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RESEARCH ARTICLE

Remediation of metal ore mine waste using combined chemical- and phytostabilisation

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Abstract

The combination of chemical stabilisation (using fly ash, lime and steel shots) and phytostabilisation (using grass mixture and two Sorghum species) were applied to remediate a highly acidic metal ore mine waste in Gyöngyösoroszi, Hungary. The change in metal mobility was monitored by chemical, biological and ecotoxicological methods. Chemical stabilisation reduced the amount of Cd from 441 to 0.42 $\mu g\ l^{-1}$*, Cu from 1510 to 11.7* $\mu g\ l^{-1}$ *and Zn from 89079 to 48.8* $\mu g\ l^{-1}$ *in drainage water and extractable As from 0.404 to 0.086* $mg\ kg^{-1}$ *in waste within two years. The high toxicity of the mine waste was reduced to non-toxic and healthy vegetation developed on the previously barren surface with metal content fulfilling animal fodder quality criteria. The technology reduced the risk on all possible pathways fulfilling all target criteria.*

Keywords

Chemical stabilisation · phytostabilisation · toxic metals · chemical soil treatment · in situ · fly ash

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1 Introduction

The lead and zinc sulphide ore mine near Gyöngyösoroszi (Mátra Mountains, Northern Hungary, main mine entrance: 47°51'01" N and 19°52'14" E coordinates) closed in 1985 after 40 years of operation, leaving the Toka-valley and the surrounding area heavily polluted with toxic metals. The 15 years intensive use of the mine and a further 20–25 years without remediation resulted in acidification, dispersion of the contaminated waste and creation of secondary pollution sources. A complex survey was carried out at catchment scale to assess the impacts of the mining activity and mine wastes on water, sediment, soil and ecosystem and to characterise the short and long-term environmental risks [1]-[6]. The results of the survey indicated, that heavy metal contamination of the Toka-valley has an unacceptably high environmental risk, therefore risk reduction is necessary by remediation of point and diffuse sources [7].

A GIS-based, complex environmental risk management strategy was developed for the catchment [8], focussed on the most sensitive environmental compartment, the surface water of the catchment and its aquatic ecosystem. The Gyöngyösoroszi mining site was the demonstration site of the DIFPOLMINE EU Life Project [9], where the differences and similarities between two metal ore mining sites – the French goldmine and the Hungarian Zn–Pb mine - were examined and integrated into the environmental risk management concepts of the two sites. The requirement of the catchment scale risk management concept at Gyöngyösoroszi is that the combined chemical and phytostabilisation technology should fulfil the target emission from the residual and diffuse pollution sources that remain after the encapsulation of the big waste dumps and the removal of smaller point sources [10].

Phytoremediation is an innovative technology that has been spreading in both Europe and the USA in the last 15 years [11]. The feasibility and efficacy of phytostabilisation combined with chemical stabilisation (CCP) has already been proven [12]: in a former field application at an abandoned zinc smelter site with soil metal contents up to 13.250 $mg \cdot kg^{-1}$ Zn a healthy and sustainable vegetation cover was established after treatment with beringite, a type of fly ash [13]-[15]. CCP technology was applied for toxic metal contaminated soil in some cases for erosion control and to promote revegetation [16]-[19].

In this paper we introduce the results of the first demonstration of CCP on highly acidic, heavily weathered sulphidic metal ore mine waste. Our aim was to select the best combination of chemical stabilisers and well growing, non-accumulative plants for remediation. To find the best stabiliser–plant combination long-term technological experiments scaled-up from laboratory microcosms and so called mini-lysimeters, through field lysimeters to field plots of different size and arrangement were performed. In our 2 years microcosm experiments fly ash reduced the water soluble ratio of Zn and Cd in Gyöngyösoroszi soil by more, than 99%, so it was selected for field application [20, 21]. Some authors examined the metal uptake of cultivated and wild plant species grown on soils and waste materials from Gyöngyösoroszi in pot and field experiments [22, 23]. They found that horseradish and different grasses (e.g. ryegrass and red fescue), are able to grow with low metal accumulation on the contaminated soils and liming can reduce their metal uptake and increase their biomass.

In our field experiments fly ash (FA) and its mixture with lime (FAL) were applied as chemical stabilisers, for the vegetation of the experimental plots grass mixture and two *Sorghum* species (sudan grass and broomcorn) were used. Our technology monitoring methodology is based on an integrated application and evaluation of mobility-related chemical analytical methods and bioavailability and effectiveness related biological tests.

2 Materials and methods

The characteristics of the mine waste and the applied amendments and plants are characterised in this chapter. The construction and setup of the field plots and the technology-monitoring tool used for the field experiments are discussed in details.

