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In situ REMEDIATION OF SOILS POLLUTED WITH HEAVY METALS. PART I. USING OF SUPPORTED MATERIALS

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Abstract. In this paper are presented principal aspects concerning remediation of soils polluted with metals by using of supported material, for their immobilisation. Soil treatment for *in situ* immobilisation of metals like Pb, Cd, Zn, etc. is realised using different materials: biosolids, synthetic or native zeolites, zeolites and clays supported with polynuclear aluminum salts, ashes. Synthetic and natural zeolites are used both for remediation of soils polluted with heavy metals and for soil quality improvement, retaining of water, ammonia and pH control. The most used supported materials are natural zeolites which decrease metals mobility and increase their retaining on imobile solide phases. Aluminum (Al_{13}) basic polychloride and montmorillonite supported with polynuclear salts, are used as immobilising agents for treatment of soils polluted with metals, e.g. 1-8 mmol Al_{13}/kg d.s. were used for zinc immobilisation, and 0.1-6% native volcanic tuff – Al_n is applied to soil in order to decrease cadmium and lead mobility.

Keywords: zeolites, montmorillonit, polynuclear salts, supported materials.

AIMS AND BACKGROUND

Classical technologies used for remediation of soils with different pollution degrees are not efficient in every circumstances, taking into account both energetic and financial problems caused by remediation of large polluted areas.

Principal soil remediation techniques applied for decreasing of heavy metals pollution are referring to: 1 – excavations, that means physical removal of polluted soil, and refilling of empty spaces; 2 – metals stabilisation *in situ*, by using of different materials for metals immobilisation; 3 – using of plants to stop pollutants widespreading and to extract them by phytoremediation; 4 – using of electrokinetic methods for remediation of soils polluted with metals.

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New techniques that were developed for metals immobilisation in soil and phytoremediation may be used for solving of different and complex pollution problems. *In situ* immobilisation of metals decreases the pollutant effects onto the environment. Soil treatment for *in situ* immobilisation of metals like Pb, Cd , Zn, etc. is realised using different materials: biosolids (from municipal sludges), synthetic or native zeolites, zeolites and pillared clays with polynuclear aluminum salts, lime, ashes, hydroxyapatites[1–5].

Mobility of metals in soil takes place due to soluble species that appear as a result of ionic exchange or sorption–desorption processes on surfaces of mineral and organic compounds. *In situ* stabilisation of metals is referring to the processes by which heavy metals can not be transported physically or biologically, in soils. These processes are combined with phytoremediation processes.

Basic processes that influence metals repartition between solid phases and solution from soil, are ionic exchange, adsorption, precipitation, complexation. Due to the formation of complexes, solubilisation of metals takes place, e.g. of Cd, Cu, Pb, Zn, etc. Metals repartition between soil and solution depends on the following factors:

– pH that influences concentration of soluble and bioavailable metals. In acidic conditions, the most important process is adsorption; pH depends on surface charge, and it is associated with protons reaction in points of mineral oxyhydroxides and some functional groups of humic substances. An important aspect is buffering capacity of soil; by carbonate adding to soils polluted with heavy metals, an increase of buffering capacity takes place, metals are blocking and their widespreding is avoided;

– soil texture has influence on metals affinity for adsorption; in case of Pb, this process is produced in the following order: clay > fine sand > gross sand. Cd, Zn, Cu, and Pb mobility is greater in sandy soils, and plants take more easy metals than from the soils with greater content of clay. Metals are accumulated in clays due to great adsorption surfaces;

– presence in soil of iron and manganese oxyhydroxides will increase intensity of adsorption processes and reduce the content of soluble metal;

– other factors like cation competition, salinity, temperature and biocenosis activity will reduce the content of soluble metals;

– organic matter is a potential accumulator for metals; it has an important role concerning metal mobility in soil. Polluted organic matter will become a storage for metals, a secondary source of pollution that can deliver pollutants in some conditions.

DISCUSSION

Immobilisation of metals from polluted soils. The answer of environment to the exposure of metals pollution like Cd, Pb, Zn from polluted soils means different risks for human health, phytotoxicity for plants, soil and water pollution, a high ecotoxicity degree of land. Chemical immobilisation is a remediation method using different chemical reagents like agricultural fertilisers, zeolites that are introduced into polluted soil in order to reduce metals mobility or solubility[6–10].

