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HEAVY METAL REMEDIATION TECHNOLOGIES IN LATVIA: POSSIBLE APPLICATIONS AND PRELIMINARY CASE STUDY RESULTS

TECHNOLOGIE REMEDIACJI OBSZARÓW ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI NA ŁOTWIE: MOŻLIWE ZASTOSOWANIA I WSTĘPNE WYNIKI BADAŃ

Abstract: Environmental contamination with heavy metals as a result of anthropogenic activities is not a recent phenomenon. Contaminated sites with heavy metals can be found in functioning as well as abandoned industrial (brownfield) territories, landfills, residential areas with historical contamination, road sides and rarely in polluted sites by natural activities. Pollution data on its amount and concentrations is known from historical studies and monitoring nowadays, but it should be periodically updated for the use of territorial planning or in case of a change of the land use. A special attention should be paid to heavy metal contamination, because in many cases this contamination is most problematic for remediation. 242 territories now are numbered as contaminated and fixed in the National Register of contaminated territories - at least 56 of them are known as contaminated with heavy metals in different amount and concentration. Legislative aspects are discussed as well as an overview of soil and groundwater contamination research and the possible remediation technologies in Latvia are given. Two case studies are described in order to give the inside look in pre-investigations done before potential start of heavy metal remediation works.

Keywords: heavy metals, contamination, remediation technologies, stabilization/solidification technology

Introduction

Soil remediation as the necessity

Soil and groundwater are environmental compartments that are primarily influenced by industrial development with increasing amount of industrial wastes and inadequate dumping of them. It causes a large number of contaminated sites that are disseminated in post industrialized countries [1, 2]. In the EU estimated contaminated sites vary from 300,000 to 1.5 million that is due to the uncertainty of the common definition for contaminated sites, different approaches to acceptable risk levels, and exposure parameters [3]. Later on, Vanheusden [4] have reported that according to the European Commission the EU counts

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~3-5 million potentially contaminated sites and 500,000 sites known as contaminated sites. The latter needs remediation activities.

Development of soil and groundwater remediation technologies is a matter of great importance to eliminate historically and currently contaminated sites because going pollution deteriorates environmental quality, the possibilities of site operation, and land of full value use. Contamination causes loss of land as a resource as well as loss of property. Importance of material property damage as pollution expression is emphasized also in [5]. Thereby a decision regarding the purchase and renovation of property quality is influenced. A single concern about environmental contamination at a site is often enough motivation to prevent an acquisition and to develop site remediation project in order to eliminate or at least to reduce contamination presence in soil and groundwater. The aim of remediation activities is to transform unusable property into available use and conserve land resources, to improve environmental conditions in the contaminated site and around it as well as to reduce the risk to humans and the environment. Remediation means actions taken to cleanup, mitigate, correct, abate, minimize, eliminate, control and contain or prevent a release of a contaminant into the environment in order to protect human health and the environment, including actions to investigate study or assess any actual or suspected release. Remediation may include, when appropriate and approved by the department, land use controls [6]. The noted definition shows that it is a broader term than cleanup and includes the management of a contaminant at a site so as to prevent, minimizes, or mitigates damage to human health or the environment [2].

Legislation in Latvia

The Law “On Pollution” (came into force on 1 July, 2001) defines the procedures in the sphere of contamination [7]. The purpose of the Law (Section 2) is to prevent or reduce harm caused to human health, property or the environment due to pollution, to eliminate the consequences of harm caused. A local government in co-operation with the relevant Regional Environmental Board of State Environmental Service has an obligation to ascertain and initially assess polluted and potentially polluted sites in a relevant administrative territory (Section 33). The Ministry of Defence has to ascertain and initially assess polluted territories in its possession and notify the relevant local government and regional environmental board thereof (Section 34).

Methods and procedures for the ascertaining of polluted and potentially polluted sites, as well as the procedures for financing, conditions for data collection and utilisation are regulated by the Cabinet of Ministers Regulations No. 483 adopted on November 20, 2001 “Inventory and registration of contaminated and potentially contaminated areas” [8].

Latvian Environmental, *Geological and Meteorological Agency* (supervised institution of Ministry of Environmental Protection and Regional Development, *MEPRD*) has an obligation to maintain all collected and processed information about contaminated sites.

A special attention is made to the territories of historical military unexploded ammunition and explosive objects that was caused by warfare during World War II. Therefore the MEPRD in co-operation with the German Ministry of the Environment and in co-operation with the Ministry of Defence implemented the draft and prepared the following Cabinet Regulations project in 2005 “On Legislative Regulations for Remediation of Contaminated Sites with Historical Military Unexploded Ammunition and Explosive Objects”. This legislative act should be governing the procedure of licensed companies to license commercials, which will be capable to investigate and remediate unexploded ordnance and explosive objects in contaminated sites [9]. At present the Regulations are not still accepted.