2.1 Characteristics of the mine waste

After the mining was terminated in the Gyöngyösoroszi mining area several mine waste dumps were left abandoned without proper isolation from the environment. One of the biggest ones is called Bányabérc mine waste dump, which consists of lumpy rock debris and loamy, acidly weathered rock material. Table 1 shows the characteristics of this mine waste. It is highly acidic, contains high amount of mobile Cd and Zn (17–22% of the total content is extractable by ammonium-acetate) and has low nutrient content.

The stepwise risk assessment of the waste depositions in the area (methodology: [24]) demonstrated that the BB waste dump is highly risky and remediation or other risk reducing intervention is needed. To stop the transport of acidic runoff and leachate and to treat the barren surface to stop solid transport CCP was chosen as a remediation option.

2.2 Pilot field-experiment with the application of combined chemical and phytostabilisation

During the fall of 2006 three field plots were constructed from the acidic mine waste material near the main entrance of the mine with the size of 6 m×15 m = 90 m^2 containing 54 m^3 of waste material. The plots were constructed for being suitable for complex monitoring of soil, leachate and plant. They were isolated from the underlying ground by a plastic foil. Above that, a 5 cm high layer of andesite gravel was placed to provide a filter layer. The water filtering through the plots was collected by a drainage system, which allowed the monitoring of the quantity and quality of the separate drainage water from each plot.

The waste material was thoroughly mixed with 5 w/w% non-alkaline fly ash "T" (pH=6.84, total metal content (mg kg^{-1}): As: 16.7, Cd: 0.478, Cu: 53.2, Pb: 9.39, Zn 56.4, water extractable metal content under detection limit (DL) – see chapter 2.3.1) originating from a power plant in Hungary (1^{st} plot; referred as FA treatment), and by the mixture of "T" and an other non-alkaline fly ash "V" (pH=6.44, total metal content (mg kg^{-1}): As: 33.6, Cd: 1.02, Cu: 32.7, Pb: 35.5, Zn 303, water extractable (mg kg^{-1}): As: 0.107, Cd, Cu and Pb: <DL, Zn: 0.235) in 5 w/w% (2.5–2.5 w/w% each) together with hydrated-lime in 2 w/w% (2^{nd} plot, referred as FAL treatment). The third plot remained untreated and was used as a control. The amendments and the combinations were selected on the bases of previous microcosm experiments where alkaline fly ashes or the combination of neutral fly ashes with lime showed the most promising results in immobilising metals: they reduced the water extractable Zn and Cd by 78–99% [20, 21].

Fly ashes cause long time stabilisation through silicate-formation and bounding metals into the molecular grid. In microcosm studies we found that alkaline fly ashes alone can stabilize metals on long term, but non-alkaline fly ashes have smaller stabilising capacity, which can be improved by lime addition [20, 25]. Additional lime was applied to lower the pH at the beginning to neutralise acidity and help the formation of hydroxides from ionic metals.

To reduce the elevated amount of arsenic found in the drainage water of the FAL treated plots steel shots (SS, elemental iron in the form of iron grit: type GP 25, Fe content 97.10–98.35%) were spread evenly in 5 kg m^{-2} concentration onto the top of the treated plots and were mixed into the upper 20 cm of the mine waste in spring 2008. SS were previously used successfully for the immobilisation of arsenic in soil [16, 19, 26] and we proved its efficiency for the stabilisation of the arsenic in the limed mine waste in laboratory microcosm and lysimeter experiments [20, 27]: the amount of water- and acetate-extractable As decreased to the third and half, respectively.

For vegetation each field plot was divided into three equal parts and preliminarily selected plants were sown: a grass mixture (10 g m^{-2}; 20.0% *Festuca arundinacea,* 20.0% *Lolium perenne,* 18.3% *Bromus inermis,* 15.0% *Dactylis glomer-*

Tab. 1. Chemical and toxicological characterisation of the mine waste

Toxic metals	Aqua regia extract	Acetate extract	Water extract	Available for plant uptake [1]	Soil chemistry[2]		Toxicity testing[2]	
	mg kg^{-1}							
As	524±38.8	< 0.080	0.103±0.011	0.403±0.059	pH	2.77±0.133	*V. fischeri* luminescence inhibition	90 % highly toxic
Cd	1.90±0.322	0.635±0.271	0.649±0.277	1.63±0.440	K_A	39.0±2.80	*S. alba* root and shoot growth inhibition	90 % highly toxic
Cu	35.1±3.08	2.08±1.15	3.39±1.42	8.73±2.36	Organic matter (%)	0.371±0.026	*T. pyriformis* reproduction inhibition	100% highly toxic
Pb	3394±1246	43.2±10.2	14.5±1.95	20.2±1.00	AL-K_2O (mg kg^{-1})	27.2±7.21		
Zn	483±110	106±51.0	109±47.2	260±63.5	AL-P_2O_2 (mg kg^{-1})	7.74±3.93		

