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Stabilization and Solidification Technology Implementation in Latvia: First Studies

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Abstract- *Soil and groundwater are environmental compartments that are primarily affected by industrial development with increasing amount of industrial wastes and inadequate dumping of them. A special attention should be paid to heavy metal contamination - at least 56 contaminated territories of National priority are known as contaminated with heavy metals in different amount and concentration in Latvia. The stabilization / solidification technology refers to binding of waste contaminants to a more chemically stable form and thus diminishing leaching of contamination. In order to choose the remediation method the pre-investigation in industrial case study area was done in stages: data analysis of previous research, sampling and testing for the future application of the S/S method. In order to select the most applicable binder material, series of experiments were done to determine leaching properties as well as compression and freezing-thawing tests in order to get information about geotechnical properties of bound soil with Portland cement additive. This was the first pilot research for implementing of this technology in Latvia as the final treatment step in cases of large amount of chemically hazardous wastes.*

Keywords: Heavy Metals, Brownfields, Remediation, Leaching Test, Compression Test

1. Introduction

Soil is a variable mixture of minerals, organic matter and water, capable of supporting the most fundamental requirements for sustainable land use. Therefore the quality of soil is basically important, and different technologies are used for the remediation of industrial contamination. 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 (9VAC20-160-10. Definitions, 1997). The soil pollution with heavy metals is an increasingly urgent problem all over the industrialized world. Excessive concentrations of heavy metals in soils often result from anthropogenic activities, such as the mining industry and the treatment of metal ores, waste incineration, road transport, and the use of fertilizers and agrochemicals (Lado et al., 2008). Soil amendments can often be used as one of *in-situ* technology for the rehabilitation process of contaminated soil.

Development of soil and groundwater remediation technologies is a matter of great importance to eliminate historically and currently contaminated sites because 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 European Directive (2008/1/EC).

Remediation technologies can be divided into two categories: in-situ and ex-situ remediation methods as well as on site and off site technologies as was previously shown (Reddy et al., 1999). Stabilization / solidification (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 as shown (Shi and Fernandez-Jimenez, 2006). Solidification encapsulates contaminants in a solid matrix while stabilization involves formation of chemical bonds to reduce contaminant mobility (Mulligan et al., 2001).

Successful results of S/S process could be achieved considering the type of solidified hazardous substances, their properties and the selected inorganic or organic binders. The possible binders used in S/S technology include: fluid fly ash, classic fly ash and cement as an additive as well as some others. Cement, however, is the most common and most often used binder (Kafka, Puncocharova, 2002; Malviya, Chaudhary, 2006; Kafka, Vosicky, 1999). The effectiveness of the applied S/S technology is assessed by leaching tests that are based on extraction to define the possibility of the solidified mass to release contaminants into the environment (Kosson et al., 2002). The compressive strength characterizes how the solidified mass ensures its safe disposal (Gailius et al., 2010). The S/S technology is an indispensable tool in waste management, remediation and port redevelopment (Wilk, 2004).

In autumn 2010 the promotion of two S/S projects was started in Liepaja and Riga prts, which were based on two previous investigations seris from 2001-2009 (Ekohelp, 2009) and 1996 (Baltec Associates, 1996). The projects should be viewed as the pilot ones for further development of remediation works in Latvia (Burlakovs, Vircavs, 2011). The use of the S/S technology is not the only solution for the remediation and immobilisation of toxic compounds; the further research might be done to draw a sketch for the use of other heavy metal remediation technologies. Case study has improved that S/S technology still would be one of most effective for active and former industrial territories, as well as areas can be used for industrial construction use in future. Leaching tests were performed at the University of Latvia laboratory, but geotechnical studies were carried out on solidified samples using assistance of "Tursons Ltd." geotechnical laboratory.

The aim of this work was to evaluate the quality of eventual application of S/S technology for remediation of real contaminated site of the National Priority List of Latvia.

2. Legislation and Study Area Description

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, thus the Registry list of contaminated and potentially sites initially was introduced in legislation of Latvia in 2001 under the power of the Law of the Republic of Latvia (2001).

The applicability of remediation technology is dependent on site-specific conditions, type of contaminants and other factors. In Latvia author outlined 56 territories contaminated with heavy metals of 242, that now are numbered as contaminated and fixed in the National Register of Contaminated and Potentially Contaminated Sites.

The area studied in this paper is situated in the northern part of Riga, the capital of the Republic of Latvia, approximately 5 km from the estuary of the River Daugava in the Gulf of Riga. Study area has been 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 were founded. In 60-ties of the 20th 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 t or 15 kg/1m^2 of slag or: 755 t of copper, lead 85 t, zinc 358 t, 66 t of arsenic (Ekohelp, 2009).

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 wastage. The filled soil almost at all of the territory is underlayed by 0.5 m thick floodplane mud and clayey sand. Marine fine sand sediments are embedded under this layer and have good filtration properties. First groundwater horizon is upper groundwater and it is found in filled soil as well as in marine fine sand sediments. 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 river. Ground and groundwater in the territory is strongly contaminated with heavy metals, separate areas also with oil products (Europroject, 2010).

