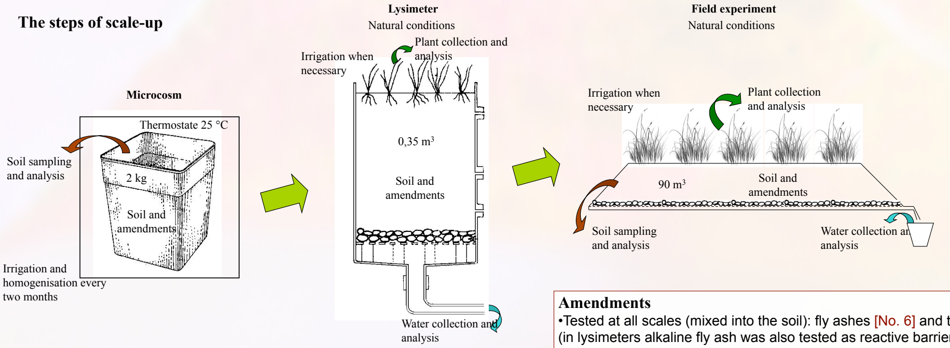
Introduction and objectives The site of Gyöngyösoroszi (Hungary) is heavily polluted with toxic metals, such as Zn, Pb, Cd, Cu and As, due to former mining in the area. The remediation strategy is to apply combined chemical and phytostabilisation on the diffuse pollution sources and the residual pollution, that remains after removal of the point sources. The toxic metals remain in the soil, but their chemical form, mobility, bioavailability, and as a result of these, their risk is drastically reduced. To select the most suitable combination of chemical stabilisers and plants several experiments were performed from laboratory to field scale: laboratory microcosm, pilot lysimeters and field plots. In the microcosms we tested 12 chemical stabilisers, while in lysimeters and field experiments we applied also plants. The most promising stabilising agents were fly-ash and lime which were applied on the field.

The steps of scale-up



Microcosm experiments

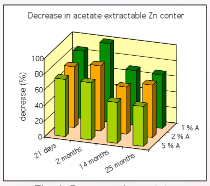


Fig. 1: Decrease in acetate extractable Zn content in fly ash 'A' treated agricultural soil

Long-term microcosm experiments were performed in laboratory for the characterisation of the effect of the different stabilising agents. Chemical analyses and rapid bioaccumulation tests showed the best ones:

1. alkaline fly ash (type 'A' and 'B'),
2. hydrated lime,
3. mixture of non-alkaline fly ash 'T' and lime,
4. mixture of hydrated lime, alginite, raw phosphate and lignite.

However, the phytotoxicity of the soils only decreased effectively in case of the alkaline fly ashes, which is very important from the point of view of the following phytostabilisation.

Table 1. Decrease in metal mobility and toxicity of mine wastes and soil after treatment (non-treated control = 0%); selected best results for each amendment

Test method	Fly ash 'A'	Fly ash 'B'	Fly ash 'T'	'T' + lime	Lime	Alginite	Phosphate	Lignite	Mixt. of 4	Prec. "R"	Prec. "C"	Red mud
Acetate extractable Cd and Zn	**49**	**34**	12	**68**	**53**	31	21	-9	**68**	53	64	62
Water extractable Cd and Zn	**99**	**98**	78	**99**	**99**	92	97	-142	**99**	71	79	83
Bioaccumulated Cd and Zn	**70**	**74**	10	**57**	**70**	70	48	-33	**70**	~0	~0	~0
Plant toxicity	**70**	**60**	62	10	20	31	20	-15	30	60	56	~0

Monitoring by an integrated methodology

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

Chemical analysis

- Soil: water- and ammonium-acetate (pH=4,5) extractable and total metal content (Aqua Regia digestion).
- Plant: nitric acid + hydrogen-peroxide (1:1) digestion.
- The metal content of these different soil extracts and the pore water was determined by ICP-AES.

Toxicity testing and bioaccumulation

In order to assess the actual risk of the treated soils toxicity measurements were also used. Therefore the stabilisation process was followed by specific ecotoxicity and bioaccumulation testing:

- *Vibrio fisheri* luminescence inhibition test,
- *Azomonas agilis* dehydrogenase enzyme-activity inhibition test,
- *Sinapis alba* (white mustard) root and shoot growth inhibition test,
- Five days bioaccumulation test with *Sinapis alba*.

Amendments

- Tested at all scales (mixed into the soil): fly ashes [No. 6] and their combination with lime (in lysimeters alkaline fly ash was also tested as reactive barrier)
- Tested only in microcosms: alginite, hydrated lime, raw phosphate, lignite, Fe-Mn-hydroxide precipitate from drinking water cleaning [No. 3 and 5], red mud from bauxite processing [No. 4].

Plants

Grass mixture, *Sorghum vulgare*, *Sorghum sudanese*, *Zea mays*

Characteristics of the soil and waste

- Agricultural soil [No. 1] and mine waste [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 926–4420 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.

Lysimeters: Stabilisation with fly ash

The stabilisation under natural conditions was examined in lysimeters. The short term results (2 months) of drain water from mine waste and agricultural soil show, that both alkaline and non-alkaline fly ashes are effective in reducing the mobility of Cd and Zn and the phytotoxicity of the drain water. The fly ash applied as a reactive barrier gave similar results to the mixed in form.