Average of 5 replicates. [1] Bioaccumulated by *Sinapis alba* in five day bioaccumulation test. [2] For detailed methodology see chapter 2.3.

ata, 13.3% *Festuca rubra,* 5.0% *Phalaris/Baldingera arundinacea,* 3.3% *Agropyron pectinatum,* 3.3% *Festuca pratensis*, 1.6% *Phleum pratensis*), *Sorghum sudanense* (50 g m^{-2}) and *Sorghum vulgare* (50 g m^{-2}). The grass mixture is able to create a closed vegetation cover, which hinders wind- and water-erosion – a main goal of phytostabilisation. A similar mixture of grasses was previously used successfully for covering red mud reservoirs in Hungary [28]. *Sorghum vulgare* (broom corn) and *Sorghum sudanense* (sudan grass) are fast growing plants, the latter with possible applicability for energy crop [29].

As the weather was drier than the average during the experimental period (precipitation was 696 mm in year 2007 and 689 mm in year 2008, average calculated from data from Hungarian National Meteorological Service between 1982–2002 is 756 mm/year,) irrigation was used to substitute the missing precipitation to supply plant seedlings with suitable amount of water. With the amount of water used for irrigation we simulated the precipitation of a normal year.

2.3 Technology-monitoring: concept and methodology

2 years monitoring of CCP field demonstration is introduced in this paper. The amount of precipitation, sprinkled water and drainage water, the pH and the electrical conductivity of the drainage water was recorded *on site* on a daily basis during the vegetation period. Samples from the drainage water, the solid waste material and the plants were regularly taken and analysed/tested, by an integrated methodology, which combined physico-chemical analysis with biological-ecotoxicological tests, to get a realistic view on the risk, and its nature [30, 31]. The concept is shown on Fig. 1. The extractants with growing acidity – distilled water, water solution of ammonium-acetate and aqua regia – characterise the extractability or the "chemical availability" of the metals. Their biological availability and effect and their changes during the stabilisation process was followed by so called direct contact ecotoxicity testing, what means that the testorganisms have the opportunity to interact with the solid waste similar to the real environment. The metal fraction available for plant uptake was measured by plant bioaccumulation test. The chemical and biological results were evaluated together based on a score system developed by the authors.

2.3.1 Mine waste sampling and analyses

The mine waste was characterised in detail before starting the stabilisation experiment (Table 1). An average sample was taken from the original location of the waste dump, then samples were taken from the transported material to the place of the experiment to get good homogeneity of waste material for the construction of the plots.

Sampling during the technology application: mine waste samples were taken monthly during the vegetation period, average samples from 20 spots/plot, from 1–20 cm depth were taken into plastic bags (Hungarian Standard 21470-1:1998), and were analysed for physico-chemical parameters, metal content and toxicity. The pH was measured according to HS 21470-2:1981, the texture according to Arany, based on a rheological method (HS 21470-51:1983), organic matter content in % by the standardized Tyurin method, based on oxidation with chromic acid (ISO 14235:1998), ammonium-lactate extractable P, K by the relevant Hungarian standard (HS 20135:1999).

The mobile metal content of the mine waste was determined after distilled water and ammonium-acetate extraction (pH=4.5) (HS 21978-9:1998), the total metal content was measured after aqua regia digestion (HS 21470-50:2006). The mobility of As was characterised by the amount extracted by sodium-hydroxide and sodium-carbonate (1:0.56 mol) (HS 21470-50:2006). The metal contents of the different extracts were measured by standardised (HS 21470-50:2006) ICP-AES method (Jobin-Yvon

ULTIMA 2, Detection limit (mg kg^{-1}): As: 0.08, Cd: 0.004, Cu: 0.05, Pb and Zn: 0.06).

For biological-ecotoxicological testing the waste samples were air dried, ground and sieved through a 2 mm sieve. The microbial activity (living cell concentration) was measured as described by Gruiz et al. [32]. The toxicity of the waste material was measured by *Vibrio fisheri* luminescence direct contact inhibition test in a soil/waste suspension, as described by Gruiz et al. [32]. The toxicity was characterised by EC_{20} values (concentration producing 20% luminescence inhibition) by comparison with brown forest soil. The *Sinapis alba* (white mustard) root and shoot growth direct contact inhibition test was developed by Gruiz et al. [32], and was applied with the modification that instead of a dilution series two replicates were measured. The growth inhibition was calculated by comparison with root and shoot lengths in distilled water. The *Tetrahymena pyriformis* (protozoon) test was developed by Leitgib et al. [33] in our lab and was modified by using 6 fold of the amount of both samples, medium and testorganism. The reproduction inhibition was calculated by comparison with growth on brown forest soil.

