Poster Session

COMBINED CHEMICAL AND PHYTOSTABILISATION OF METAL POLLUTED SOILS – FROM MICROCOSMS TO FIELD EXPERIMENTS

Viktoria Feigl[1], Attila Anton[2], Ferenc Fekete[3], Katalin Gruiz[1]
[1] Budapest University of Technology and Economics, 1111 Szent Gellért tér 4., Budapest, Hungary, +36-1-463-2347, vfeigl@mail.bme.hu; gruiz@mail.bme.hu
[2] Research Institute of Soil Science and Agrochemistry of the Hungarian Academy of Sciences, 1022 Herman Ottó u. 15., Budapest, Hungary, +36-1-356 4682, anton@rissac.hu
[3] Mecsek-Öko Inc., 7633 Esztergár Lajos u. 19., Pécs, Hungary, +36-72-535-260, feketeferenc@mecsekoko.hu

Keywords: soil, remediation, stabilisation, toxic metals, stabilising agents, fly ash, combined chemical and phytostabilisation, mining site remediation

Abstract

The metal polluted area of a former zinc and lead mine will be subjected to combined chemical and phytostabilisation. To select the suitable chemical immobilising agent for soil and mine waste materials laboratory and field experiments were performed. The metal immobilisation process was monitored by an integrated methodology, a combination of physico-chemical analysis and ecotoxicity testing. During the development we applied a stepwise scale-up from 2–5 kg microcosm, through laboratory and open-air pilot lysimeters to the field plots. According to the microcosm experiments alkaline fly ashes showed the best results in the long term (2 years) immobilisation of toxic metals (Zn, Cd, Pb and Cu) in the soil. The addition of 5 w/w% fly ash to the soil decreased the water soluble metal content by 99% and the acetate soluble fraction by 50%. In addition to the extractability of metals the bioavailability and as a consequence the toxicity also decreased. The combination of 5 w/w% non-alkaline fly ash and 2 w/w% lime was as effective as the alkaline fly ash, while the non-alkaline fly ashes alone also decreased metal mobility and toxicity, but a bit slower. The lysimeter results proved the toxicity reducing effect of the fly ashes on soil and drain-water and the advantages of fly-ash application as a reactive barrier. The plot experiments completely confirmed the results of the microcosm and pilot lysimeter experiments: the toxic metal content and toxicity of the pore water was reduced, the growth of the vegetation was stimulated, the efficiency of the vegetation in controlling runoff and erosion increased significantly.

1. Introduction

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. A complex survey was carried out in the area to assess the impacts of the mining activity (Gruiz and Vodicska, 1992, 1993; Horváth et al., 1996). The results of the environmental survey indicated that heavy metal contamination of the examined area creates a high environmental risk therefore risk reduction is necessary on the site (Gruiz et al, 2005, 2007).

The remediation strategy for diffuse pollution sources and residual pollution areas that remain after removal of the point sources will be subjected to a combined chemical and phytostabilisation. The aim of the chemical stabilisation is to reduce the mobility and bioavailability of contaminants in the soil, and as a result to stop transport by water and plants and lower risk of the contaminants for surface water system and food chain. The plant cover normalises water cycle of the soil, hinders leaching of metals by precipitation, stops wind and water erosion, therefore reduces metal transport on all possible transport pathways. The metal amount that gets into the food chain is further diminished by the application of plants which take up small quantity of metals and do not transport from the roots to the shoots.

The feasibility and efficiency of phytostabilisation combined with chemical stabilisation has already been proven by Vangronsveld et al. in 1995a; and applied for toxic metal contaminated land in some cases (Mench et al., 2003; Vangronsveld et al., 1995b). Chemical stabilisers are added to the soil before settling of plants. Chemical stabilisers lower bioavailable toxic metal content in the soil, therefore enable germination and growth of the plants. Since less metal gets into the plant it becomes healthier and produces a higher biomass. The addition of chemical additives to the soil also reduce water solubility and transport by water of toxic metals from soils and as a final result lower the environmental risk of the polluted soil and plants grown on it.