These stabilisation processes decrease metals bioavailability for plants. By introducing chemical reagents in soil, heavy metals may react with them to form minerals *in situ*. So, metals can remain in soil in a less dangerous form. This approach gained attention in the last decade, and many tests for metals immobilisation in experimental sites or even in polluted zones were realised.

For metals immobilisation are used pillared materials, organic and inorganic that are introduced in soil in one or more stages. Pollution degree of soil will influence doses of supported materials and plant species used for phytoremediation. Monitoring of system, polluted soil – supported material – plants, must be realised during entire vegetation period, for determination of metals accumulation degree both in supported materials and in plants tissues.

In a study on a soil polluted with Pb, Cd, Zn, the following immobilising agents were used: municipal biosolids stabilised with lime, municipal biosolids anaerobic stabilised, phosphatic rock or ammonium phosphate, zeolites, composts. The results of immobilisation treaments are analysed by evaluation of metals bioavailability decreasing to plants, used in the phytoremediation process[11–15].

Thus, by using of ammonium phosphate, a fertiliser, it will react with lead from polluted soil to form pyromorphite, an insoluble mineral; the time necessary for this process is similar with that used for excavation. To evaluate the stability of chemical products formed by immobilisation processes, it is necessary to determine metals solubility, especially when acidic conditions are present in soil.

Chemical reagents used for immobilisation are pH dependent, and many times, rain changes soil acidity.

In Table 1 are presented costs for soil treatment; in case of immobilising, costs are smaller with 50% than for excavation.

Table 1. Comparative prices for different remediation processes of soil polluted with heavy metals

Remediation	Costs/m^3	Time for operation
Excavation	100-400 USD	6-9 months
Immobilising *in situ*	90-200 USD	6-9 months
Phytoremediation	15-40 USD	18-60 months

Treatment with supported materials. The most used supported materials are natural zeolites, which decrease metals mobility and increase their retaining on imobile solide phases. The influence of these agents onto mobility, bioavailability, and metals toxicity is followed by modified distribution coefficient, bioavailability factor, transfer and recalcitrant factors which give informations concerning metal quantity retained in soil, comparatively with mobile metal quantity. Application of these remediation techniques for soils polluted with different metals (cadmium, zinc, lead, chromium) gave satisfactory results in Poland, Italy, France and Gemany[16–22].

Synthetic and natural zeolites are used both for remediation of soils polluted with heavy metals and for soil quality improvement, retaining of water, ammonia and pH control. Their selectivity is determined by several factors: ion dimensions and their solvation state, Si:Al ratio, skeleton geometry, temperature[5, 8].

Volcanic tuff, synthetic zeolites, dolomites, are pillared materials for hetero-polynuclear complexes from iron and aluminium oxyhydroxides, other solid materials with blocking properties for mobile metallic ions from soils. These heteropolynuclear complexes consist of aggregate which retain mobile ions from neutral and weak acids soils, and thus metal toxicity and solubility is reduced.

Now, pillared materials are used together with phytoremediation for polluted soil remediation. Pollution degree of soil influences necessary doses of supported material, and plant species used for phytoremediation.

The use of pillared materials consisting of native volcanic tuff – Al_n, is realised in different proportions, 0.6-6%, for metallic ions blocking and decreasing of their mobility. For a waste mining zone, consisting of gross sand 65%, fine sand 15%, organic matter 5%, and dust 15%, it is used 4% native zeolite, to reduce metals mobility with 50-80%, during one year.

Pillared materials are introduced in soil by specific tillages. Inorganic and organic materials are introduced in polluted soil in one or successive steps. It is necessary to introduce in polluted soil organic materials, in order to assure both organic matter and necessary NPK. Like organic material are used manure, bio-solides, composts, that are introduced in soil through agricultural works. Doses of organic fertilisers may reach up to 8-10 t/h.

Aluminum (Al_{13}) basic polychloride and montmorillonite supported with poly-nuclear salts are used as immobilising agents for treatment of soils polluted with metals. In case of aluminum basic polychloride, 1-8 mmol Al_{13}/kg d.s. were used for zinc immobilisation, and supported material montmorillonite – Al for cadmium and lead retaining. Native volcanic tuff – Al_n is applied in different proportions to soil, 0.1-6%, in order to block metals and decrease their mobility.