The metal uptake of plants was predicted by an innovative five-day plant bioaccumulation test – developed for this purposes by the authors – using *Sinapis alba.* 5 g waste sample was placed into a Petri-dish, watered to its total water holding capacity and 40 *Sinapis alba* seeds were sown. The plants were incubated in the dark at 20 °C for 5 days. At day 3 the missing water was compensated. After 5 days the shoot of the plants were separated with a plastic knife, washed with water and dried. The metal content of plant was measured by ICP-AES (HS 21470-50:2006) after digestion with 10 ml nitric acid and 4 ml hydrogen peroxide for 3 hours at 105 °C.

2.3.2 Drainage water sampling and analyses

Drainage water samples were taken weekly during the vegetation period and were analysed for physico-chemical parameters, metal content and toxicity. The samples were stored in plastic bottles at 4 °C until processing. The pH was measured according to HS 260-4:197, the SO_4^{2-} content was measured according to HS 11885:2000. The metal content of the drainage water was determined according to HS 1484-3:2006 by ICP-AES.

The toxicity of the drainage water was measured by *Vibrio fisheri* luminescence inhibition test as described for water samples by Gruiz et al. [32]. The luminescence inhibition was calculated by comparison with 2% NaCl solution. The *Sinapis alba* (white mustard) root and shoot growth inhibition test was carried out according to HS 22902-4:1990. The growth inhibition was calculated by comparison with root and shoot lengths in distilled water.

2.3.3 Field plant sampling and analyses

Plant growth and characteristics were monitored in details, including plant size measurements (average lengths of 20 plants weekly) and metal content. Plant samples (average sample of 20 plant shoots and leaves) were collected monthly for analysis. Plant material was rinsed thoroughly with deionised water and dried at room temperature. Plants' metal content was determined by ICP-AES (HS 21470-50:2006) after digestion with 60% nitric acid and 30% hydrogen peroxide solutions applied in 5:1 ratio (plant:solution=1:50, destruction with microwave). The results were given for dried plant material and evaluated in time.

2.3.4 Integrated evaluation and interpretation of the results

For each test method applied for monitoring a score system was developed. Scores were given from 0–5, the maximum was 5 for each type of chemical and biological measurement (Fig. 1). The scores of metal concentrations in waste and leachate were established in comparison with the Maximum Effect Based Quality Criteria ($EBQC_{max}$) for metals in surface waters, set by Gruiz et al. [34] and the score of metal concentration in plant was calculated from the Hungarian quality criteria for human food and animal fodder. The scores of different toxic effects are based on comparison with the effects of uncontaminated controls. The final score for a technology-version is the sum of the scores for each test (in this system total 210 points) and given also in % of the maximum score. The higher the score the less the risk of the treated mine waste, so the final score shows the efficacy and applicability of the technology.

2.3.5 Statistical analysis

Analysis of variance (ANOVA) was performed by using StatSoft® Statistica 8.0 program to see if the treatments significantly reduced the metal mobility and toxicity of the waste material. The level of significance was established at $p<0.05$. Fisher LSD test was used for comparison of the treatments.

3 Results and discussion

The chemical-analytical and biological-ecotoxicological results of the field experiment are presented for the treated waste material, its drainage water, and the plants grown on the treated mine waste, respectively.

3.1 Effect of stabilisers on the mine waste

The effect of stabilisers was followed in time by several samplings. The mobility/stability of the metals were characterised by the metal content of water- and acetate extracts of solid mine waste.

In the untreated waste the water and acetate extractable metal content (especially Cd, Cu and Zn) decreased during the 2 years to the fifth (Table 2). From the isolated waste material, laid in a relatively thin layer (0.6 m) the metals and other components are leached out easily by the precipitation, as there is no new supply. In larger (thicker) waste depositions the source of metals is quasi endless in the timeframe of a few years. The not weathered or leached wastes represent higher risk, as they are a long time source of metals [35].