2. Objectives

Our aim was to select suitable chemical stabilisers, well growing plants and their combination for the typical mine wastes and contaminated soils of the area. To find the best stabiliser and stabiliser–plant combination scaled-up experiments were performed with selected immobilising agents. The main goal of the experiment was to develop an innovative remediation technology, which is able to reduce the risk of the former mining site and as a priority to ensure surface water quality at catchment scale. The risk reduction by combined chemical and phytostabilisation is a part of a complex risk management strategy, which uses GIS based, catchment scale risk assessment. On the basis of the GIS-based risk model of the catchment, the target emission of diffusely spread mine-waste and non vegetated surfaces after removal of point-type waste sources has been calculated. The requirement of the catchment scale risk management concept is, that the combined chemical and phytostabilisation technology should fulfil the reduced target emission from the diffuse sources (Gruiz et al., 2008)

3. Experimental setup

To find the best stabiliser and stabiliser–plant combination scaled-up experiments were performed with selected immobilising agents. The scale-up had three steps: laboratory microcosm experiments in pots and flow-through columns (mini-lysimeters), pilot experiments in open-air lysimeters and field experiments of different size field plots. Some of the field plots were equipped with a drain-system for collecting and sampling pore water to follow the water-cycle and contaminant transport by water. In the microcosm experiments we tested the effect of chemical stabilisers, and the leaching of toxic metals. Open-air lysimeters are suitable for following the fate of water, the effect of reactive barriers and also plants can be grown on their surface. Field experiments were carried out on typical soils and wastes of the area: mine waste rock, highly weathered mine waste, agricultural soil polluted by contaminated sediment through floods. On the fields chemical stabilisation was combined with phytostabilisation, using grasses or grass mixtures, agricultural cultivars, like maize and industrial plants like *Sorghum sudanense* and *Sorhum vulgare*.

Microcosms for chemical stabilising experiments: Two types of alkaline (type A, B) and two types of non-alkaline (type T, V) fly ash from different origins, lime and other additives, such as raw-phosphate, alginite, lignite, Fe-Mn-hydroxide precipitate, red mud and the mixture of some additives were tested in microcosms including toxic metal contaminated mine wastes and soils. The microcosms were composed of 2 kg soil mixed with different stabilisers and were incubated at 25 °C for 2 years. After 2 years stabilisation the mobility of the metals was tested in the chemically treated soil in mini-lysimeters.

The open-air lysimeter setup: 0.34 m^3 soil and stabiliser mixture was placed in a concrete cylinder and exposed to natural conditions. In the open-air lysimeters we tested 3 fly ash types (A, T and V) mixed to agricultural soil and mine waste material. We also applied one of the fly ashes (A) as a flow through layer in the lysimeter, simulating a reactive barrier.

In the field experiments 3 different treatments were tested on 6x10 and 15x40 m field plots. The metal stabilising effect of the fly ash and of its mixture with lime was tested on different mine waste materials: intensively weathered acidic waste-rock and contaminated soil of flooded agricultural area. In the field experiments we combined chemical stabilisation with phytostabilisation, therefore four plant species were sowed on the chemically treated and control soils: grass mixture, two *Sorghum* species and sweet corn. The lysimeter and the field experiments have been run for one year so far.

4. Technology-monitoring

Technology monitoring aims to follow the effect of the additives on toxic-metal concentrations and chemical forms in soil, dissolved concentration in pore water and accumulated amount in plants. The addition of stabilizers result complex changes in the soil. The metal mobility, solubility and bioavailability are changing continuously until the new equilibrium. In our experiments the process was monitored on long term, to reach the equilibrium state for most of the soil-processes, and differentiate reversible and irreversible processes. It may occur that a stabiliser seems to be effective on short term, but does not immobilize metals during a longer period.

