Combined chemical and phytostabilisation of an acidic mine waste – Long-term field experiment

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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 a highly acidic metal ore mine waste in a field experiment. The change in metal mobility was monitored by chemical, biological and ecotoxicological methods. Chemical stabilisation reduced the amount of Cd from 441 to 0.120 µg/l, Cu from 1510 to 9.85 µg/l and Zn from 89079 to 29.3 µg/l in drain water and extractable As from 0.404 to 0.086 mg/kg in waste within three 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

stabilisation, pytostabilisation, mine waste, toxic metals, fly ash

Introduction

The area of the former lead and zinc sulphide ore mine in Gyöngyösoroszi, Hungary is heavily polluted with toxic metals, such as Zn, Cd, Pb, Cu and As. A complex survey was carried out in the former mining area to assess the impacts of mining activity (Gruiz and Vodicska, 1993; Horváth and Gruiz, 1996) and a complex risk management strategy was developed, which uses GIS based, catchment scale risk assessment (Gruiz et al., 2007, 2008, 2009a). As part of this complex environmental management concept the diffusely polluted area is planned to be remediated with an *in situ* technology, the combination of chemical stabilisation with phytostabilisation (CCP).

For the selection of effective stabiliser and plant combinations scaled up experiments were performed in laboratory microcosms, field lysimeters and filed plots (Feigl et al., 2008, 2009a, 2010). In this paper we present the long term results of the field experiments with an acidic mine waste from the area.

Bányabérc is one of the biggest waste heaps in Gyöngyösoroszi. The stepwise risk assessment of the waste depositions in the area based on the method developed by Gruiz (2006) showed that the waste dump is highly risky and remediation or other risk reducing intervention is needed. As a remediation option CCP was chosen.

For the stabilization of the highly acidic, heavily weathered sulphidic metal ore mine waste, based on the microcosm and lysimeter experiments fly ashes and their combination with lime and steel shots were applied (Feigl et al., 2007, 2009b). As phytostabilizing plants grass mixture and two *Sorghum* species (*Sorghum sudanense* and *Sorghum vulgare*) were chosen. The demonstration of the CCP technology was followed for three seasons by integrated monitoring and evaluation method.

Materials and methods

Three 6 m × 15 m field plots were constructed from waste material taken from the acidic waste heap at Bányabérc. The plots were isolated from the underlying ground by a plastic foil, above that, a 5 cm thick layer of andesite gravel was placed to provide a filter layer. The water filtering through the plots was collected by a drainage system. The first plot was amended with 5% by weight non-alkaline fly-ash (FA) T originating from a power plant in Hungary; the second was treated with two non-alkaline fly-ashes T and V in 5% by weight (2.5% by weight each), together with hydrated-lime in 2% by weight (FAL). The plots were amended with steel shots (SS) after the first year in 5 kg/m^2. The third plot remained untreated and was used as a control. Three plant types were grown on the field plots near each other: a grass mixture and two Sorghum species (*Sorghum sudanense* and *Sorghum vulgare*).

The experiment was monitored during three growing seasons by an integrated methodology, the combination of chemical-analytical methods with biological and toxicity testing (Gruiz et al., 2009b). The mobile metal content of the soil was determined after distilled water and ammonium-acetate extraction (pH=4.5), the total metal content was measured after aqua regia digestion by ICP-AES according to Hungarian Standards (HS 21470-50:2006 and HS 21978-9:1998).

The soil's biological activity was evaluated by determining the aerobic living cell number in soil. The toxicity of the soil was measured by *Vibrio fisheri* luminescence inhibition test, *Sinapis alba* root and shoot growth inhibition test and *Tetrahymena pyriformis* reproduction inhibition test applying direct contact with soil. The methods were developed by Gruiz et al. (2001). The metal amount available for plant uptake was estimated by a self-developed 5 days *Sinapis alba* rapid bioaccumulation test.

Dry weights (drying at 70℃, 10 hours) of field-gro wn plants were determined at the end of the growing season. The metal amount accumulated by plants was analysed after nitric acid and hydrogen peroxide (5:1) digestion by ICP-AES.

Results and discussion

During the three years of monitoring water, soil and plant samples were taken from the plots. The water collection from the plots allow us to get kind of 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 precipitate. In Table 1 the metal content of the drain water from the field plots is shown. In the drain water from the untreated waste the amount of Cd, Cu, Pb and Zn was highly above the Maximum Effect Based Quality Criteria ($EBQC_{max}$) set by Gruiz et al. (2006). During the three years of monitoring the metal amount leached out from the untreated plot decreased to the third, but it was still more than a 100 times higher than the $EBQC_{max}$ in case of Cd and Zn. The FA treatment decreased the mobile metal amount in the waste material, but not sufficiently and even increased its mobile Pb content. However, the FAL treatment was effective, as it reduced the metal contents under the $EBQC_{max}$ by the second year. Only the As content remained 3 times higher than the $EBQC_{max}$. The pH of the drain water increased from 2.9 to 4.2 by FA and to 7.6 by FAL treatment. 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 in case of both treatments.