General classification of remediation technologies and contaminated sites

Remediation technologies can be divided into two categories: *in-situ* and *ex-situ* remediation methods [10] as well as on site and off site technologies. On site remediation is carrying out on the contaminated site using *in situ* or *ex situ* approaches. In off site treatment process contaminated soil and/or groundwater are removed from the excavated site (*ex situ* approach). It demands the transportation of the contaminated soil and/or groundwater to the treatment facilities. An *in-situ* method means that a contaminated substance in soil or groundwater is treated in the place where the contamination is determined. *In-situ* technologies are used for treatment of unexcavated soil or unextracted groundwater that remains relatively undisturbed after cleanup process. The following *in-situ* and *ex-situ* remediation technologies are used for reduction of heavy metal contamination level:

a) *in-situ* and *ex-situ* technologies - bioremediation, *stabilization/solidification* (S/S), and separation/concentration;
b) *in-situ* technologies - soil flushing, electrokinetics, barriers/treatment walls, chemical treatment, soil amendments, and phytoremediation;
c) *ex-situ* technologies - soil washing.

Technologies based on the used processes include biological, physical separation, chemical, physical-chemical, thermal, and containment techniques. In bioremediation technologies microbiological metabolism is used to transform or degrade soil or groundwater contaminants into harmless substances. Physical and chemical treatment technologies are based on the physical and/or chemical properties of the contaminants as well as on the contaminated media to chemically convert, separate, or contain the contamination.

Contaminated sites with heavy metals, oil products and other contaminating substances and materials can be found in current industrial areas as well as in abandoned industrial territories, illegal dumping sites, harbours, agricultural and residential areas with historical contamination, road sides and somewhere else. Contaminated sites from the list of national importance generally can be grouped in subcategories, as of the former or the present economic use. The following contaminated sites can be divided in Latvia. Further in the Table 1 main contaminated sites with heavy metals are shown as well as possible technology could be applied for the remediation. The type of remediation must be approved, of course, after the appropriate evaluation of geology, hydrogeology, contamination quantity, environmental risks and at the end also economic prerequisites.

The first subcategory, which can be outlined in a distinct way, contains the *former dump sites* of mixed waste. In former USSR municipal, residential, housing, and building waste as well as hazardous substances and materials were often dumped in these dump sites. Table 1 shows main contaminated sites of the first category, type of contamination as well as probable recommendations for remediation actions of some of the noted sites.

Another very important group is *former military territories*, after the collapse of the former USSR. After the World War II more than 1,000 units of Soviet Army forces were located in about 600 military objects that occupy ~10% of Latvia territory. The largest firing-grounds were Zvarde, Liepajas Navy port (Karaosta), Rudbarzi missile base, and Lielvarde airfield. Site pre-investigations and remediation has been carried out in some of former military territories, *eg* Rumbula airfield where soil and groundwater was contaminated with oil products. Total area of 6 ha is contaminated with oil products and during 2000-2002 there were pumped out 1730 m^3 contaminated groundwater (~80 m^3 pure oil product) [11]. Contamination with heavy metals, toxic organic substances, and also with oil products was determined in about 11 military territories. In spite of the remained historical contamination some of these territories are readjusted for the use of another purpose, *eg* the area of Riga Freeport.

Areas of *industrial contamination (brownfields)* - in these territories a lot of raw materials including heavy metals, various their compounds, inorganic and organic substances have been used. Industrial development simultaneously caused site contamination that in many cases is set as historical contamination. The former military industrial areas could also be included in this subcategory, but in the frame of the current paper we separate those for better understanding.

Especially hazardous sites must be counted separately, *eg* liquid toxic substances dump site in Jelgava (mostly groundwater contamination), biomedical and chemical industry dump site (Olaine), former treatment facilities of the city Riga and similar ones.

General group of contaminated areas comprises ex-warehouses, former and existent fields of ironscrap, the well-worn industrial facilities, territories with various contaminating materials and substances, *eg* agricultural chemicals. Their further use is frequently liable after adjustment activities in these territories however the environmental and risk assessment must be done in order to obtain information on environmental situation and quality of those territories.

In the middle 1990s the European Union framework cooperation for remediation of historically contaminated sites has been started in Latvia [12], the base legislation Act is the Law "On Pollution" [7]. At present the following remediation technologies are applied in Latvia: 1) stabilization/solidification; 2) soil flushing; 3) electrokinetic treatment; 4) phytoremediation and 5) bioremediation. The applicability of remediation technology is dependent on site-specific conditions, type of contaminants and other factors. List of contaminated sites is regulated by one main legislation Act [8]. In Latvia there are 56 territories contaminated with heavy metals, most important are given in Table I. Approximately half of these territories are concentrated in Riga, and more than a half of those are situated in the territory of the Freeport of Riga (Fig. 1).