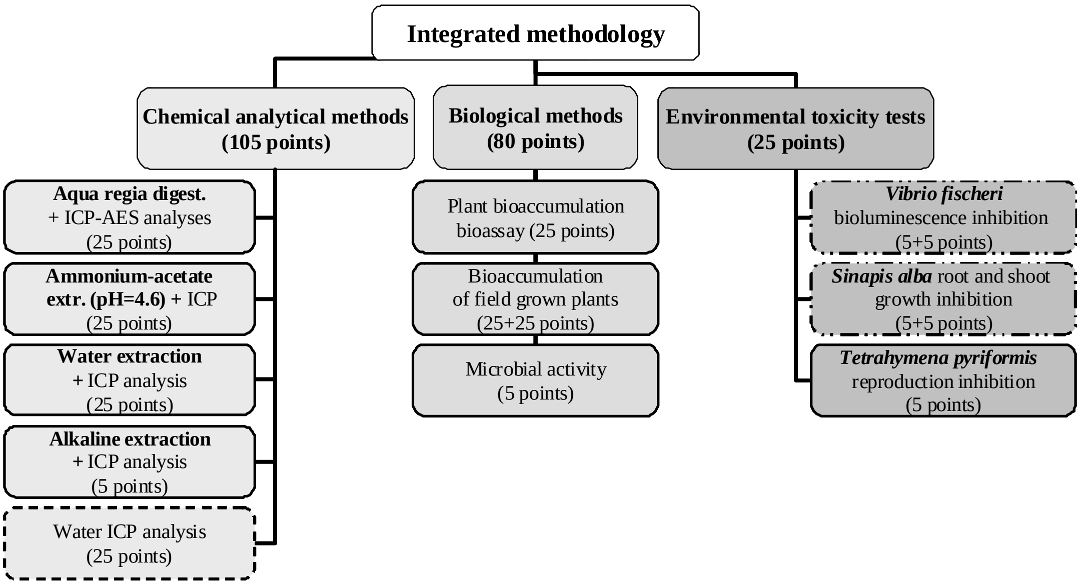

Fig. 1. Integrated technology monitoring and score system with maximum points
Continual frame: applied for waste, intermittent: for drainage water, point and line: both. In case of chemical analysis and plant bioaccumulation 5–5 points can be given for each metal (As, Cd, Cu, Pb, Zn), except alkaline extraction, where only As was examined.

The water and acetate extractable metal content of the waste decreased considerably after stabilisation (Table 2), as expected from former microcosm results [21]. It also agrees with the drainage water quality of the field plots (3.2). By 2008 in the FAL+SS treated waste material the water extractable Zn, Cd and Pb concentration decreased by more than 99% and in the acetate extract we observed 55–97% decrease. FA+SS treatment was also effective for Cd, Cu and Zn, but to a smaller extent than the FAL+SS treatment (81–95% decrease in water extractable amount).

The mobilisation of As as the effect of alkaline treatment conditions (FAL) is shown by both water and acetate extracts, but during the experiment the extractable amount of As in both extracts decreased due to elemental iron (SS) application in 2008. In the alkaline (sodium-hydroxide + sodium-carbonate) extract the concentration of As decreased from 220 to 154 mg kg^{-1}, in the water extract from 0.302 to 0.122 mg kg^{-1}and in the acetate extract from 0.404 to 0.086 mg kg^{-1} in 2008, it is 60% and 79% decrease, respectively. In parallel microcosm experiments the addition of SS (1 w/w %) highly reduced As mobility in the mine waste: with 48% in the water and 78% in the acetate extract in a 3 months experiment [25].

As the effect of fly ash (FA) treatment higher concentration of Pb was found in the acetate extract, but lower in the water extract compared to untreated. Both the water and acetate extracts the extractable amount of Pb decreased due to SS application in 2008, with 62% and 32%, respectively. In the above mentioned microcosm experiment SS reduced the concentration of Pb with 48–52% both in the acetate and the water extracts [25].

The nutrient content of the mine waste also improved due to the treatments: by 2008 the organic matter content increased from 0.374% to 0.808% (FA) and 0.925% (FAL), the K content from 27.6 mg kg^{-1} to 97.3 mg kg^{-1}(FA) and 202 mg kg^{-1} (FAL), P content from 6.60 mg kg^{-1} to 17.0 mg kg^{-1}(FA) and 36.7 mg kg^{-1} (FAL), respectively.

The chemical analytical results of the mobile metal contents represent the extractability (availability for water and acidic water). This kind of risk endangers subsurface and surface waters. The second transport route, plant uptake of metals was measured by the rapid bioaccumulation test performed on the waste material in laboratory by using very young seedlings, which have maximal uptake potential, so that this test can be considered as a pessimistic model of plant uptake. Plant bioaccumulation test proved the efficacy of FAL treatment in stabilising the plant-available toxic metal content of the waste (Table 3), and neither As, nor Pb were found amongst the bioaccumulated toxic metals, which means that they are in a form that is not available for plants.

The third type of risk is the toxic effect of the metals on the soil ecosystem. Microbiological activity of the waste material is 5 order of magnitude less than in an average soil. The microbial activity significantly increased after FA and FAL treatments (Table 3). Toxicity decreased immediately after the treatments and remained low during the two years of experiment. All toxicity tests proved the strong toxicity of the original waste material, but contrary to the chemical results FA treatment decreased toxicity more efficiently than FAL in some cases. This might be due to the fact that during chemical stabilisation nutrients are also immobilised. The decreased availability of important nutrients in the FAL treated waste compensates the higher amount of available toxic metals and their inhibitory effect in the FA treated waste.