Area is included in the Registry list of contaminated and potentially contaminated areas (web-1), the National Register of Contaminated and Potentially Contaminated Sites was created according to this Registry and the *Jaunmīlgrāvis* area is included in it.

3. Materials and Methods

Choosing of potential remediation method was done in 2 stages using the pre-investigation. The first stage involved existing material analysis and gaining of the pollution distribution in whole industrial area. The second was more detailed stage and was carried out after gaining results from the first stage and included sampling and testing for the future potential application of the S/S method.

Firstly 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 7 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), second interval in the depth of 2.00-3.00 m, third interval 3.00-4.00 m and the last one 4.00-5.00 m.

The pilot study area was chosen based on results of the first stage research. More detailed soil sampling from the upper part during the pilot study covered 1.82 ha. The studied territory was chosen because it is not industrially used at the moment. During the second stage 5 soil samples were taken from pilot study area (Fig. 1) in order to choose the sample for the leaching and compression resistance testing.

In 2010 soil samples were analysed in the "Eurofins" laboratory in Finland. The following heavy metal concentrations were determined: Pb, Zn, Cu, Ni, Cd, Cr, Hg in accordance with ISO 17294-2 method and As by NEN 6966. Study in 2012 included additional contamination studies in industrial area for 10 samples.

Fig. 1. Study and pilot research area (marked with green). Groundwater flow directions are shown as arrows.

In 2010 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). The leaching test BS EN 12457-2 was used in order to study the behaviour of the solidified mass in the environment. The final part of the research in 2010 included geotechnical testing for compressive strength parameters after 7 day testing in order to get know the parameters for the construction on stabilized / solidified soil in the pilot study area.

Additional research in 2012 was done for soil samples from whole industrial area. Leaching tests were performed for 6 heavy metal contaminated samples with and without Portland cement binder additive. The primary purpose of Portland cement grade PC500-D20 (CEM II/A-S 42,5N) is fabrication of concrete and reinforced concrete structures, surface, underground and underwater structures affected by fresh water. It is also used for building mortars preparation. Portland cement clinker is manufactured by burning at high temperature a raw meal consisting mainly of limestone and clay (Gineys et al., 2010). Soil samples without binder were used for batch testing as "zero samples", but cemented samples were put as small cubes with size 1cm of the edge length. Setting time of a cementitious mixture is referred to as the period when water is introduced into the mixture system to the onset of hardening. Final setting time is defined as that at which the 5-mm cap ring left no noticeable mark when placed on the surface of the mortar mixture (Yin et al., 2006). Stabilized / solidified waste acceptance criteria can be used to evaluate the effectiveness of the treatment. This criterion is chosen because S/S technology is widely used for treatment and two main parameters are measured for determination of the effectiveness of remediation – UCS and leachability limits. Regulatory leachability limits are most important in this case, in order to see the effectiveness of binding. Therefore regulatory limits at a disposal site in the United Kingdom (Sollars C.J., Perry R, 1989) is given, which is 5 mg/L or comparing to results in Table 2, would be 50 mg kg^{-1}, if the L/S ratio 10 is applied like in this study case.

During the batch leaching test vessels were filled with distilled water till a liquid-to-solid-ratio 10:1 (referred to the dry cube or not stabilized soil sample). Under continuous agitation at the rate 100RPM the batch leaching test was done for samples with agitation time period of 24 hours. pH$_{H2O}$ level was measured for all samples before and after the period. After this time the liquid was let to set down for about 10 minutes. For the determination of inorganic compounds the liquid was filtered over a 0,45µm filter. Afterwards content of leached metals was determined by atom absorption spectrometry method.

Further experiments for geotechnical parameters were done in order to know geotechnical parameters for soil bound in various proportions. Three different cubes (10x10x10 cm) and cones (diameter 10 cm, height 5 cm) were made (Fig. 2) and geotechnical tests performed. Concrete is an artificial conglomerate stone made essentially of Portland cement, water and aggregates.

Fig. 2. Solidified soil samples for compressive strength and freeze thaw resistance studies.

When first mixed the water and cement constitute a paste which surrounds all the individual pieces of aggregate to make a plastic mixture. A chemical reaction called hydration takes place between the water and cement, and concrete normally changes from a plastic to a solid state in about 2 hours. Thereafter the concrete continues to gain strength as it cures. The industry has adopted the 28-day strength as a reference point, and specifications often refer to compression tests of cylinders of concrete which are crushed 28 days after they are made (web 2), the same principle was used during this research. Samples were bound with Portland cement (PC500-D20) with the mixing ratio 20:1 (5%), 10:1 (10%) and 5:1 (20%). Compressive strength and freeze thaw resistance parameters were tested in "Tursons Ltd." geotechnical laboratory using PSY-125 compression testing equipment and CT-700 freezing camera.

4. Results

The obtained results of the pre-investigation in 2010 shown that the studied territory is contaminated with As, Cu, Zn, Pb and some also 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.