Table 1

List of main heavy metal contaminated sites of the first category and recommendations for probable remediational action after preliminary research [11]

1.	Location, name	Type of contamination	Recommendations for probable remediation actions
2.	JSC Lokomotīve, Daugavpils, industrial area	HM[1], OP[2]	Environmental contamination assessment
3.	Liquid toxic substances dump, Jelgava	HM, elements in anionic form, OP	Groundwater treatment methods
4.	Zvārde tank polygon, former military area	OP, HM	Phytoremediation
5.	Liepāja Port Channel	HM	Stabilization/solidification
6.	Former Pesticides Warehouse, Viļāni	DDT[3], HM	Environmental contamination assessment

7.	"BIOLAR" dump of toxic substances, Olaine,	Toxic hazardous substances, HM	Groundwater treatment methods
8.	Olaine dump site	HM	Risk assessment, monitoring, re-cultivation
9.	Mārupe Landfill	COD[4], N, P	Risk assessment, monitoring, re-cultivation
10.	Priedaine dump site	COD, ammonia, OP, HM, N	Risk assessment, monitoring, re-cultivation, reactive walls
11.	Bangas, former Soviet Army missile base, former military area	OP, HM	Risk assessment, stabilization / solidification, phytoremediation
12.	Ventspils fishing port, fuel base	OP, HM (Zn, Cu, Pb)	Environmental contamination assessment
13.	Ķilupe Landfill, Ogresgals	COD, elements in anionic form, N	Risk assessment, monitoring, re-cultivation, reactive walls
14.	Getliņi Landfill, Riga	Elements in anionic form, N, COD	Risk assessment, monitoring, reactive walls, soil flushing
15.	JSC Bolderāja Former Sewage Treatment System, Riga Port	COD, surfactants, Fe, sulphates, N, OP, HM	Stabilization/solidification
16.	Lacon Ltd., former Soviet Army fuel base, Riga Port	OP, HM (Pb)	Stabilization/solidification
17.	Bolderāja ship repair yard, Riga Port, brownfield	OP, COD, alcohols, phenols, surfactants, N, HM (Pb, Cd, Cu)	Stabilization/solidification
18.	Mekora, Ltd., Former 145. Military Factory	OP, COD, HM (Ni, Zn, Cu, Pb)	Environmental contamination assessment
19.	Kleisti dump site, Riga	HM (Zn, Pb, Cr), COD, N, elements in anionic form	Risk assessment, monitoring, recultivation, reactive walls, soil flushing
20.	KRS Ltd., Riga Port industrial area	Adhesive waste from paints, varnishes, inks, OP, HM, Hg	Environmental contamination assessment, groundwater treatment methods
21.	Freja Ltd., former Soviet Army Territory, Riga Port	HM, OP	Risk assessment, monitoring, stabilization/solidification
22.	Russo-Balt Ltd., Riga former military factory	HM (Pb, Zn, Cd), OP	Environmental contamination assessment
23.	JSC Latvijas Krāsmetāli, Riga, brownfield	HM, OP	Environmental contamination assessment
24.	Former "Alfa" area, Riga, brownfield	Trichlorethylene, COD, SAS, OP, alcohols, phenols, HM	Risk assessment, stabilization/solidification, phytoremediation
25.	Deglava Street dump site	COD, N, V, elements in anionic form	Risk assessment, monitoring, re-cultivation
26.	Former Alfa Area 2, Riga, brownfield	Ammonia, acids, HM	Risk assessment, stabilization/solidification, phytoremediation
27.	Latvijas Nafta, Riga, brownfield	COD, OP, HM (Zn, Pb)	Environmental contamination assessment
28.	Bieķengrāvis, former hazardous waste dump	COD, OP, N, HM (Cu)	Environmental contamination assessment,
29.	Viva Color Ltd., Riga, brownfield	Phenols, N, HM (Pb, Zn)	Risk assessment, stabilization/solidification, phytoremediation
30.	Eko Osta, Riga Port, former Soviet fuel base	OP, HM	Risk assessment, stabilization/solidification, phytoremediation