Tab. 2. The water and acetate extractable metal content of untreated and stabilized waste material

Treatment	Year	As water	As acet.	Cd water	Cd acet.	Cu water	Cu acet.	Pb water	Pb acet.	Zn water	Zn acet.	pH water
Metal content of untreated mine waste (mg kg^{-1})												
Untreated	2007^1	0.103^a	0.080^a	0.649^a	0.635^a	3.39^a	2.08^a	14.5^a	43.2^a	109^a	106^a	3.03
	2008^2	0.081	0.088	0.025	0.136	0.726	0.738	1.92	36.8	12.8	25.3	3.65
Metal content of stabilised mine waste (mg kg^{-1})												
FA	2007	0.091^a	$< 0.080^a$	0.341^a	0.585^a	0.486^b	1.13^a	6.39^b	110^b	41.8^a	67.3^{ac}	4.35
FAL	2007	0.302^b	0.404^b	$< 0.004^b$	0.128^b	0.388^b	0.465^{bc}	0.079^c	2.30^c	0.198^b	15.3^b	6.97
FA+SS	2008	$< 0.080^a$	$< 0.080^a$	0.044^c	0.296^{ac}	0.351^b	0.899^{ab}	2.40^d	75.0^{ab}	5.55^c	38.0^c	4.43
FAL+SS	2008	0.122^a	0.086^a	$< 0.004^b$	0.254^c	0.168^b	0.062^c	$< 0.060^c$	5.32^d	0.281^b	47.4^{ac}	7.43
% decrease in metal content due to stabilisation compared to untreated, 2007												
FA	2007	11.7	0.0	47.5	7.9	85.7	46.0	55.9	-154.5	61.5	36.6	
FAL	2007	-193.2	-405.0	99.4	79.8	88.6	77.7	99.5	94.7	99.8	85.5	
FA+SS	2008	22.3	0.0	93.2	53.4	80.8	56.9	83.4	-73.8	94.9	64.2	
FAL+SS	2008	-18.4	-7.5	99.4	60.0	95.0	97.0	99.6	87.7	99.7	55.3	

^{1}: average of 5–11 months (5 sampling)

^{2}: average of 20–23 months, (3.5 months period after SS treatment) (2 sampling)

Means having the same letter per column are not significantly different (level of significance: $p<0.05$).

In the LSD test untreated 2007 was used for comparison.

Tab. 3. Bioaccumulation of metals in *S. alba* test plants, microbial cell concentration and adverse effects of mine waste before and after treatment

Treatment	Year	Metal content of *S. alba* plants					Activity	Ecotoxicity			
		As	Cd	Cu	Pb	Zn	Microbial cell concentration	*V. fischeri* luminescence inhibition^4	*S. alba* root growth inhibition^5	*S. alba* shoot growth inhibition^5	*T. pyriformis* growth inhibition^6
		mg kg dry weight^{-1}					CFU g soil-1	%	%	%	%
Untreated	2007^1	0.403^a	1.63^a	4.66^a	20.2^a	260^a	$6.06 \cdot 10^4$	100.0	100.0	100.0	100.0
FA	2007	0.346^a	1.26^{ab}	1.93^a	18.3^{ab}	207^a	$2.74 \cdot 10^7$	60.2	−7.0	4.7	97.1
FAL	2007	0.373^a	0.401^b	1.99^a	5.03^b	75.4^b	$1.38 \cdot 10^6$	42.9	21.1	13.0	99.9
Untreated	2008^2	11.7^d	1.75^d	3.13^d	98.3^d	300^d	$9.71 \cdot 10^4$	100.0	100.0	100.0	100.0
FA+SS	2008	1.83^d	1.18^d	0.763^d	46.9^d	223de	$1.09 \cdot 10^6$	65.5	35.8	−6.8	−18.7
FAL+SS	2008	1.79^d	0.429^e	0.990^d	16.7^d	101^e	$5.58 \cdot 10^6$	40.0	43.9	−22.5	16.9
HCQ for fodder / fresh vegetable		2.00/ 2.00	1.00/ 1.00	- / 100^3	10.0/ 3.00	- / 100^3					

^{1}: average of 5–11 months (4 sampling); ^{2}: average of 20–23 months, (3.5 months period after SS treatment) (2 sampling). Means having the same letter per column are not significantly different (level of significance: $p<0.05$). In the LSD test samples from 2007 (marked with letter “a”) and from 2008 (marked with letter “d”) was compared to their own untreated control. No comparison was done between the two years. HQC = Hungarian Quality Criteria. ^{3} Specified only for tinned food.

Inhibition percentage: 100%: total inhibition, 0%: no inhibition. Untreated was set as 100%.

^{4}Luminescence inhibition compared to 2% NaCl solution. ^{5} Root and shoot growth inhibition compared to distilled water. ^{6} Reproduction inhibition compared to unpolluted brown forest soil.