Table 2: Effect of fly ashes on Cd and Zn in drain water from heavily weathered waste material containing lysimeters

Treatment	Cd (μg/l)	Zn (μg/l)	Decrease Cd (%)	Decrease Zn (%)
Non-treated	311	53 677		
Fly ash, type 'T'	30.4	6 405	90.2	88.0
Fly ash, type 'V'	0.2	72.5	>99.9	99.9
Fly ash, type 'A'	0.1	15.2	>99.9	>99.9
'A' as reactive barrier	0.1	26.7	>99.9	>99.9

Type 'T' and 'V': non-alkaline, type 'A': alkaline

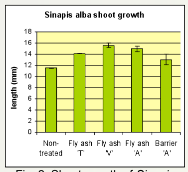


Fig. 2: Shoot growth of *Sinapis alba* test plant on drain water

Field scale: stabilisation of an intensively weathered acidic waste-rock with fly ash and lime

The stabilising effect of fly ashes and their mixture with lime was studied in constructed field plots. Lime addition was needed because of the strongly acidic character of the waste. The water collection from the plots allow us to predict the risk connected to the transport of toxic metals by water (e.g. the infiltrated precipitate). The combination of fly ashes and lime was highly efficient in reducing the mobile metal content and the toxicity of the waste and a healthy vegetation was developed on the treated plots. The metal content of plants grown on the field plots was under or close to the limit value for food and fodder.

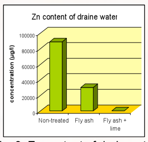


Fig. 3: Zn content of drain water from the field plots

Table 3: Cd and Zn content of drain water from field plots, decrease according to non-treated

Treatment	Cd	Zn	pH
Non-treated (μg/l)	441	89 079	2.9
Fly ash (μg/l)	138	30 380	4.1
Fly ash + lime (μg/l)	2.3	226	7.2
Fly ash (% decrease)	68.8	65.9	
Fly ash + lime (% decr.)	98.5	99.7	

Hungarian limit value for underground water is 5 μg/l for Cd and 200 μg/l for Zn.

Table 4: Effect of fly ash + lime treatment on the waste material

Monitoring	Decrease
Acetate extracted metal conc.	85%
Water extracted metal conc.	99%
Bioaccumulated metal conc.	84%
Toxicity	75%
Soil activity (increase)	100×

Fig. 4: Non-treated plot in August

Fig. 5: Grass on fly ash + lime treated plot in August

Fig. 6: *Sorghum* species on fly ash + lime treated plot in August

Field scale: Stabilisation of agricultural soil with fly ash

In this field experiment agricultural soil (pH=6,6) contaminated with metal containing river sediment was treated with the non-alkaline fly ash 'T'. The other half of the area was left untreated and used as a control. The acetate and water extractable metal content of the soil, and also the bioaccumulated metal amount in the plants applied for phytostabilisation decreased by 80–92% due to the treatment. In the treated area higher biological activity was measured in the soil and the toxicity decreased with 25–30%.

Table. 5: Effect of fly ash treatment on agricultural soil

Test method	Non-treated (mg/kg)	Fly ash treated (mg/kg)	Decrease (%)
Acetate extracted Cd	1.54	0.275	82
Water extracted Cd	0.051	<0.004	92
Bioaccumulated Cd	6.63	0.72	89
Acetate extracted Zn	237.4	47.7	80
Water extracted Zn	4.106	0.315	92
Bioaccumulated Zn	503	108	79

Total metal content of soil: 5.23 mg/kg Cd and 1102 mg/kg Zn.
Hungarian limit value for food and fodder is 1.0 for Cd and 100 for Zn.

Fig. 7: *Sorghum* species and *Zea mays* on the agricultural experimental area in July

Conclusions Combined chemical and phytostabilisation is an effective technology for the risk reduction of toxic metal polluted soil and waste. The unvegetated, barren, diffusely polluted surface of the former mining site became a suitable habitat for plants and as a consequence the quality of runoff and infiltrated waters improved. The best chemical stabilizer, which could be used in combination with phytostabilisation on the metal polluted site was selected after microcosm and lysimeter experiments. The alkaline 'A' fly ash showed the best immobilizing effect on the acidic mine waste on long term (2 years), but the not alkaline ones mixed with lime gave similar results. One single treatment with 5 w% 'A' fly ash reduced the acetate extractable metal content by 45–49% and the water soluble part by more than 99%. Soil toxicity and bioaccumulation decreased by 70%. The Zn and Cd concentration in the drain water of the field plot decreased with 98–99% and the phytotoxicity of the soil diminished to 25%. The non-alkaline fly ash without lime was efficient in reducing the water and acetate extractable Zn and Cd amount in contaminated agricultural soil by 92% and the plants grown on the treated area accumulated 70–90% less Zn and Cd. According to the results from both experiments the fly ash treatment combined with phytostabilisation is an effective tool in reducing metal mobility and the risk of metals to surface and subsurface waters and living organisms in the contaminated area of the former lead and zinc mine in Hungary.

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