The stabilisation of metals was monitored by an integrated methodology, which combined physico-chemical analysis with toxicity testing. The chemical analyses of the soil included the measurement of the toxic metal in extracts prepared by distilled water, acetate (ammonium-acetate, pH=4.5) and a stronger organic acidic extractant (ammonium-acetate + acetic acid + EDTA, called Lakanen-Erviö), as well as the total metal content measured after aqua regia extraction by atomic emission spectrometry (ICP/AES). By water extraction we aim to model the mobile metal amount, which can be washed out by rain water. The acetate extract is the pessimistic model of water extraction, simulating the maximal water soluble metal amount.

To study the dynamics of leaching in soil and the irreversibility of the chemical stabilisation beside batch extraction we applied a more realistic model using a filled-column leaching test in mini-lysimeters. 200 g stabilised soil was washed with rain water for 10 days. 12 fractions were collected and their toxic metal content was analysed.

In order to assess the actual risk of the treated soils toxicity was tested. The experiments were monitored by bacterial, plant and animal toxicity tests and plant bioaccumulation tests. To follow bioavailability and accumulation a rapid plant accumulation test with *Sinapis alba* was developed and performed. The bacterial tests for predicting the risk of the soil included *Vibrio fisheri* luminescence inhibition test and *Azomonas agilis* dehydrogenase enzyme-activity inhibition test. The *Sinapis alba* (white mustard) root and shoot growth inhibition test and a five days bioaccumulation test were used for getting direct information on the suitability of the chemical stabiliser from the point of view of the plant: its growth and its metal uptake. These are important technological and risk parameters in support of the selection and growing of the plants and assess food-chain risk due to vegetation. The *Tetrahymena pyriformis* growth inhibition test was applied to predict the toxic effect of the treated soils on animals.

The chemical analytical results were evaluated together with the toxicity and bioaccumulation results. In addition to soil sampling, pore-water sampling was possible from the lysimeters and field plots. The field plots allowed detailed plant assessment (growth rate and density) and plant sampling/collection for chemical analyses.

5. Results

5.1 The diffuse pollution and the contaminants of the former mining site

The soil in Gyöngyösoroszi is mainly contaminated with As, Cd, Cu, Hg, Pb and Zn, but of these metals Cd (total content 4.2–23.3 mg/kg) and Zn (total content 926–4420 mg/kg) are the most mobile, endangering surface waters and food chains through plants. For that reason their availability was more closely studied. According to the acetate-extracted ration, 26–34% of total Cd and 23–24% of total Zn are in mobile form. 7–13% of total Cd and 6–11% of total Zn are water-soluble. Mine wastes and soils containing a high amount of As or Pb, their mobility has to be decreased by the use/addition of other amendment, such as zero valent iron (Kumpiene, 2006). In our study/case we concentrated on Cd and Zn, because they represent the highest risk for the water quality of the catchment area in Gyöngyösoroszi.

5.2 Effect of the chemical stabilisers

Before the establishment/start of lysimeter and field experiments long-term microcosm experiments were performed in laboratory (Feigl et al., 2007) for the characterisation of the effect of the different stabilising agents. Chemical analyses of the different extracts from the long term stabilisation showed that the alkaline fly ash (Type A and B), hydrated lime, and the mixture of hydrated lime, alginite, raw phosphate and lignite showed the best results in immobilising the toxic metals in Gyöngyösoroszi agricultural soils (Table 1). A non-alkaline fly ash (type “T”) together with lime proved to be as efficient as the alkaline fly ash alone in a six moths experiment. Due to the treatments the Cd and Zn concentrations in the pore water go under the limit values for groundwater (given by the Hungarian law), which are 5 μg/l for Cd and 200 μg/l for Zn. In the fly ash “A” treated soil 0,3 μg/l Cd and 32 μg/l Zn was measured (in 1:10 water extract) two years after the treatment.