Leaching test in 2010 has shown that from "zero sample" is leaching unacceptable amounts of heavy metals – Cd, Cu, Ni and Zn. Stabilized soil has it diminished level of leaching and it is at the acceptable level. The results show that S/S remediation method has high efficiency on heavy metals (Table 1, 2). Further research of 2012 at the University of Latvia gave additional information on leaching behaviour of the contaminated soil and stabilized soil by Portland cement of various proportions.

Table,1. Concentration of heavy metals (mg kg^{-1}) in upper layer of soil. (pilot study area, 2010) (Fig.1.)

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

Table, 2. BS EN 12457-2 leaching test results compared to soil contamination (mg kg^{-1}). (sample for S/S testing from pilot study area, 2010).

	Contamination in original sample	Zero sample (pH level 3.2)	5% cement (pH level 10.5)	13% cement (pH level 10.5)	Allowed leaching 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
Pb	400	0.02	<0.01	<0.01	0.5
Zn	1200	**36**	0.04	0.03	4

Results of laboratory works at the University of Latvia are given further in Table 3 and Table 4.

The pH_{H_2O} values of all leachates from bound samples were essentially alkaline in all cases, but not bound samples have lower pH_{H_2O} (Table 4).

Table, 3. Heavy metal content (mg kg^{-1}) in *Jaunmīlgrāvis* area soil samples (2012).

Nr.	Depth (m)	Cu	Zn	Cd	Pb
1.1	0.5-2.0	**588**	442	3.2	**2067**
3.1	0.5-2.0	**350**	**1394**	0.3	**240**
5.1	0.5-2.0	**493**	315	0.5	**648**
5.3	3.0-4.0	**1044**	**1358**	2.6	**352**
5.4	4.0-5.0	**417**	392	3.7	66
14.1	0.5-2.0	**394**	614	0.9	**742**
C level for sandy soil[1]		**150**	**700**	**8**	**300**

Compression strength testing in 2010 represented data that after 7 days the solidified soil with 5% of the cement had the value of 3 MPa, but further analysis of freeze thaw resistance was not done because of the recommendation type of the research. The main idea for this study was the outlining main aspects and problems for technical economic analysis of S/S technology application in contaminated area.

Table, 4. Leaching of heavy metals (mg kg^{-1}) from soil and leaching from stabilized soil from *Jaunmīlgrāvis* area (2012).

Nr.	pH	Cu	Zn	Cd	Pb
1.1	7.4 / 12.3 with 20%	**4.60 /** 1.23	**7.42 /** 0.06	**0.08**/ n	**2.92 / 1.18**
3.1	7.9 / 10.8 with 5%	0.57 / 0.72	**4.84 /** 0.02	n / n	0.33 / 0.22
5.1	7.9 / 12.6 with 10%	0.08 / 0.65	0.08 / 0.02	n / n	0.27 / 0.22
5.3	7.8 / 11.0 with 20%	0.35 / 0.85	0.13 / 0.04	n / n	**0.69 /** 0.33
5.4	6.4 / 12.6 with 5%	**50.64/** 0.13	**110.3 /** 0.07	**1.19**/ n	0.41 / n
14.1	8.0 / 12.7 with 10%	0.46 / 1.09	3.69 / n	n/ 0.02	**0.61 /** 0.24
Leaching level[2]		**2.0**	**4.0**	**0.02**	**0.5**

[1] *Regulation of the Cabinet of Ministers Nr. 804 Instructions on Environmental Quality Standards for Soils*

[2] *Acceptable leaching threshold after the use of S/S method (Finland), n- not detectable amount of leaching from sample*

Repeat compression strength testing and additionally freeze thaw resistance studies for solidified samples bound with 5%, 10% and 20% Portland cement was done. Results are given in Table 5.

Table, 5. Compression strength and freeze thaw resistance for solidified samples with Portland cement. (2012).

Nr.	Content of Portland cement PC500-D20 (%)	Compression strength (28 days) (MPa)	Compression strength (28 days) after 50 freeze thaw cycles (MPa)
1	5	1.6	0.3
2	10	3.8	1.5
3	20	8.4	8.5

Compression strength of samples is highly dependent of proportional content of the cement, as it can be seen in Table 5 testing results. Freeze thaw testing has shown that physical impact of natural processes will be harmful for 5 and 10% cemented soil without special additives for improving geotechnical parameters. Interesting detail is that soil bound with 20% Portland cement after 50 cycles of freeze thaw impact has increased the compressive strength. All of samples after the freeze thaw impact experienced mass loss, inversely proportional to the content of cement in the sample.

5. Conclusion

Remediation of contaminated areas by stabilization / solidification (S/S) technology is closely connected with the development degree of engineering science and empirical knowledge supported by new research done in this field. Leaching tests provide information about behaviour of different contaminants in stabilized soils. Two series of research were performed in industrial area with considerable heavy metal contamination level and both improved the effectiveness of S/S technology. Freeze thaw resistance and compression strength data analysis indicates that soil bound just using Portland cement without other additives do not provide satisfactory geotechnical properties for further solidified land use in construction, therefore further leaching and geotechnical properties of contaminated and stabilized soils are necessary in order to implement S/S technology in Latvia as the remediation tool.

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