31.	Riga Gardening Pesticide Warehouses (former)	OP, HM	Risk assessment, stabilization/solidification, phytoremediation
32.	”Energoautomātika” former industrial area, Riga	Pb, As	Environmental contamination assessment
33.	Vega Stividors, Riga Port, industrial area	HM, As	Stabilization/solidification, phytoremediation
34.	BLB, Riga Port, industrial area	HM, OP, HM (As)	Stabilization/solidification, phytoremediation
35.	Magnāts Ltd., Riga Port, industrial area	OP, HM (Pb)	Stabilization/solidification, phytoremediation
36.	Grand Ltd. former light bulb factory, brownfield	OP, HM (Pb, Cu)	Environmental contamination assessment
37.	JSC Starts Riga, industrial area	COD, HM (Pb)	Environmental contamination assessment
38.	SJSC Latvenergo TEC-1, Riga, brownfield	OP, elements in anionic form, ammonia, HM	Environmental contamination assessment
39.	Former mordant site, Ancene	Amines, HM (Cu, Zn)	Environmental contamination assessment

[1] HM - heavy metals; [2] OP - oil products; [3] DDT - dichlorodiphenyltrichloroethane (pesticide)

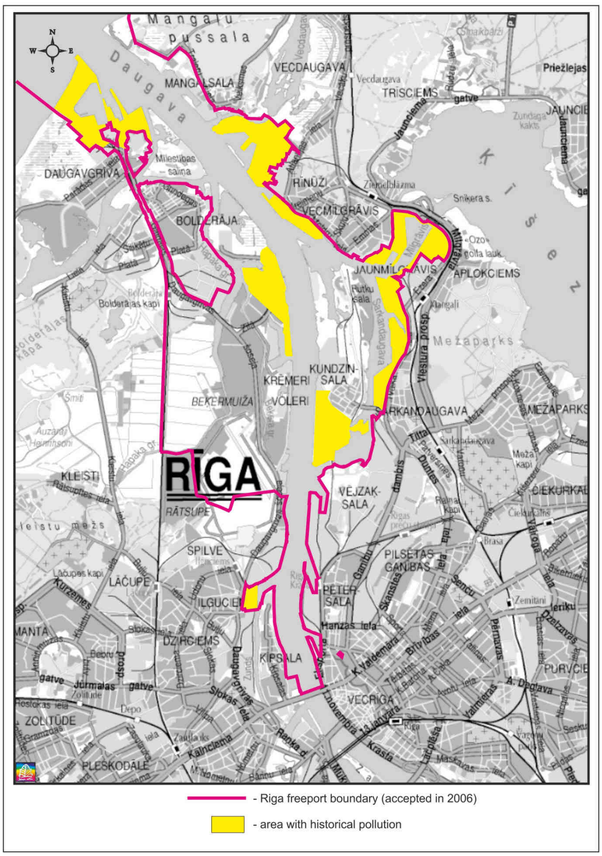

Fig. 1. Historically contaminated sites in the freeport of Riga

In autumn 2010 the promotion of two great scale stabilization/solidification projects were started in the sites of Liepaja and Riga ports. The projects should be viewed as the pilot ones for further development of remediation works in Latvia. The use of the S/S technology is not the only solution for the remediation and demobilisation of toxic compounds; the further research might be done to draw a sketch for the use of other heavy metal remediation technologies, but the case study has improved that S/S technology still would be one of most effective for active and former industrial territories, because stabilized areas does not threat the environment around and also can be used for industrial construction use in future. The present study is carried out, mainly, to give an overview to the problems concerning heavy metal contaminated areas in Latvia and describe preliminary research before one of the application - stabilization / solidification technology preliminary research in the Freeport of Riga. This site is situated in Riga, Jaunmīlgrāvis (Fig. 1).

Before the representing of the preliminary research results, this paper describes some other methods / technologies, which could be potentially used in Latvia for heavy metal contaminated sites treatment.

Description of main applicable technologies

Stabilization / solidification technologies are based on the treatment of contaminated soils with materials such as cements and siliceous pozzolans and it can be employed *in situ* or to the excavated material. As a result, the mobility of the contaminant is reduced by physical-chemical processes. Solidification of the polluted substrate with cement restricts its contact with groundwater and air. Cement and siliceous pozzolans react with metals and cause the formation of hydroxides, carbonates and silicates of very low solubility. This treatment is not efficient for heavy metals that form soluble hydroxides or anions species. It should be emphasized that the mixing process and the heat generated by cement hydration reaction can increase the vaporization of organic pollutants (Fig. 2) [13].

S/S technologies have been used for decades as the final treatment step prior to the disposal of both radioactive and chemically hazardous wastes. The stabilization refers to an alteration of waste contaminants to a more chemically stable form, thereby resulting in a more environmentally acceptable waste form. Typically, the stabilization processes also involve some form of physical solidification [14].

Soil flushing is based on leaching with water, acids or other flushing solvents. The choice of washing solution has to address the contaminant presented in the soil and the possible environmental side effects. The contaminated fluid is collected and pumped to the surface where it can be recirculated, removed, or treated or re-injected. Technology can be combined with physical barriers to avoid the deep percolation. The technique can be used for *in-situ* treatment of soils contaminated with organics, metals and radionuclides (Fig. 3).

