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Proposal of Solidification/Stabilisation Process of Chosen Hazardous Waste by Cementation

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Abstract**—**This paper presents a part of the project solving which is dedicated to the identification of the hazardous waste with the most critical production within the Czech Republic with the aim to study and find the optimal composition of the cement matrix that will ensure maximum content disposal of chosen hazardous waste. In the first stage of project solving – which represents this paper – a specific hazardous waste was chosen, its properties were identified and suitable solidification agents were chosen. Consequently solidification formulas and testing methodology was proposed.

Keywords**—**Cementation, solidification, waste, binder.

I. Introduction

THE most commonly used binder for solidification of various types of wastes is cement. Above all a frequent reason for utilization of cementation process is the simplicity of the process. However, this advantage is on the other side not fully compensated by significant disadvantage which means quite high cost of this type of binder and also the ecological aspect cannot be forgotten - high CO_2 emissions associated with cement production [1]-[3].

The advantage of cementation process is that the process itself takes place under normal temperature. This process is particularly suitable for inorganic materials (ashes and dehydrated sludge from industrial wastewater treatment plants), and also for mere solidification of waste going to landfill. Currently a wide range of combinations of different types of binders is being used.

Cement itself is energy-intensive material; therefore it is necessary to ensure optimum composition of the solidification mixture. The disadvantage is its sensitivity to the presence of certain substances that affect the hydration reactions leading to the formation of the solid structure. There is also disadvantage of an increase in the volume of solidified waste, which is inappropriate for depositing on landfills. Also a low resistance to corrosion agents is a disadvantage. The addition of fly ash to the Portland cement has a positive effect on the immobilization capacity and reducing the permeability of [4].

The wastes are usually mixed with Portland cement and additives that in a positive way influence the properties of the cement and with sufficient quantity of water to initiate the hydration reactions. After this, the process of stabilization and solidification begins and waste and are thus incorporated into the cement structure.

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The waste reacts with water and cement to form hydroxides of metals or carbonates, which are generally less soluble than the original metal compounds in waste. Cementation technology can mostly be carried out on the available equipment – solidification technology lines (mobile / stable).

Cement can be used as an activator for other potentially binding materials as e.g. glassy slags or fly ashes, which is economically advantageous. Finally these secondary binders become an integral part of the cement matrix, which utilizes one type of waste to immobilize other type of more dangerous wastes.

The formation of less soluble hydroxides of metals or carbonates during hydration reactions results in meeting the required limits for leachability tests. The advantage of solidification technology is also the possibility of processing of amorphous metals. Also solidified/stabilized waste product can be handled easily and the risk of dust creation is very low. The release of heavy metals from the product is also relatively low. Output solidification product can be often used as a backfill or construction material in mining activities or in transport construction engineering as a base layer. [5]

II. Materials and Methods

A. Description of the Project

The aim of the solved project is for the representative of hazardous waste that will be identified as a hazardous waste with the most critical production within the Czech Republic to study and find the optimal composition of the cement matrix that will ensure maximum content disposal of chosen hazardous waste. Properties of the cement matrix with incorporated waste at various content of hazardous waste and at different composition cement matrix will be verified by the set of suitably designed tests those will enable the study of the inbuilt hazardous waste impact on the cement matrix properties and those will prove the effectiveness of the formula.

In the first stage of project solving different types of cement matrix will be designed with different contents of hazardous waste those properties will be examined by the set of appropriately designed physical-mechanical, physical-chemical and microstructural tests.

B. Selection of the Hazardous Waste

The first stage was dedicated to the selection and identification of input raw materials and design of cement matrix formulas. The selection of hazardous waste (HW) was the first step. For HW selection the most up-to-date data available in statistic databases were used. As first the

Integrated Pollution Register of the environment (IPR) was used where it was found in the Polluted Integrated Register Summary Report for 2012, that in the same year the production of HW was announced by total 4 104 plants while other wastes were produced in 995 plants only. The total amount was 665.000 tons of HW which was mostly handed over for removal. The highest share (19%) in the announced amount of HW had metal processing plants. These producers belonged among the most important producers of HW also in the past.