Amongst the tested fly ashes the alkaline fly ash type “A” was the most efficient in reducing the mobile metal content of the soil. Its immobilising effect was observed 21 days after addition and remained unchanged after 2 years. The higher the amount of fly ash added (1, 2, 5 w%), the greater was the decrease in the metal mobility. Fly ash “B” was also efficient, but the non-alkaline fly ash “T” and “V” (not shown in the table) did not reduce the acetate extractable metal content effectively. These differences in efficiency might be due to the different origin and composition of fly ashes, which is reportedly (Vangronsveld et al., 1996) the two crucial factors determining the metal immobilising potential of ashes. Besides sorption and crystal growth, the alkalizing effect also reportedly contributes to the immobilising effect of fly ash, therefore the differences in effectiveness might be due to the different alkalinity of the tested ashes. The fly ashes originating from the Oroszlány power plant are highly basic: fly ash “A” pH=12.60; fly ash “B” pH=9.66, while fly ash “T” from Tata (pH=7.2) and “V” from Visonta (pH=6.4) are not alkaline ones, therefore they were not able to shift the pH of the acidic Gyöngyösoroszi soil (pH= 5.54) to the alkaline domain.

Amongst the other amendments tested the best results after 1–1,5 years treatment were given by the mixture of hydrated lime, alginite, raw phosphate and lignite. Lime alone reduced metal mobility effectively, alginite was highly efficient for all present metals, and raw phosphate was effective in reducing the mobility of Zn. The examined wastes showed surprisingly high efficiency: comparing the two Fe–Mn precipitates from drinking water treatment type “C” was more effective than type “R”, especially in reducing the mobility of Zn, and both types were more effective for Cd than for Zn. Red mud reduced the mobility of all of the metals in the contaminated soil. In all cases, when an additive was tested at more than one concentration, the higher amount was more efficient. Lignite highly enhanced the water solubility of toxic metals in the soil, so it is not suitable for stabilisation of metals like Cd and Zn.

Table 1: Decrease in acetate extractable and water soluble metal contents in treated soils – selected best result of each chemical stabiliser

	Fly ash “A”	Fly ash “B”	Fly ash “T”	“T” + lime*	Lime	Algi nite	Raw phosph	Lignite	Mixt. of 4	Prec. “R”	Prec. “C”	Red mud
Soil type	Agricult ural	Agricult ural	Agricult ural	Mine waste	Agric ult.	Agricu ltural	Agricult ural	Agricul tural	Agric ult.	Mine waste	Mine waste	Mine waste
Cd acetate extracted (mg/kg, non-treated)	2.3	2.3	1.2	1.1	3.1	3.1	3.1	3.1	3.1	2.5	2.5	2.5
Zn acetate extracted (mg/kg, non-treated)	302	302	171	198	455	455	455	455	455	221	221	221
Cd acetate extracted (%, treated)	**45%**	30%	2%	**48%**	**41%**	24%	12%	-9%	**64%**	**53%**	**64%**	42%
Zn acetate extracted (%, treated)	**49%**	34%	12%	**68%**	**53%**	31%	21%	-31%	**68%**	26%	**63%**	**62%**
Cd water soluble (mg/kg, non-treated)	1.8	1.8	0.01	0.34	1.17	1.17	1.17	1.17	1.17	0.02	0.02	0.02
Zn water soluble (mg/kg, non-treated)	152	152	0.48	57	236	236	236	236	236	0.62	0.62	0.62
Cd water soluble (%, treated)	**99%**	94%	53%	**99%**	**99%**	84%	45%	-142%	**99%**	71%	79%	71%
Zn water soluble (%, treated)	**99%**	**98%**	78%	**99%**	**99%**	**92%**	**97%**	-199%	**99%**	27%	51%	83%

*6 months results for fly ash “T” + lime. Other results represent 2 years stabilisation. % decrease is expressed compared to the untreated control = 0%, which values are given in mg/kg