Table 1: Metal content of the drain water from the filed plots
Values under the $EBQC_{max}$ are marked with bold

Treatment	Year	Metal content					pH
		As µg/l	Cd µg/l	Cu µg/l	Pb µg/l	Zn µg/l	
Untreated	2007	**<1.8**	441	1510	17.0	89079	2.91
Untreated	2008	**<1.8**	180	714	16.2	37286	2.88
Untreated	2009	11.2	157	433	12.5	24126	3.25
FA	2007	**<1.8**	138	**88.7**	131	30380	4.12
FA+SS	2008	**<1.8**	124	**77.4**	192	26009	4.13
FA+SS	2009	**4.23**	111	**85.2**	184	17111	4.39
FAL	2007	20.7	2.30	**14.1**	**1.96**	226	7.23
FAL+SS	2008	20.9	**0.42**	**11.7**	**<1.50**	**48.8**	7.77
FAL+SS	2009	33.3	**0.120**	**9.85**	**<1.50**	**29.3**	7.85
$EBQC_{max}$		10.0	1.0	200	10.0	100	

The water and acetate extractable metal content of the waste has also decreased as expected from the drain-water (Table 2). In the FA treated plot the amount of water extractable Zn, Cd and Pb decreased by 81–95%, in the FAL treated plot by more, than 99%. The reduction of extractable metal amounts in the untreated plot was also observed in the upper 20 cm (from which the samples were taken), but it was smaller than in the treated plots. The mobilisation of Pb in the FA treated plot, and that of As in the FAL treated plot. However, laboratory microcosm studies proved that SS can reduce the mobile As and Pb contents in the mine waste by 48–78% when it is thoroughly mixed with material (and not only placed on the upper layers) (Bertalan, 2009).

Table 2: Water and acetate extractable metal content of waste
Values representing more than 90% (water extract) 50% (acetate extract) of decrease in metal content compared to "untreated 2007" are marked with bold

Treatment	Year	As water	As acet.	Cd water	Cd acet.	Cu water	Cu acet.	Pb water	Pb acet.	Zn water	Zn acet.
Untreated	2007	0.103	0.080	0.649	0.635	3.39	2.08	14.5	43.2	109	106
Untreated	2008	0.081	0.088	**0.025**	**0.136**	0.726	**0.738**	1.92	36.8	12.8	**25.3**
Untreated	2009	<0.080	<0.080	**0.083**	**0.135**	0.701	**0.456**	2.83	**7.88**	16.43	**24.7**
FA	2007	0.091	<0.080	0.341	0.585	0.486	1.13	6.39	110	41.8	67.3
FA+SS	2008	<0.080	<0.080	**0.044**	**0.296**	**0.351**	**0.899**	2.40	75.0	**5.55**	**38.0**
FA+SS	2009	<0.080	<0.080	**0.040**	**0.205**	0.409	1.10	**0.396**	45.5	**7.88**	**27.3**
FAL	2007	0.302	0.404	**<0.004**	**0.128**	**0.388**	**0.465**	**0.079**	**2.30**	**0.198**	**15.3**
FAL+SS	2008	0.122	0.086	**<0.004**	**0.254**	**0.168**	**0.062**	**<0.060**	**5.32**	**0.281**	**47.4**
FAL+SS	2009	0.102	0.093	**<0.004**	**0.160**	**0.213**	**0.141**	**0.064**	**3.67**	**0.307**	**28.8**

The microbial activity in the mine waste increased 10 times in the FA treated plot and 100 times in the FAL treated plot compared to the non-treated one (Figure 1). The activity slightly decreased within the 3 years in all plots. The toxicity of the waste decreased due to both treatments by the same rate. As an example the root growth of *S. alba* test plants is shown in Figure 2. The shoot growth showed the same pattern. The root lengths in the treated waste were 5 times longer than in the untreated one and they slightly decreased within the 3 years. In the untreated waste a natural reduction of toxicity was seen due to the reduction of metal content in the upper layers of plots. The luminescence inhibition of *V. fischeri* decreased to the half in the first year, and by the third year the treated samples showed no inhibition to the test organism. The inhibition of the reproduction of *T. pyriformis* also decreased due to the treatments to 40-15% compared to an unpolluted control soil, meanwhile the untreated samples caused total inhibition in the first two years.