Electrokinetic technology can be applied in wide areas, where there are no economic activities at the moment. Such places are former industrial and military firing-grounds, left after the collapse of the USSR. Electrokinetics is a quiet expensive technology. Electrokinetic technology (Fig. 4) is applicable to water soluble contaminants at sites with homogeneous soils that are fine-grained and exhibit both high permeability and high moisture contents.

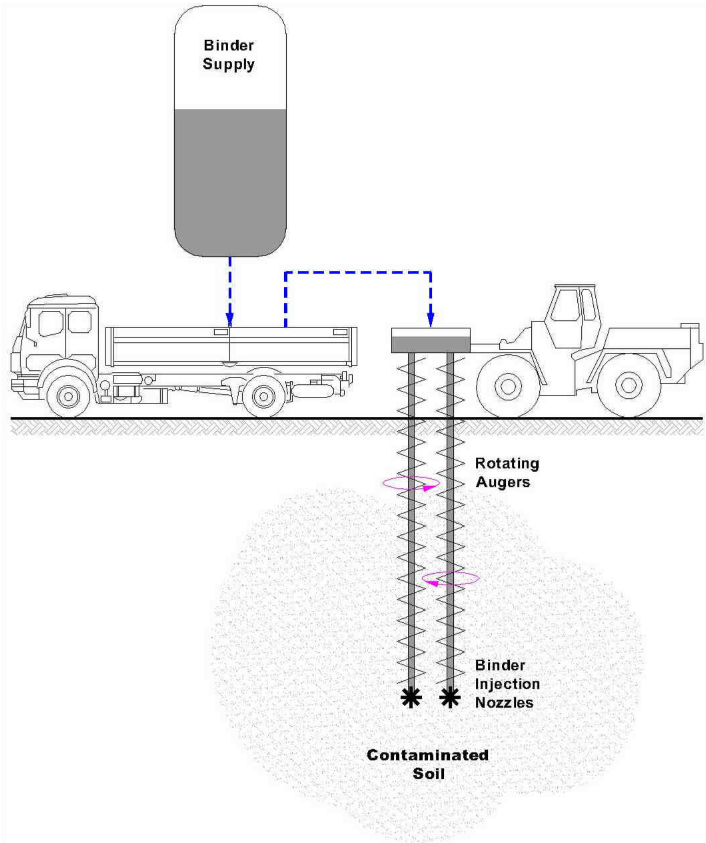

Fig. 2. Stabilization/solidification technology for remediation of various contaminants - heavy metals, oil products, PCB's etc.