The results of the toxicity tests in most cases agreed with the results of the chemical analysis, the toxicity of the soil was best reduced, by the addition of fly ashes “A” and “B” (Table 2). The bacterial *Vibrio fisheri and Azomonas agilis* test showed that the toxicity decreased by ~30% particularly after 2 and 5 w% of fly ash treatment and the *Sinapis alba* plant growth test showed 60–70% reduction in plant toxicity. The rapid bioaccumulation test showed that addition of 5 w% “A” fly ash to the soil diminished the Cd and Zn uptake of the test plant by 60–70%. One year after treatment with 2 w% fly ash “T” the toxicity for plants decreased with 26–62%, but 5 w% of the amendment caused 5–37% increase in plant toxicity, although the results from chemical extractions showed higher effectiveness for higher concentrations of fly ash. The same results were obtained from the plant bioaccumulation test: 2 w/w% of fly ash “T” caused 3–11% decrease in the metal uptake, while 2 w/w% caused 5–18% increase. The non-alkaline fly ash together with lime caused 70% decrease in bacterial toxicity and increased the growth rate of *Tetrahymena pyriformis* 10 times, but it was only slightly effective in reducing plant toxicity, which was also observed in case of non-alkaline fly ash and lime, when they were applied separately. The fly ash in combination with lime diminished the metal uptake of plants by 35–57%, which can be considered as a suitable reduction, fulfilling environmental and food quality criteria, which is 0.5 mg/kg for Cd and 100 mg/kg for Zn according to the Hungarian law. It is important to notice, that the test plants in the beginning of their growth period accumulate a large amount of metals, ten times more than other plants and also as the test plant itself when it gets older. The metal amounts measured in the plants grown on the non-treated control are above limit value, but the suitable stabilisers are able to reduce the metal uptake of the test plant, ensuring lower value, that the quality criteria.

Table 2: Highest decrease in toxicity and metal bioaccumulation in treated soils

	Fly ash "A"	Fly ash "B"	Fly ash "T"	"T" + lime	Hydr lime	Alginite	Raw phosph.	Lignite	Mixture of 4	Prec. "R"	Prec. "C"	Red mud
Bacterial toxicity	**30%**	**30%**	~0%	**70%**	**80%**	~0%	~100%	~0%	**60%**	0%	0%	0%
Plant toxicity	**70%**	**60%**	62%	10%	20%	31%	20%	-15%	**30%**	60%	56%	~0%
Bioaccumulated Cd (mg/kg)	3.0	3.0	2.2	0.72	2.6	2.6	2.6	2.6	2.6	2.1	2.1	2.1
Bioaccumulated Zn (mg/kg)	743	743	118	190	585	585	585	585	585	217	217	217
Bioaccumulation	**70%**	**74%**	10%	57%	70%	70%	48%	-33%	**70%**	~0%	~0%	~0%

Decrease is given in %, compared to the non-treated control = 0%, bioaccumulated amounts given for dry weight

The toxicity and bioaccumulation test-result refine the picture got on the basis of chemical analyses. The mixture of hydrated lime, alginite, raw phosphate and lignite was nearly as effective as fly ash "B" relevant to bioaccumulation, but plant toxicity reduction of the mixture is less than that of fly ash A and B. Hydrated lime reduced the toxicity of the soil for bacteria and the bioavailability of metals effectively, but did not reduce the toxicity of contaminated soil for plants, which is an important criterion from the point of view of phytostabilisation. Alginite was effective in reducing bioavailability and toxicity for plants, but not for bacteria. Raw phosphate effectively decreased bacterial toxicity, but did not efficiently reduce plant toxicity and metal bioaccumulation. It is also possible that the additive itself has a toxic effect on the testorganisms. The toxicity and bioaccumulation results proved the results of the chemical extractions for lignite, which means that lignite addition enhanced metal mobility and availability. Two-month results from the application of the two Fe–Mn precipitates from water treatment and the red mud showed no change in toxicity and bioavailability, while after one year the plant toxicity test showed that both two Fe–Mn precipitates decreases toxicity with 60%.

5.3 Chemical stabilisation under natural conditions: pilot experiment in lysimeters

Lysimeters were applied to examine the stabilisation processes under natural conditions. Their advantages are that they are cheaper than field tests, they need less space for construction, allow pore-water collection and the number of parallels and different combinations is not as much restricted by space and costs than in case of field experiments. Therefore we constructed ten lysimeters to study the stabilizing effect of fly ashes on mine waste and agricultural soil.

The short term results (2 months) from water analysis for the mine waste material shows, that both the alkaline fly ash "A" and the non-alkaline fly ash "V" caused 99% decrease in the concentration of Zn and Cd according to the non treated control (mine waste), while the non-alkaline fly ash "T" caused 88–90% decrease (Table 3).

