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

Viktória Feigl[1,a], Ágota Atkári[1], Attila Anton[2,b], Katalin Gruiz[1,c]

[1]Budapest University of Technology and Economics, Department of Applied Biotechnology and Food Science, 1111 Szt. Gellért tér 4, Budapest, Hungary
[2]Research Institute of Soil Science and Agrochemistry of the Hungarian Academy of Sciences, 1022 Herman Ottó u. 15, Budapest, Hungary

[a]vfeigl@mail.bme.hu, [b]anton@rissac.hu, [c]gruiz@mail.bme.hu

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

Introduction

Gyöngyösoroszi is an area of a former lead-zinc sulphide ore mine situated in the Mátra Mountains, Northern Hungary. A complex survey was carried out in the area to assess the impacts of the mining activity [1]. The results of the environmental survey indicated that heavy metal contamination of the examined area creates a high ecological risk, therefore the remediation of the site has to be started. According to the approach used successfully on other large metal contaminated sites [2], the identified diffuse pollution sources and the residual pollution area that remains after removal of the point sources will be subjected to phytostabilisation combined with chemical stabilisation.
Phytostabilisation is a proven technology, as indicated by successful studies performed in both Europe and USA [3]. To enhance the effectiveness of phytostabilisation it can be combined with in situ chemical stabilisation. The chemical stabilisers lower the mobility and bioavailability of toxic metals in the soil, therefore reduce erosion and leaching and enable settling of plants. The complex stabilisation system lowers the environmental risk of diffuse pollution and of plants grown on it.

Objectives

Before establishing full-scale demonstrations of the combined chemical- and phytostabilisation on the former mining site of Gyöngyösoroszi, the type of vegetation and the stabilising additive that fits to the local parameters (soil type, slope, exposition, metal concentrations…etc.), has to be determined. Prior to field experiments preliminary modelling tests were done in microcosm at laboratory scale to select the most suitable chemical stabilizer for the Gyöngyösoroszi soil and mine-waste. The requirement towards the good immobilising additive is that it should be able to reduce the mobility and biological availability of the toxic metals on long term, to reach an acceptable risk level.

Experimental

Microcosm tests. The soil samples from the phytostabilisation experimental area in Gyöngyösoroszi were treated with three different types of fly ashes, two from the power plant in Oroszlány, Hungary (fly ash "A" and "B") in 1 w%, 2 w% and 5 w% and one from Tata, Hungary (fly ash "T"), which was added to the soil in 2 and 5 w%. Fly ash (also called cyclonic ash) was used successfully for full scale combined chemical and phytostabilisation in Belgium [4,5]. We also tested other commonly used soil amendments: alginite (1,5 w%), hydrated lime (1 w%), raw phosphate (1 w%), lignite (10 w%), two types of Fe-Mn-hydroxide precipitate from drinking water cleaning in Budapest (precipitate "R" and "C", in 2 and 5 w%), and red mud (2 and 5 w%) from bauxite processing.

The soil samples treated with different additives and the untreated control sample were placed in 2 kg pots each. They were incubated at 25 °C, were mixed and watered every two months. The duration of the experiments varied from 1 to 2 years.

Monitoring of the stabilising experiment. Due to the addition of stabilizers to the soil complex processes are going on in the microcosms. The metal mobility, solubility and bioavailability are changing continuously until the new equilibrium. The process was monitored on long term, to reach the equilibrium state. It also occurs that a stabiliser seems to be effective on short term, but does not immobilize metals through a longer period.

The stabilisation and as a consequence the decreased mobility, solubility and bioavailability of toxic metals in the soil was monitored by an integrated methodology, which combined physico-chemical analysis with biological and ecotoxicity testing.

Monitoring by chemical analysis included metal-analyses in the water-, the ammonium-acetate- (pH=4,5) and the ammonium-acetate + acetic acid + EDTA-extract. The total metal content was measured after Aqua Regia digestion. The metal content of these different extracts was determined by IPC-AES: Inductive Plasma Coupled Atomic Emission Spectrometry.

In order to assess the actual risk of the treated soils toxicity measurements are also needed. Therefore the microcosm tests were monitored also by bacterial and plant ecotoxicity tests and plant bioaccumulation tests. The bacterial tests for predicting the risk of the soil included *Vibrio fisheri* luminescence inhibition test and *Azotobacter agile* dehydrogenase enzyme-activity inhibition test. The *Sinapis alba* (white mustard) root and shoot growth inhibition test and a self-developed five days bioaccumulation test were used for getting direct information on the suitability of the chemical stabiliser from the point of view of the following phytostabilisation process.

Results

The diffuse pollution and the contaminants. The soil in Gyöngyösoroszi is mainly contaminated with As, Cd, Cu, Hg, Pb and Zn, but out of these metals Cd (total content 4,2–23,3 mg/kg) and Zn (total content 926–4420 mg/kg) are the most mobile and for that reason their availability was more closely studied. 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.

Chemical analytical results. According to the different extractions, one type of fly ash, hydrated lime, and the mixture of hydrated lime, alginite, raw phosphate and lignite showed the best results in immobilising the toxic metals in Gyöngyösoroszi soils (Table 1).

Amongst the tested fly ashes 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 fly ash "T" did not reduce the acetate extractable metal content effectively. These differences in efficiency might the be due to the different origin and composition, which is reportedly [6] the two crucial factors determining the metal immobilising potential of ashes. Besides adsorption and crystal growth, the alkalizing effect also reportedly contributes to the immobilising effect of fly ashes [6], 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 is not alkaline (pH=7,2), therefore it was not able to shift the pH of the acidic Gyöngyösoroszi soil (pH= 5,54) to the alkaline domain.

Amongst the other additives 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: out of 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 the metals.

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

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

Toxicity testing and bioaccumulation. The results of the toxicity tests proved the results of the chemical analysis, that is the toxicity of the soil was reduced by the addition of fly ashes “A” and “B” (Table 2). The bacterial *Vibrio fisheri and Azotobacter agile* 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 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%. In case of “T” fly ash none of the toxicity or bioaccumulation tests showed any changes in toxicity and bioavailability of metals to the non-treated control in the first two months of the experiment. 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.

Table 2. Highest decrease in toxicity and metal bioaccumulation in treated soils (decrease in the non-treated control = 0%)

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

–: no change in the first two months, one year results under evaluation

The mixture of hydrated lime, alginite, raw phosphate and lignite was nearly as effective as fly ash “B” relative to bioaccumulation, but plant toxicity reduction was less for the mixture. 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 would be very important 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. 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 according to the plant toxicity test the two precipitates show promising results.

Conclusions

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

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