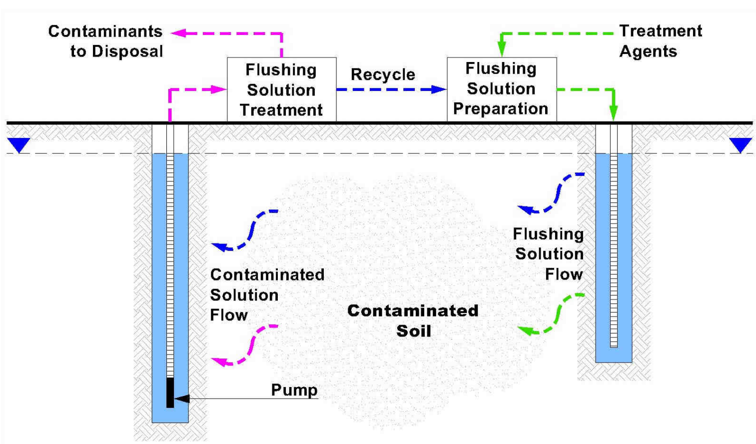

Fig. 3. Soil flushing technology

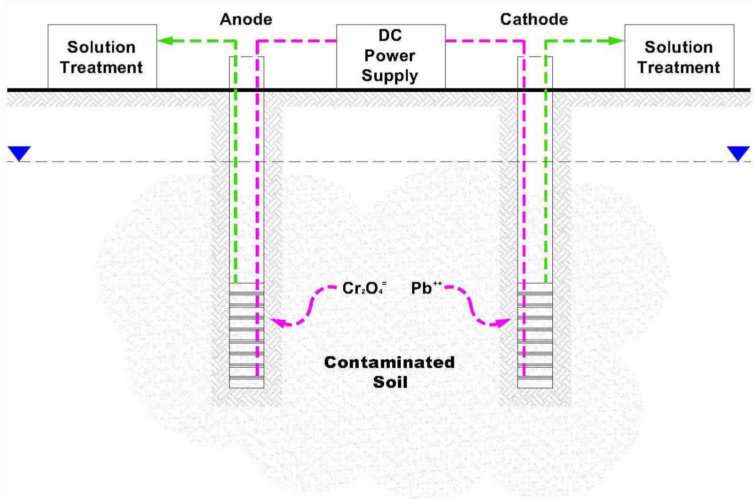

Fig. 4. Electrokinetic technology for heavy metal contamination remediation

The technology is most efficient when salinity and cation exchange capacity are low. Electrokinetic technology has the following advantages: 1) may be able to treat soils not accessible for excavation; 2) potentially effective in both the saturated and unsaturated zone; 3) applicable in soils of low hydraulic conductivity, particularly with high clay content; 4) can treat both organic and inorganic contaminants. Applicability limitations of electrokinetic technology includes the successive aspects: 1) contaminant solubility and the desorption of contaminants from the soil matrix may limit the success of the technology; 2) the process may not be efficient when the target ion concentration is low and the non-target ion concentration (background) is high; 3) the technology requires the presence of a conducting pore fluid to mobilize contaminants; 4) heterogeneous or anomalies found at sites, such as submerged foundations, rubble, large quantities of iron or iron oxides, and large rocks or gravels that may reduce removal efficiencies [15].

Phytoremediation is a relatively new approach to removing contaminants from the environment. It may be defined as the use of plants to remove, destroy or sequester hazardous substances from the environment. Unfortunately, even plants, that are relatively tolerant of various environmental contaminants, often remain small in the presence of a contaminant. Phytoextraction is very dependent on plant and soil factors, such as soil suitability for plant growth, depth of the contamination, depth of the plant root system, level of contamination, and urgency in cleaning up. Furthermore, there is need for a full understanding of the physiology, biochemistry, uptake etc., of the plants employed [16]. The climatic conditions and bioavailability of metals must be taken in consideration using phytoremediation. The plants will have to be isolated from wildlife and agricultural lands. Once contaminated, the plants will have to be disposed of in an appropriate fashion. Some techniques include drying, incineration, gasification, pyrolysis, acid extractions, anaerobic digestion, extract of the oil, chlorophyll fibres from the plants or disposal since plants are easier to dispose of the soil [17]. Phytoremediation will be most applicable to shallow soils with low levels of contamination (2.5÷100 mg/kg). In comparison with other remediation technologies phytoremediation is permanent technology. More research is needed to enhance the extraction of the metals by the plants through genetic breeding or other technologies and how to correlate bioavailability with metal uptake. Crop plants that grow fast may be viable for phytoremediation [18]. In spite of slow process of phytoremediation that is limited by specific metal hyperaccumulator species and some other factors phytoremediation mitigates environmental problem without the need to excavate the contaminated soil. Sarma [19] has reported that more than 750 terrestrial and aquatic plants have potential value for phytoremediation. They are used to reduce wide spectra of heavy metal concentrations in contaminated land and groundwater, for example, Ni, Cu, Cd, Cr, Hg, As, Ag, Se, Zn. Results of Sas-Nowosielska et al [20] indicate the potential for using some species of plants to treat Hg contaminated soil through stabilization rather than extraction. However in Latvia phytoremediation has not been done in contaminated industrial sites, but this approach should be used in further decontamination works, where the concentration of metals is not so high.

Biological technologies for remediation take advantage of the pathways developed by microorganisms to protect themselves from oil products and metals. Common protection mechanisms include oxidation/reduction, sorption and methylation. Biotechnologies that incorporate these mechanisms are in an advanced state of development for the remediation of organic compounds, but experience is limited for inorganic contaminants. Such processes as bioleaching, biosorption, biovolatilization, and biological oxidation and reduction may provide *in situ* treatments without the use of environmentally aggressive chemicals [13]. Techniques for the extraction of oil products and heavy metals by microbiological means are rather limited at this time. The main technologies include bioleaching and oxidation/reduction reactions. At present biological treatment technologies are in development stage and will be experimentally tested in some brownfield areas in the near future. Microorganisms are also known to oxidize and reduce heavy metals, *eg* Hg and Cd can be oxidized while As and Fe can be reduced by microorganisms but Cr(VI) can be reduced to Cr(III) that is less mobile and toxic. Bacteria such as *Bacillus subtilis* and sulfate reducing bacteria in the presence of sulfur can perform this reaction. Another process (called mercrobes) has been developed and tested in Germany at heavy metal concentrations greater than 100 ppm. Since the mobility is influenced by its oxidation state, these reactions can affect the contaminant mobility [18].

Reactive walls, isolation and containment approaches are used in order to stop the contaminating groundwater flow in combination with other remediational technologies. The advantages of this technique are that it is *in situ*, a wide variety of contaminants can be treated and flow control can be used. Further research is required in the areas of matching the contaminant with the media in the barrier, optimization of the flow and retention time through the barrier, and technologies of regenerating the media [18].