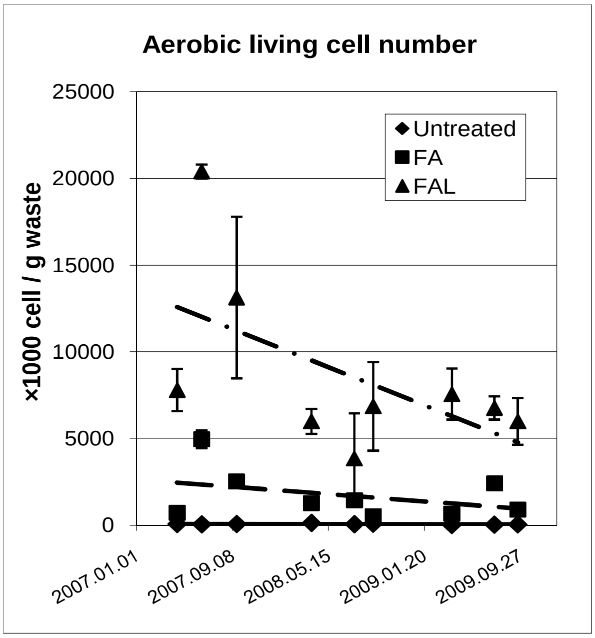

Figure 1: Aerobic living cell number in the waste

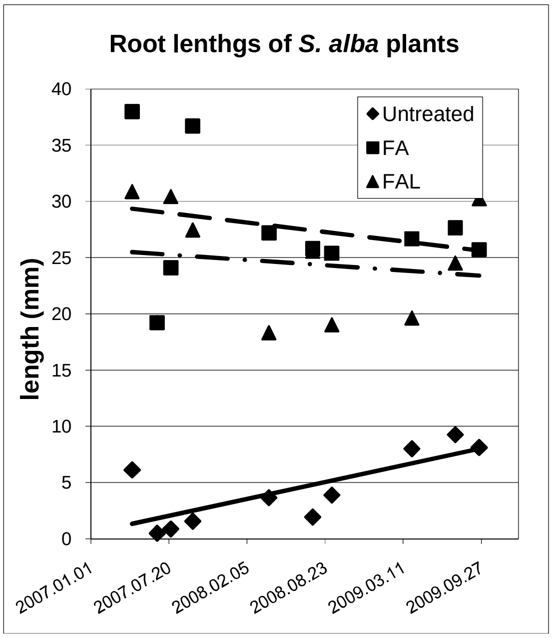

Figure 2: Root lengths of *Sinapis alba* test plants on mine waste

The metal content of the plants grown on the FAL field plots was under the Hungarian limit value for fodder, which is 2 mg/kg for As, 1 mg/kg for Cd, 100 mg/kg for Cu, 10 mg/kg for Pb and 100 mg/kg for Zn (in dry weight). The metal amount available for plant uptake was predicted by a 5 days laboratory bioaccumulation test with *Sinapis alba*. The results are shown on Figure 3. In Figure 4. the amount of metals accumulated in field grown plants are shown. On the untreated plot the plants were not able to grow at all in field conditions, which proves the importance of the application of chemical stabilisers before the sowing of plants. On the treated plots there were no significant difference between the metal accumulation of the three plant types used for phytostabilisation. However, the amount of metals accumulated in plants on the FAL treated plot was smaller than in the ones grown on the FA treated plot.

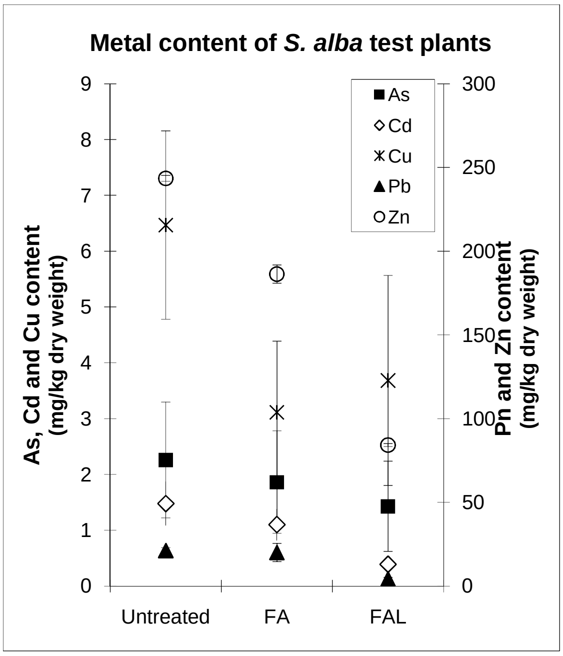

Figure 3: Metal content of *Sinapis alba* test plants (average of three years)

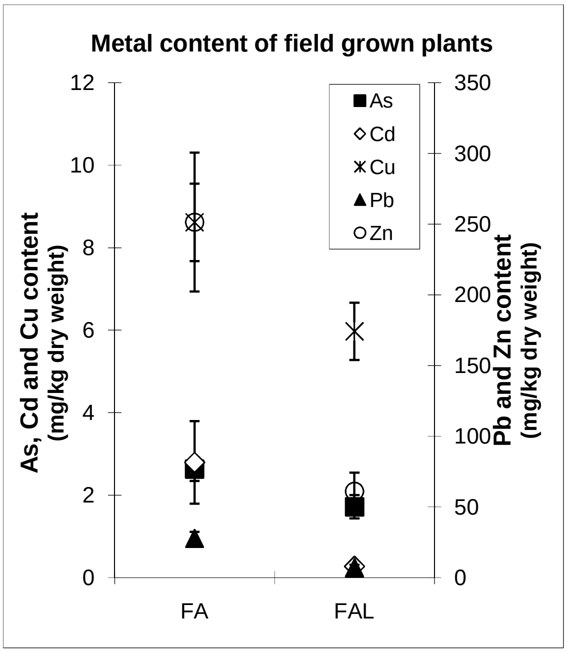

Figure 4: Metal content of field grown plants (average of three years)

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 animal fodder.

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