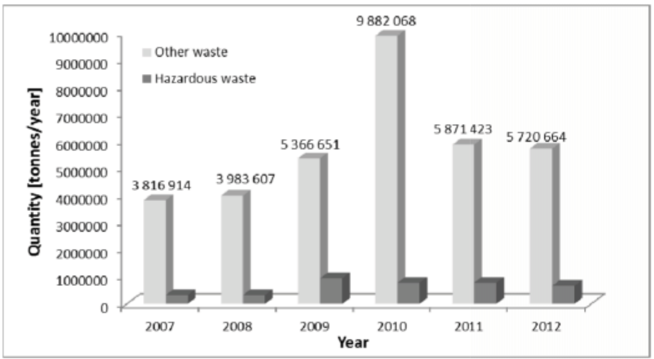

Fig. 1 Total reported amount of hazardous and other waste in Czech Republic in years 2007 – 2012

The difference between both categories – hazardous and other waste – was also in the way of waste treatment. By both monitored categories were wastes passed for recovery as well as for waste disposal. Other wastes were in most cases passed on for further utilization (more than 63% of the total announced amount of other waste), while hazardous wastes were disposed primarily (almost 71%). (IPR)

Utilization of public Waste Management Information System (ISOH) was another step, which, upon entering its catalogue code, makes possible to determine production of the given waste at the monitored area during particular year. This Waste Management Information System is managed by CENIA, the Czech Agency for the Environment. This system gathers data on production and management of waste in the Czech Republic, reported by waste generators and authorised bodies according to § 39, clause 2) of the Waste Act no. 185/2001. The data are aggregated and filtered in this system according to codes of wastes subject to the Regulation no. 381/2001, (Waste Catalogue), waste categories subject to the Waste Act and territory, in which these wastes were handled with in order the aggregation parameters, can be changed arbitrarily. Within the solution of the project, the database was used as follows: as input parameters for searching the last three years for which data are available in the system, i.e. 2010, 2011 and 2012 were selected, further the entire Czech Republic territory was selected as monitored territory, HW as waste category and waste production as waste management. A big amount of output data was subsequently processed and evaluated. From the evaluated production of HW particular types, the wastes whose production exceeded 20 thousand tons in particular monitored years were selected. Subsequently 5 representatives with the highest production during the monitored years were evaluated from this numerous data file. Among these selected wastes the following HWs subject to waste catalogue codes belonged: 17 05 03 - Soil and stones containing dangerous substances, 19 03 04 - Wastes marked as hazardous, partly stabilised, 10 02 13 - Sludges and filter cakes from gas treatment containing dangerous substances, 19 02 05 - Sludges from physico/chemical treatment containing dangerous substances, 10 02 07 - Solid wastes from gas treatment containing dangerous substances.

In order to obtain samples of the selected HWs an official Application for provision of information subject to the Act no. 106/1999 on free access to information was prepared and sent to the Ministry of the Environment of the Czech Republic, Department of Waste. The objective of this Application was to obtain information on particular producers of wastes from Czech industrial sphere in order to get samples for laboratory testing. The application was then assigned by the Head of the Department to CENIA Head for processing. The official announcement of the Ministry of the Environment of the Czech Republic and Cenia was, that the required information could not be provided due to not to provide the precedent in providing this type of information to third person even though in previous years these information were by Cenia provided. Considering the non-provision of the information by the Ministry of the Environment of the Czech Republic and CENIA, the next logical step to obtain the samples was to address one of the most important European waste management companies. Subsequently a list of selected HWs was handed over to this company from which the HW 190205 - Sludges from physico/chemical treatment containing dangerous substances was identified as the one accepted in highest amounts. The company handed over a sample of this waste for laboratory testing.