Materials and methods

Site description

The studied territory is situated in the northern part of Riga, approximately 5 km from the estuary of the River Daugava in the Gulf of Riga (see Fig. 1, Jaunmīlgrāvis). Study area is economically active from the beginning of the 20th century. In earlier years (1894-1967) the territory was used for several industrial purposes including the manufacturing of superphosphates, but just nearby the dump site for tailings was made. Later in this area the oil product storage, reloading and transit terminal was founded. In 60-ties of the 20^{th} century the factory-workshop was functioning, but later the oil product terminal facility overtook the area. Soil pollution source mainly was superphosphate production waste (slag), where the highest concentration was received for lead, copper, zinc and arsenic. Total amount of toxic heavy metals throughout the whole research area was estimated 1264 Mg (tons) or 15 kg/1 m^2 of slag or: 755 Mg (tons) of copper, lead 85 Mg (tons), zinc 358 Mg (tons), 66 Mg (tons) of arsenic.

Territory geomorphology is slightly undulating and technogenically changed. Earlier the area was the floodplane of the armlet of the River Daugava, but now it is covered by approximately 4 m thick technogenic filled soil layer, which is made of sand, debris, glass, slag and other civilisation wastage. The filled soil almost at all of the territory is underlayed by 0.5 m thick flood plane mud and clayey sand. Thick Littorina Sea fine marine sand sediments are embedded under this layer by several meters.

Hydrogeologically the first groundwater horizon is upper groundwater and it is found in filled soil as well as in marine fine sand sediments. Areas, where there is no mud or clayey sand, groundwater makes the common groundwater horizon. Groundwater level in the territory depending of the season is at the depth of 1.5 m till 2.5 m from the surface. The wider amplitude of levels can be seen in filled soil layer (up to 0.6 m). The direction of the groundwater flow is to the River Daugava. Ground and groundwater in the territory is strongly contaminated with heavy metals, separate areas also with oil products [21].

Sampling methods and research stages

According to the earlier made researches by "Ekohelp" Ltd. the contamination oversize includes ~1,000 Mg (tons) of different metals. Mostly they are concentrated in calces (tailings) of sulphuric acid manufacturing process and widely distributed in the area as filled soil. The thickness of calces is changed from 1-4.5 m. Toxic heavy metals gain high mobility by precipitation and infiltration processes. Therefore, the remediation method must be chosen to decrease the mobility of heavy metals. In order to choose the remediation method the pre-investigation was done in 2 stages. The first stage involved existing material analysis and gaining of the pollution distribution in whole industrial area. The second is more detailed stage and was carried out after gaining results from the first stage and included sampling and testing for the future application of the S/S method.

First research stage. Drilling sites were chosen after careful analysis of historical research study materials. Drilling works were done with *Fraste „Terra - in"* drilling machine. The auger drilling method has been chosen, and boreholes up to 5 m of depth were drilled.

Sampling of soil was made from the upper part that covers interval of 0.50-2.00 m in the depth (for estimation of soil quality at the upper layer), but the second interval was in the depth of 3.00-4.50 m. The total area of soil sampling covered 1.82 ha.

Second research stage. The pilot study area was chosen based on results of the first stage research. The studied territory was chosen by economic reasons (not directly industrially used at the moment). We estimated that the contamination level of this part is more or less characterized for the whole area on average. During the second stage 5 soil samples were taken in order to choose the one for the testing needed for stabilization purposes [22].

Sample analysis and results

All soil samples were analysed in the "Eurofins" laboratory in Finland. The following heavy metal concentrations were determined: Pb, Zn, Cu, Ni, Cd, Cr and Hg in accordance with ISO 17294-2 method and As by NEN 6966 [23].

Afterwards at the second research stage stabilization testing with the leaching test was done in "Eurofins" laboratory in Germany. One sample from five was chosen in order to test the possible stabilization. The sample was chosen, because the contamination level in soil was the closest to the average level in the pilot study area of 1.82 ha.

The sample was mixed and afterwards divided into three parts: one part was cemented with 5% cement of weight, second - 13% cement of weight, but the third - was left without cementing (zero sample) [22]. The special leaching test BS EN 12457-2 was used in order to study the behavior of the solidified mass in the environment [24].

The final part of the testing included geotechnical compression testing in order to get know the parameters for the construction on stabilized / solidified soil (results are not described in the present study).

Results and discussion

The obtained results of the pre-investigation show that the studied territory is contaminated with As, Cu, Zn, Pb and some sites are also contaminated with Cd, Ni, Cr and Hg. The average soil contamination level exceeds the acceptable legal norms: 13.5 times for As, 20.6 times - Cu, 6.6 times - Pb, also the legal acceptable level is reached for Zn and Hg. Table 2 shows testing results from the pilot study area: the average value of heavy metal concentrations obtained from 5 sample analysis, taken in 1.82 ha area, as well as testing result for the sample, which was taken for leaching test.