Table 3: Decrease in the metal concentrations of drain-waters of the lysimeters, 2 months after mine waste stabilisation, compared to untreated control (0%)

Treatment	Cd	Cu	Pb	Zn	pH
Untreated	311 µg/l	111 µg/l	5.3 µg/l	53 677 µg/l	4.34
Fly ash "T"	90.2%	97.6%	39.6%	88.0%	6.90
Fly ash "V"	>99.9%	98.8%	71.7%	>99.9%	7.42
Fly ash "A"	>99.9%	98.0%	71.7%	99.8%	7.23

The *Vibrio fischeri* bacterial toxicity test could not show any difference between the treatments, but the shoot growth of *Sinapis alba* was increased by 23% in the non-alkaline fly ash treated waste, while fly ash "V" and "A" caused 30–35% increase in plant growth which correlates well with the analytical results. The fly ash "A" applied as reactive barrier only decreased plant toxicity 12% although according to the analytical results it showed as good efficiency when it was mixed to the soil.

The lysimeter results for the agricultural soil indicates that the three applied fly ashes have nearly the same effectiveness in decreasing metal mobility. The 300 µg/l Cd and 51 938 µg/l Zn measured in the drain-water decreased with 92–96% in case of Cd and 97–98% in case of Zn. According to the *Sinapis alba* shoot growth test on drain-water only the fly ash "V" was effective in reducing toxicity of the agricultural soil.

To understand the processes in the lysimeters the experiments are planned to be continued at least for one more year.

5.4 Field experiments

5.4.1 Stabilisation of an intensively weathered acidic waste-rock with fly ash and lime

The stabilising effect of fly ashes was studied in three field plots which were constructed from intensively weathered mine waste. One plot was treated with fly ash "T" and "V" mixed with lime, the second only with fly ash "T" and the third plot was applied as untreated control. Each plot's drain-waters were separately collected with drainage systems, the drain-water, the waste material and the plants were sampled periodically.

The water collection from the plots allow us to get kind of average sample from the highly heterogenous waste material and makes possible to predict the risk connected to the transport of toxic metals by the infiltrated precipitate. The Zn and Cd concentration of the collected drain-water on the effect of the treatment with fly ash "T" alone decreased with 66–69%, while the combination of fly ash and lime was able to reduce it with 98–99%. Due to the fly ash + lime treatment the Cd concentration measured in the drain-water goes under the limit value for groundwater (given by the Hungarian law) which is 5 µg/l and close to the one for Zn, which is 200 µg/l. The close vegetation will further decrease the metal concentrations in the drain-water. The concentrations measured in the drain-water and the rate of decrease due to the treatments is shown in Table 4.

Table 4: Decrease of metal content in the drain water from the filed plots (average value of 7 samples) compared to the non-treated control (0%)

	Cd	Cu	Zn	pH
Metal content of the drain-water from the untreated plot (µg/l)				
Untreated	441	1 510	89 079	2.9
Fly ash "T"	138	89	30 380	4.1
Fly ash "T" and "V" + lime	2.3	14	226	7.2
Decrease in metal content due to the treatments (%)				
Fly ash "T"	68.8	94.1	65.9	
Fly ash "T" and "V" + lime	98.5	99.1	99.7	

The ecotoxicological measurements proved the efficiency of the treatments, the toxicity of the water samples changed from toxic to non-toxic according to the *Vibrio fischeri* bacterial test and the plant growth of *Sinapis alba* increased 5 times.

The water and acetate extractable metal content of the waste has also decreased as expected from the drain-water. The amount of Zn, Cd and Pb extractable by distilled water decreased by more than 99% in the fly ash + lime treated waste material. The fly ash treatment alone was also proved to be effective, but to a smaller extent. The microbial activity in the soil increased 100 times due to the treatment with the mixture of fly ash and lime, and toxicity of the waste after both treatments decreased by the same rate.