C. Identification of Chosen Waste

The chosen waste is ta neutralization sludge, which can be characterized as waste produced after neutralization of waste acids from various industrial processes containing dangerous substances.

Fig. 2 Chosen waste under catalogue code 19 02 05

After the acceptance of the sample from the company, the selected waste properties were identified. It is a waste sludge classified as HW subject to the Annex no. 1 of Ministry of the Environment of the Czech Republic Regulation no. 381/2001, Waste catalogue - included in the group 19 02 05 - Sludges from physico/chemical treatment containing dangerous substances. This waste is generated during the production of steel galvanised wires in neutralisation station which serves for optimization of sewage waters pH value. The waste produced in this way is separated and subsequently drained on relevant equipment. The identification of the waste was carried out in accordance with the Regulation no. 294/2005 on conditions of waste depositing at dumping sites and their use on terrain surface. The leachability, ecotoxicity and setting of pollutant content in dry mass are the basic monitored features subject to which the Regulation assesses the wastes. From the tests it resulted that higher concentrations were shown in water leachate with dissolved solid substances indicator; at assessment of pollutant content in dry mass this one was then a significant contaminant whose values strongly exceeded limit values set by the Annex no. 10 of the Regulation no. 294/2005.

TABLE I
RESULTS OF LEACHABILITY TESTS

Indicator	Unit	Resulting value	Limiting values for leachability class IIa
pH	-	11.4	≥6
DOC	mg/l	11.9	80
Chlorides	mg/l	2760	1500
Fluorides	mg/l	0.200	30
Sulphates	mg/l	15.9	3000
Dissolved solid substances (105 °C)	mg/l	5250	8000
Hg	mg/l	<0,00100	0.2
As	mg/l	<0,0500	2.5
Ba	mg/l	0.0457	30
Cd	mg/l	<0.00500	0.5
Cr	mg/l	<0.00500	7
Cu	mg/l	0,152	10
Mo	mg/l	0.0309	3
Ni	mg/l	0.0328	4
Pb	mg/l	<0.0500	5
Sb	mg/l	<0.050	0.5
Se	mg/l	<0.025	0.7
Zn	mg/l	0.0327	20

In terms of ecotoxicological tests the waste did not met the limits set by this Regulation.

D.Selection of Solidification Agents and Design of Cementation Matrix

Then selection of suitable solidification agents proceeded [1]-[7]. Upon the inland and abroad literature search on cement utilization for various waste types, the following three cement types were selected as the most suitable ones due to their properties: CEM I 42,5 R and two representatives of Portland mixing cements CEM II/B-S 32,5 R and CEM II/B-M (S-LL) 32,5 R. From sorbents then 6 commercial available types on different bases were selected. As other solidifying admixtures also the fluid fly ash and classic fly ashes were selected. Subsequently the identification of these selected solidifying agents was carried out.

TABLE II
POLLUTANT CONTENT IN DRY MATTER

Indicator	Unit	Resulting value	Limiting values for utilization on the surface ground
Dry matter (105 °C)	%	42.89	-
As	mg/kg of dry matter	1.49	10
Cd	mg/kg of dry matter	0.38	1
Cr	mg/kg of dry matter	159	200
Hg	mg/kg of dry matter	0.009	0.8
Ni	mg/kg of dry matter	77.8	80
Pb	mg/kg of dry matter	1870	100
V	mg/kg of dry matter	6.99	180
BTEX	mg/kg of dry matter	<0.0005	0.4
PAU	mg/kg of dry matter	0.052	6
EOX	mg/kg of dry matter	<0.5	1
hydrocarbons $C_{10} – C_{40}$	mg/kg of dry matter	23.1	300
PCB	mg/kg of dry matter	0.0003	0.2

Once finished the selection and identification of the input raw materials, it was proceeded to design of cement matrix formulas, the final phase of the project first solution stage. Two basic principles were followed during the formula designing: 1.) Direct mixing of HW into the cement matrix, 2.) Pre-treatment of HW in solidified inter-stage, subsequently in-built into the cement matrix:

1. With the first principle the formulas were formed by combination of selected cements, dangerous waste and flyashes in various weight ratios. The bases of cement matrices are always made by one of particular cement type, whose content is always verified in three weight contents (5%, 10%, and 15% by mixture total weight). The HW content was also designed in four weight contents (0%, 30%, 40%, and 50% by mixture total weight). The rests of the mixture were always formed by fly-ashes which were suggested as completion to the total sum 100% of mixture total weight invariably in the same ratio 50 : 50, fluid fly ash : classic fly ash. According to this procedure 12 basic formulas were designed.
2. Other formulas were proposed with formation of solidifying intergrade. The acquired sorbents will be used to this purpose. In order to get more transparent mutual comparison of formulas proposed subject to the principles 1. and 2., the formulas according to the principle 2. were suggested according to the basic formulas of the principle 1. – i.e. cement in amount 5%, 10%, 15% by weight, HW content 0%, 30%, 40%, 50% with the difference that the rest to 100% of mixture total weight was formed by sorbents (for each sorbent always four formulas were designed, the sorbent amount depended on particular sorbent type, however always moved within 5–30% by weight) and the rest of fly-ashes in ratio 50 : 50. Subject to this procedure also 36 basic formulas were designed. In the event that during the evaluation of basic laboratory verification is found that the set of basic formulas is to be completed with other formulas in order to obtain more

comprehensive summary of influence of particular input raw material contents, these will be completed as necessary.

E. Proposal of Methodology for Testing of Cement Matrices

The last step of this phase solution was to define an exact methodology for testing of cement matrices with in-built HW. The designed methodology of testing of cement matrix with in-built waste consists of the tests determined for verification of cement matrix physical and mechanical properties (compressive strength, absorptivity, frost resistance, porosity), further from the tests considering the risk of contaminant release into the environment (leachability test /static test, dynamic test, ecotoxicity setting – acute ecotoxicity, contact ekotoxicity, monitoring of pH value). The last type of the tests will be the tests for monitoring and study of cement matrix microstructure with in-built HW with objective to clarify and understand the way of neutralisation of contaminants and their binding in the cement matrix structure. The test sample will undergo the X-ray diffraction analysis, differential thermal analysis, high pressure mercury porosimetry and electron microscopy. The properties like compressive strength, leachability, pH and microstructure study will be monitored in intervals of 28, 180 and 360 days.

In 2014 also the second stage of project solving has been started – the very testing of designed cement matrices with in-built HW. The solution of this stage is planned for the period 10/2014 – 9/2015. First two months of this stage were dedicated to the preparation of test specimen according to the designed formulas. The preparation of the test samples shall further continue also in 2015 together with gradual evaluation of test results, which will be summed in 2015 Project Solution Progress Report.

III. Conclusion

This paper presents a part of the project solving which is dedicated to the identification of the hazardous waste with the most critical production within the Czech Republic with the aim to study and find the optimal composition of the cement matrix that will ensure maximum content disposal of chosen hazardous waste. In the first stage of project solving – which represents this paper – a specific hazardous waste was chosen, its properties were identified and suitable solidification agents were chosen. Consequently solidification formulas and testing methodology was proposed.

In the second year of project solving – in 2015 – the project solving will continue according to the approved project proposal. In the first step the preparation of test specimens, which started already in year 2014, will be completed. After sufficient aging of sample specimens according to the proposed testing methodology, the experimental verifying of sample specimens will start.

In the first stage of laboratory testing the attention will be paid to the study of the effect of HW content on the process of setting and hardening of the cement matrix. Also the verification of the physic-mechanical properties (unconfined compressive test, water absorption, frost resistance, porosity), as well as the study of environmental impact (static and dynamic leaching tests, acute ecotoxicity and contact ecotoxicity tests, pH factor monitoring) according to the defined methodology and time periods will be performed. The results of the tests will be continuously evaluated and in the case of need the modified formulas will be defined or supplementary tests will be performed..

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