Table 2

Heavy metal average concentrations [mg/kg] in soil upper layer of the pilot study area [22]

	Cd	**As**	**Ni**	**Cr**	**Cu**	**Zn**	**Pb**	**Hg**
Average in pilot study area	2.26	255	6.85	9.35	1145	1455	620	0.475
Sample for S/S testing	2.3	350	8.1	13	2100	1200	400	0.54
Acceptable legal norms (Latvia)	8	40	200	350	150	700	300	10

Table 3

BS EN 12457-2 leaching test results compared with soil contamination [mg/kg] [22]

Parameter	**Soil contamination in sample for S/S testing**	**Zero sample (pH level 3.2)**	**5% cement (pH level 10.5)**	**13% cement (pH level 10.5)**	**Acceptable leaching level after the use of S/S method (Finland)**
As	350	0.02	0.02	0.08	0.5
Cd	2.3	0.27	<0.002	0.002	0.02
Cr	13	<0.01	0.03	0.01	0.5
Cu	2100	600	0.25	0.27	2
Hg	0.54	<0.002	<0.002	<0.002	0.01
Ni	8.1	0.65	<0.01	<0.01	0.4
Pb	400	0.02	<0.01	<0.01	0.5
Zn	1200	36	0,04	0,03	4

The average sample was taken to leaching test and main results of solidified soil of 5 and 13%, as well as of “zero sample” are given in Table 3.

Leaching test has shown that “zero sample” is leaching out unacceptable amounts of heavy metals - Cd, Cu, Ni and Zn, but in the stabilized solidified form leaching is diminished and are at the acceptable level. Besides, the emission of cadmium and nickel leaches more even the total amount is under the acceptable level. The results show that S/S remediation method has high efficiency on heavy metals. As, Hg and Pb are not very mobile heavy metals in this case, as can be seen in Table 3.

Further research must be done while the remediation is in process in order to improve the chemical composition of the binder material for soil stabilization/solidification. After the end of remediation risk analysis must be done as well as monitoring network developed.

Conclusions

The *in situ* and *ex situ* technologies are used for remediation of the contaminated sites. Heavy metal remediation is mostly connected with the treatment of soil and demobilizing of toxic elements or excavation and *ex situ* after remediation. In large scale and high concentration level of contamination the stabilisation/solidification, electrokinetic, separation/concentration technologies are applied. Leaching test shows that in the stabilized solidified form leaching is diminished and is at the acceptable level. It certifies effectiveness of the applied S/S technique for heavy metal (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) remediation in industrial area.

The future of contaminated brownfield remediation in Latvia mostly could be done by S/S, soil flushing, electrokinetic, phytoremediation technologies or combined.

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TECHNOLOGIE REMEDIACJI OBSZARÓW ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI NA ŁOTWIE: MOŻLIWE ZASTOSOWANIA I WSTĘPNE WYNIKI BADAŃ

Abstrakt: Zanieczyszczenie środowiska metalami ciężkimi, w wyniku działalności człowieka, nie jest nowym zjawiskiem. Miejsca skażone metalami ciężkimi można znaleźć na wielu obszarach, m.in. na terenach poprzemysłowych, składowiskach odpadów, obszarach mieszkalnych, poboczach dróg, rzadziej zanieczyszczenia pojawiają się w sposób naturalny. Poziom zanieczyszczeń można ocenić na podstawie źródeł historycznych, a także na podstawie współczesnych badań. Informacje o zanieczyszczeniach powinny być okresowo aktualizowane na użytek planowania przestrzennego lub w przypadku zmian sposobów zagospodarowania. Szczególną uwagę należy zwrócić na zanieczyszczenia metalami ciężkimi, ponieważ w wielu przypadkach właśnie ten rodzaj zanieczyszczeń jest najtrudniejszy w remediacji. Obecnie wymienia się 242 obszary skażone, wpisane do Krajowego Rejestru Skażonych Obszarów - co najmniej 56 z nich to obszary skażone różnymi ilościami metali ciężkimi, występujących w różnych stężeniach. Przedyskutowano aspekty prawne, a także wyniki badań zanieczyszczenia metalami ciężkimi gleby i wód gruntowych na Łotwie oraz omówiono ewentualne technologie remediacji. Opisano dwa przykłady wstępnych wyników badań, poprzedzających remediację metali ciężkich.

Słowa kluczowe: metale ciężkie, zanieczyszczenia, technologie remediacji, technologia stabilizacja / zestalania