The metal content of the plants grown on the field plots was diminished under the limit value for food and fodder. On the untreated plot the plants were not able to grow at all, which proves the importance of the application of chemical stabilisers before the sowing of plants.

5.4.2 Stabilisation of agricultural soil with fly ash

In an other field experiment agricultural soil 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 efficiency of the treatment was followed by the change in the water and acetate extractable metal content and the toxicity of the soil and the measurement of the accumulated metal amount in the plants grown on the plots. Since the area closer to the Toka-creek is more contaminated with metals due to floods, we divided the area into two parts: one within 5 meters distance from the creek and the other, which was further than 5 meters.

In Table 5 the results of water and acetate extracts of the treated and untreated soil near the creek are shown. The acetate extractable Zn, Cd and Pb content of the soil decreased by 80–82% due to the treatment with fly ash "T", while the water extractable metal content decreased with 92%. The amounts of Cu measured are not significant, because the area was treated with copper containing pesticides previously.

The biological activity measurements of the soil show that the soil microflora is active despite of the high toxicant contamination, the microflora of the flooded area has already been adapted to the long term toxic metal contamination. In the treated area higher activity was measured than in the non-treated one. The *Sinapis alba* root and shoot growth inhibition test showed that the fly ash treatment causes 25–30% increase in plant growth and the *Vibrio fischeri* luminescence inhibition test showed 15% decrease in the toxicity, which value is still in the toxic category.

Table 5: Decrease of metal content in acetate and water extracts of the stabilised agricultural soil compared to the non-treated control (0%)

	Non-treated (mg/kg)	Fly ash treated (mg/kg)	Decrease compared to non-treated (%)
Total Cd	5.23		
Acetate extractable Cd	1.54	0.275	82.2
Water extractable Cd	0.051	<0.004	92.1
Total Zn	1101.7		
Acetate extractable Zn	237.39	47.70	79.9
Water extractable Zn	4.106	0.315	92.3

(Total metal content measured after aqua regia digestion)

The next table shows the metal content measured in the plants grown in the field (Table 6). The grass mixture was not able to grow in the area because of the weeds, which overgrow grasses. The metal concentrations in the plants grown in the area (*Zea mays, Sorghum sudanense, Sorghum vulgare*) decreased under the limit value for food and fodder given by the Hungarian regulation. In the two *Sorghum* species the Zn and Cd concentration decreased with 70–90% due to the fly ash treatment, in the *Zea mays* root and leaves reached only 35–80 %.

Table 6: Metal content of plants grown in the agricultural experimental area compared to the non-treated control (0%)

Plant	Treatment	As	Cd	Cu	Pb	Zn
Metal content of plants close to the creek (mg/kg)						
Sorghum sudanense	Non-treated	0.78	3.00	7.90	3.32	348
	Treated	0.45	0.90	6.00	2.20	104
Zea mays	Non-treated	4.66	5.29	21.10	25.42	665
	Treated	1.00	1.59	13.30	5.62	301
Sorgum vulgare	Non-treated	0.51	6.63	11.10	6.25	503
	Treated	0.53	0.72	10.50	1.86	108
Decrease compared to non-treated (%)						
Sorghum sudanense		42.3	70.0	24.1	33.7	70.1
Zea mays		78.5	69.9	37.0	77.9	54.7
Sorgum vulgare		-3.9	89.1	5.4	70.2	78.5
Limit value for animal fodder		2.0	1.0		10.0	
Limit value for fresh vegetable		2.0	0.5	100	3.0	100

These result show that the non-alkaline fly ash “T” was able to reduce metal mobility in the soil.

6. Conclusions

The aim of the experiments performed in laboratory, pilot and field scale was to select the best chemical stabilizer, which could be used in combination with pytostabilisation on the metal polluted site, Gyöngyösoroszi to reach fast growth and complete cover to stop transport by water and erosion. Amongst the additives tested in microcosms 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 were tested in field experiments in Gyöngyösoroszi.