3.2 Effect of stabilisers on the drainage water

Drainage water from each plot was collected separately. The water collection from the plots allows us to obtain an average sample from the highly heterogeneous waste material and makes possible to predict the risk connected to the transport of toxic metals by the infiltrated precipitation.

The amount of toxic metals measured in the drainage water is presented in Table 4. By 2008 the Cd and Zn concentration of the collected drainage water decreased on average by 70–72% due to FA treatment, while FAL treatment was able to reduce it by more than 99%, under the Maximum Effect Based Quality Criteria set by Gruiz et al. [34] for the natural surface water

Tab. 4. Decrease in the metal and sulphate content, increase of pH and decrease in toxicity of drainage water from field plots

		Metal content					Other contents		Toxicity	
Treatment	Year	As	Cd	Cu	Pb	Zn	SO_4^{2-}	pH	*S. alba* root growth inhibition	*S. alba* shoot growth inhibition
		μg l^{-1}					mg l^{-1}		%^{3}	%^{3}
Untreated	2007^1	$< 1.8^a$	441^a	1510^a	17.0^a	89079^a	2988^a	2.9^a	100.0	100.0
FA	2007	$< 1.8^a$	138^b	88.7^b	131^b	30380^b	2092^b	4.1^b	4.7	-6.4
FAL	2007	20.7^b	2.30^c	14.1^c	1.96^c	226^c	1606^c	7.2^c	6.4	-7.4
FA+SS	2008^2	$< 1.8^a$	124^b	77.4^b	192^d	26009^b	1846^{bc}	4.1^b	-1.7	-11.1
FAL+SS	2008	20.9^b	0.42^d	11.7^c	$< 1.50^c$	48.8^d	1426^{cd}	7.8^d	36.1	-14.3
EBQC$_{max}$		10.0	1.0	200	10.0	100				
% decrease in content due to treatments compared to untreated 2007										
FA	2007	<DL	68.8	94.1	-669	65.9	30.0			
FAL	2007	-1050	98.5	99.1	88.2	99.7	46.3			
FA+SS	2008	<DL	71.8	94.9	-1047	70.8	38.2			
FAL+SS	2008	-1061	99.9	99.2	91.2	99.9	52.3			

[1]: average of 5–11 months (7 sampling)

[2]: average of 20–23 months; average of 3.5 months period after SS treatment (7 sampling)

Means having the same letter per column are not significantly different (level of significance: $p<0.05$).

EBQC$_{max}$: Maximum Effect Based Quality Criteria set by Gruiz et al. [34]

Inhibition percentage, 100%: total inhibition, 0%: no inhibition. Untreated was set as 100%.

[3] Root and shoot growth inhibition compared to distilled water.

system, the Toka-catchment. Cu, Pb (FAL) and As (FA) were also under this value.

The concentration of As was below detection limit (0.08 mg kg^{-1}) in the drainage water from the untreated mine waste and the FA treated waste, but increased due to FAL treatment. The increase in As mobility is due to the elevation of pH, since As (arsenate ion) is more mobile in the environment under alkaline conditions [36]. The addition of SS to the treated plots did not reduce the concentration of As in the drainage water within 3.5 months, but proved to be effective in the parallel column experiment, where the concentration of As in the drainage water decreased to the third due to SS addition [25]. The reason for the insufficiency of SS on the field can be that they were only mixed into the upper 20 cm of the mine waste, which was not enough to reduce the content of arsenic in the drainage water after 3.5 month. Friesl et al. [37] also concluded that the small depth (10–15 cm) of amendment placement can be the reason for insufficient As immobilisation. The water, acetate and sodium-hydroxide + sodium-carbonate extractable As in the mine waste (samples taken from the upper 20 cm) decreased due to the steel shot addition, which proves the theory that the arsenate washed out by the precipitation was located in the pores of the waste under the SS treated layer.

In the FA treated plot Pb concentration increased due to the treatment compared to the untreated plot. Increased mobility of Pb was also found by Ruttens et al. [38] due to the addition of fly ash, which might be due to the variability of stability constants of metallo-organic complexes depending on pH and other properties of the medium [39]. The mobilisation of Pb was also observed in the acetate extract of the mine waste (Table 2), and the same was found in a column experiment, in which the effect of two years precipitation on the FA treated mine waste was modelled [25].

The amount of SO_4^{2-} in the drainage water decreased considerably, due to the treatments with 30–53%, as a result of increased pH.

The toxicity of the drainage water proved the efficacy of the treatments, the toxicity of the water has changed from very toxic to non-toxic according to the *Vibrio fischeri* bacterial test. The plant growth test using *Sinapis alba* showed that both root and shoot growth of the test plant is higher in the treated waste than in the untreated. There was no difference in plant growth between FA and FAL in 2007, but in 2008 the root grew bigger in case of FA+SS, than of FAL+SS treatment (Table 4).