Two immobilising reagents, aluminum basic polychloride and montmorillonite supported with aluminium polynuclear salts, were used for treatment of two different soils: one soil from Zurich canton, Swiss, with a medium pollution level due to successive treatments with municipal sludge, containing 2.5% organic matter; the other soil, a sandy soil, from one very industrialised zone, Upper Silezia, Poland: due to metals processing industry, soil is polluted with cadmium, zinc, lead, and contained 1.5% organic matter.

The destroying of organic matter from soil of Silezia, produced great quantities of cadmium and zinc in liquid phase. By treatment of this soil with 8 mmol Al_{13}/kg d.s., metals immobilisation took place. It is appreciated that this effect is due to interaction of aluminum basic polychloride with organic matter from soil, which is followed by metals solubilisation. Both reagents, aluminum basic polychloride and montmorillonite supported with aluminium polynuclear salts, had a strong effect for metals immobilisation. In case of soil from Swiss, the same immobilisation effects for cadmium, zinc, and lead were recorded, for 1-2 mmol Al_{13}/kg d.s.

In neaby of Sevilla town, Spain, due to an accident at basins containing pyrite sludge and waste water, a large area was polluted, with surface of 40 km length and 0.50 km width; this area was polluted with a layer of 3-30 cm sludge. For zone remediation, it was took into consideration metal immobilisation, followed by phytoremediation[10].

Immobilisation treatment was realised with synthetic zeolite, manufactured from flaying ashes, produced at two electric power plants from Teruiele, NaP1-TE and Narcia, NaP1-NA. Alcalinity of zeolitic products reduced soil acidity. Four experimental areas were chosen in 1999, and eight in 2000. Zeolites were mixed with soil up to a deep of 25 cm, with doses of 10–25 t/ha, for zeolite NaP1-TE, and 18-54 t/ha for NaP1-NA.

In Table 2 are presented metals concentrations from soil and of water used for soil washing after treatment with zeolites, after one and two years. Small content of metals in waters used for soil washing, showed that mobility of Cd, Co, Cu, Ni and Zn, was reduced in great extent due to the treatment with zeolite. It may be observed that pH of soil after treatment with synthetic zeolite, increased to 7.5.

Table 2. Soil and washing water parameters after treatment with zeolites[10]

Parameter	Blank sample		Samples treated with NaP1-TE zeolite, after 2 years				Samples treated with NaP1-NA zeolite, after 1 year			
	soil	washing water	soil		washing water		soil		washing water	
Zeolite (t/ha)	0	0	10	25	10	25	18	54	18	54
pH		3.5			3.9	7.5			3.3	7.2
Cadmium	1	0.5	1	1	0.4	0.1	2	2	0.7	0.1
Cobalt	10	3.3	11	13	2.2	0.1	11	16	3.3	0.1
Copper	97	8.8	103	72	2.7	0.2	144	114	11	0.3
Nickel	18	1.9	21	23	1.6	0.1	21	25	2.7	0.1
Zinc	260	151	283	241	110	0.3	302	400	107	0.1

CONCLUSIONS

1. New techniques that were developed for metals immobilisation in soil and phytoremediation may be used for solving of different and complex pollution problems. *In situ* immobilisation of metals decrease the pollutant effects onto the environment. Soil treatment for *in situ* immobilisation of metals like Pb, Cd,

Zn, etc. is realised using different materials: biosolids (from municipal sludges), synthetic or native zeolites, zeolites and pillared clays with polynuclear aluminum salts, lime, ashes, hydroxyapatites.

2. For metals immobilisation are used supported (pillared) materials, organic and inorganic, that are introduced in soil in one or more stages. Pollution degree of soil will influence doses of supported materials, and plant species used for phytoremediation. Monitoring of systems, polluted soil – supported material – plants, must be realised during entire vegetation period, for determination of metals accumulation degree both in supported materials and in plants tissues.

3. The most used supported materials are natural zeolites, which decrease metals mobility and increase their retaining on imobile solide phases. The influence of these agents onto mobility, bioavailability and metals toxicity is followed by modified distribution coefficient, bioavailability factor, transfer and recalcitrant factors, which give informations concerning metal quantity retained in soil, comparatively with mobile metal quantity.

Aluminum (Al_{13}) basic polychloride and montmorillonite supported with polynuclear salts, are used as immobilisating agents for treatment of soils polluted with metals: 1-8 mmol Al_{13}/kg d.s. were used for zinc immobilisation, and 0.1- 6 % native volcanic tuff – Al_n is applied to soil, in order to block metals and decrease their mobility.

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