The experiments in lysimeters and field plots proved the efficiency of fly ash, especially when it was applied together with lime on mine waste material. The Zn, Cd and Pb concentration in the leachate from the field plot decreased with 98–99% and the phytotoxicity of the soil diminished to the fifth. The non-alkaline fly ash "T" 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 in the contaminated area of the former lead and zinc mine in Hungary.

7. Acknowledgement

The research work was performed with the financial support of the "DIFPOLMINE" EU Life 02 ENV/F000291 Demonstration Project (www.difpolmine.org), the "BANYAREM" Hungarian GVOP 3.1.1-2004-05-0261/3.0-R&D Project (www.eugris.info/Projects) and the "MOKKA" Hungarian R&D Project, NKFP-020-05 (www.mokkka.hu).

References

Feigl, V., Atkári, Á., Anton, A., Gruiz, K.: Chemical stabilisation combined with phytostabilisation applied to mine waste contaminated soils in Hungary, Advanced Materials and Research, Vols. 20-21, pp. 315-318, 2007

Gruiz, K. and Vodicska, M.: Assessing Heavy Metal Contamination in Soil Using a Bacterial Biotest – Soil Decontamination Using Biological Processes, International Symposium (Karlsruhe, 1992) Preprints, pp. 848–855, Dechema, Frankfurt am Main, 1992

Gruiz, K. and Vodicska, M.: Assessing Heavy-metal Contamination in Soil Applying a Bacterial Biotest and X-ray Fluorescent Spectroscopy – In: Contaminated Soil '93, Eds. (F. Arendt, G.J. Annokkée, R. Bosman and W.J. van den Brink) Kluwer Academic Publ., The Netherlands, pp. 931–932, 1993

Gruiz, K.; Vaszita, E. and Siki, Z.: Environmental Risk Management of Mining Sites with Diffuse Pollution – In: Conference Proceedings, CD (9th International FZK/TNO Conference on Soil-Water Systems, 3–7 October, 2005, Bordeaux) Theme F, Eds. O. Uhlmann, G.J. Annokkée, F. Arendt, pp. 2568–2574, 2005

Gruiz, K., Vaszita, E., Siki, Z. and Feigl, V.: Environmental risk management of an abandoned mining site in Hungary, Advanced Materials Research, Vols. 20–21, pp. 221–225, 2007

Gruiz, K., Vaszita, E., Zaletnyik, P., Siki, Z.: GIS-based catchment scale modelling of toxic metal transport by erosion in an abandoned mining area, In: Conference Proceedings of Consoil 2008, CD, 2008

Horváth, B. and Gruiz, K.: Impact of metalliferous ore mining activity on the environment in Gyongyosoroszi, Hungary, The Science of the Total Environment, Vol. 184, pp. 215-227, 1996

Kumpiene, J., Ore, S., Renella, G., Mench, M., Lagerkvist, A., Maurice, C.: Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil, Environmental Pollution 144, pp. 62–69, 2006

Mench, M., Bussiere, S., Boisson, J., Castaing, E., Vangronsveld, J., Ruttens, A., De Koe, T., Bleeker, P., Assunção, A., Manceau, A.: Progress in remediation and revegetation of the barren Jales gold mine spoil after in situ treatments, Plant and soil, Vol. 249, pp. 187–202, 2003

Vangronsveld, J., Sterckx, J., Van Assche, F., Clijsters, H., Rehabilitation studies on an old non-ferrous waste dumping ground: effects of revegetation and metal immobilization by beringite, Journal of Geochemical Exploration, Vol. 52, pp. 221–229, 1995 a

Vangronsveld, J., Van Assche, F., Clijsters, H.: Reclamation of bare industrial area contaminated by non-ferrous metals: in situ metal immobilization and revegetation, Enviromental Pollution, Vol. 87, pp. 51-59, 1995 b

Vangronsveld, J., Ruttens, A., Clijsters, H.: The use of cylonic ashes of fluidized bed burning of coal mine refuse for long-term immobilization of metals in soils. In: Sajwan, K.S., Alva, A.K., Keefer, R.F. (Eds.), Biogeochemistry of Trace Elements in Coal and Coal Combustion Byproducts. Plenum, New York, pp. 223-233, 1996