3.3 Effect of chemical stabilisers on the field grown plants

The metal content of plants used for phytostabilisation and therefore grown on the field plots is important from the point of view of their food chain effects, so non-accumulator plants should be applied.

On the untreated plot no vegetation was grown, and the sown plants used for phytostabilisation of the mine waste were not able to survive due to high toxicity, high pH and the lack of nutrients. This proves the importance of the application of chemical stabilisers prior to the sowing of plants. On the FAL treated plot the two *Sorghum* species were able to grow quicker and 1.5 times higher than on the FA treated one according to length measurements in the first month after sowing. There was no

Tab. 5. Accumulated metal concentration in plants grown on the field plots at the end of the vegetation period

Treatment	Year	Metal content (mg/kg dry weight)	As	Cd	Cu	Pb	Zn
FA	2007 Sept.	Grass mixture (4 months old)	7.08	1.17	13.9	60.2	192
		Sorghum vulgare (4 months old)	4.78	7.06	12.9	95.3	184
		Sorghum sudanense (4 months old)	4.06	8.33	14.6	103	343
FAL	2007 Sept.	Grass mixture(4 months old)	2.27	0.164	9.30	7.67	57.6
		Sorghum vulgare (4 months old)	2.56	0.273	7.20	10.6	43.2
		Sorghum sudanense(4 months old)	2.87	0.428	9.00	12.6	59.3
FA+SS	2008 Sept.	Grass mixture (1.5 years old)	2.30	3.44	6.48	22.4	248
		Sorghum vulgare (4 months old)	2.90	0.785	5.46	70.3	74.1
		Sorghum sudanense (4 months old)	5.51	3.27	7.31	126	164
FAL+SS	2008 Sept.	Grass mixture(1.5 years old)	1.17	0.512	3.33	3.47	39.5
		Sorghum vulgare (4 months old)	1.27	0.052	4.49	2.75	27.8
		Sorghum sudanense(4 months old)	1.96	0.207	4.41	6.47	46.3
Hungarian quality criteria for animal fodder			2.00	1.00		10.0	
Hungarian quality criteria for fresh vegetable			2.00	1.00	100[1]	3.00	100[1]

[1] Specified for tinned food.

significant difference in grass growth.

Plant samples were taken 3 times during each growing seasons. Metal uptake is usually faster during the first period of growth, and decreases with plant age. In this paper the results at harvest are presented (Table 5). The three plants accumulated the metals to different extent. To the time of harvest, the metal concentrations were below or close to the limit value for food and fodder in all plants using the FAL treatment. This means that the growing of plants on the stabilised mine waste do not add an additional risk and they can be used for phytostabilisation purposes.

3.4 Integrated evaluation of the chemical analytical, biological and ecotoxicological test results by a score system

The integrated evaluation was carried out as described in chapter of methods. Here we only present the final scores for each treatment (Table 6). FAL treatment proved to be better, the single FA treatment and the addition of SS improved the efficacy of both treatments by 5–10%. The best technology (FAL+SS) reached the 75% of the maximum score, which means 49% improvement compared to the initial (untreated).

Tab. 6. Efficacy of treatments

Treatment	Total score of 210 points	Percentage of maximum (100%)[1]
Untreated	58.5	25.8
FA	109.3	50.6
FAL	151.0	70.0
FA+SS	128.5	60.0
FAL+SS	160.5	75.2

[1] 50%: points for chemical- analytical tests divided by their maximum (105 points), 30%: points for biological tests divided by their maximum (80 points), 20%: points for ecotoxicological tests divided by their maximum (25 points).

4 Conclusions

The aim of the field demonstration of CCP, the combination of chemical and phytostabilisation in Gyöngyösoroszi applied to toxic metal containing mine waste material was to verify the efficacy of this innovative remediation technology. With the integrated methodology applied for technology monitoring we proved that both the metal mobility and the toxicity of the waste material can be decreased by the application of fly ash (FA) as chemical stabiliser. Its efficacy can be further enhanced with lime (FAL) and steel shot (SS) addition. As a consequence of chemical stabilisation a healthy vegetation was able to develop on the previously barren mine waste material with concentration of metals in the above ground parts under the Hungarian limit value for food and fodder. According to the results presented in this paper and other field experiments on metal polluted agricultural soil from the Toka catchment area [40], the fly ash treatment combined with phytostabilisation is an effective tool in reducing metal mobility. The complex verification of the technology – by setting a material balance, calculating residual risk and characterising eco- and cost-efficiency [41] – also proved the efficacy and applicability of CCP for toxic-metal contaminated sites. The first demonstration of CCP for a typical acidic mine waste of the former lead and zinc mine in Gyöngyösoroszi, Hungary can be considered as a successful demonstration, hopefully increasing the chance for market-entry and trust in technologies based on the immobilisation of contaminants in soils and solid wastes.

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