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Solidification of hazardous waste with the aim of material utilization of solidification products

Jakub Hodul[a,*], Božena Dohnálková[a], Rostislav Drochytka[a]

[a]*Brno University of Technology, Faculty of Civil Engineering,Veveri 331/95, 602 00 Brno, Czech Republic*

Abstract

In order to reduce the amount of hazardous waste this work deals with the possibility of using solidification technology to transform the hazardous waste with the aim to achieve the material utilization of solidification products. For this purpose, it is necessary to determine a suitable solidification formula for solidification product made of the chosen hazardous waste – neutralization sludge. Particular solidification formula is chosen on the basis of advanced experimental examination of solidification products. Solidification products have to comply with the environmental requirements and physical and mechanical properties arising from their suitable further use in building industry or for land rehabilitation processes.

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Keywords: neutralization sludge; hazardous waste; solidification; environmental requirements; mechanical requirements; solidification agents

1. Introduction

Due to the continuous production of neutralization sludge (NS) in industry and in the context of the necessary remediation of old ecological burdens in The Czech Republic (removal and remediation of substandard and unsecured landfills, which contain such neutralization sludge (NS)), it is necessary to find a suitable technology to solve this problem. The technology of solidification seems to be the most suitable way, through which the hazardous waste (HW) can be reprocessed to a new usable product – solidification product. In order to use the

* Corresponding author.
E-mail address: hodul.j@fce.vutbr.cz

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treated waste in the most efficient way, primarily as a replacement for primary sources of raw materials, it should have required properties resulting from its further use.

Meeting of the requirements resulting from the future use of solidification product is achieved mainly by selecting the appropriate neutralization sludge and economical-efficient solidification binders. At first, it is therefore necessary to design and then examine large amount of solidification formulas.

The suitability of various solidification recipes need to be checked first on a laboratory scale and then subsequently the most technologically and economically acceptable option must be chosen. After the thorough examination of the properties of solidification products, this new material may be used in practice. To prevent any release of contaminants from solidification product resulting in environmental pollution, it is inevitable to monitor the long-term durability of the solidification product (steady required properties at any time on the place of its use).

The trend of waste maximum utilization is also provided in national legislation. Waste Act No. 185/2001 in force is based on Directive of the European Parliament and Council No. 98/2008/ES and states hierarchy of waste management, which emphasizes the prevention of the waste production. The waste disposal (landfill without further use) is in this hierarchy of waste management in the last place.

For the possibility of further use of solidification product it is necessary to maintain certification (conformity assessment). Government Directive No. 163/2002 offers the possibility how to make the conformity assessment or it can be through a voluntary certification (used in building within the meaning of Act No. 183/2006), while it would be possible to use it only in the Czech Republic. Because of currently missing standards or other technical regulations in the Czech Republic dealing with the possibilities of use solidification products, the building technical certificate (BTC) has to be provided at first. BTC provide technical determining of the product properties by the authorized person. When the BTC is drafted it can be based on standards and technical regulations developed for a similar type of material (e.g. a stabilized fly ash). Authorized person on the basis of BTC defines the technical characteristics associated with the basic requirements and also determines their levels due to the intended use of solidification product in construction. When BTC is released, the certification of solidification product can be processed. After release of the certificate, solidification product can be used for its intended use, which is specified in the relevant technical documents.

2. Future applications of solidification product and optimal testing methodology

The use of solidification products (SPs) should have predominantly ecological benefits - environmental protection. The most of possible future applications of solidification product result from technical manuals that have been developed mainly for the product group - ashes and mixes with fly ash, while defined use is closest to the appropriate application of the solidification product. Vacenovska et al. [1] discovered that a possibility of application of this product, which contains HW is closely related with the technology of its production. It is mostly produced on solidification lines, in form of granules, so the principal possibility of its utilization are various dustings, backfill material, base layers, material shaping the terrain and especially as material for landfill reclamation and remediation of old ecological burdens. The use of the product as a building material in common earthwork is unlikely due to the usual high pollutant content in dry matter, which is not permitted by applicable strict standards.

Based on the selected optimum application of solidification product, the optimal testing methodology was created. The proposed testing results mainly from the requirements arising from the aforementioned technical manuals. The tests can be divided, as shown in Figure below, into physical and mechanical tests – for detecting and defining the technical characteristics of the product and the ecological tests – dealing with the protection the environment and human and animal health. Recent results from Al-Tabbaa and Perera [2] indicate that the final physical and mechanical properties of solidification product (SP) influence also the future suitable technology of

its application. Environmental protection requirements are set out in the relevant legislation (Regulation No. 294/2005) and among the monitored parameters belong leaching in water, the concentration of pollutants in the dry matter and acute toxicity test. In foreign countries, legislation deals with protection of the environment also based on other types of tests.

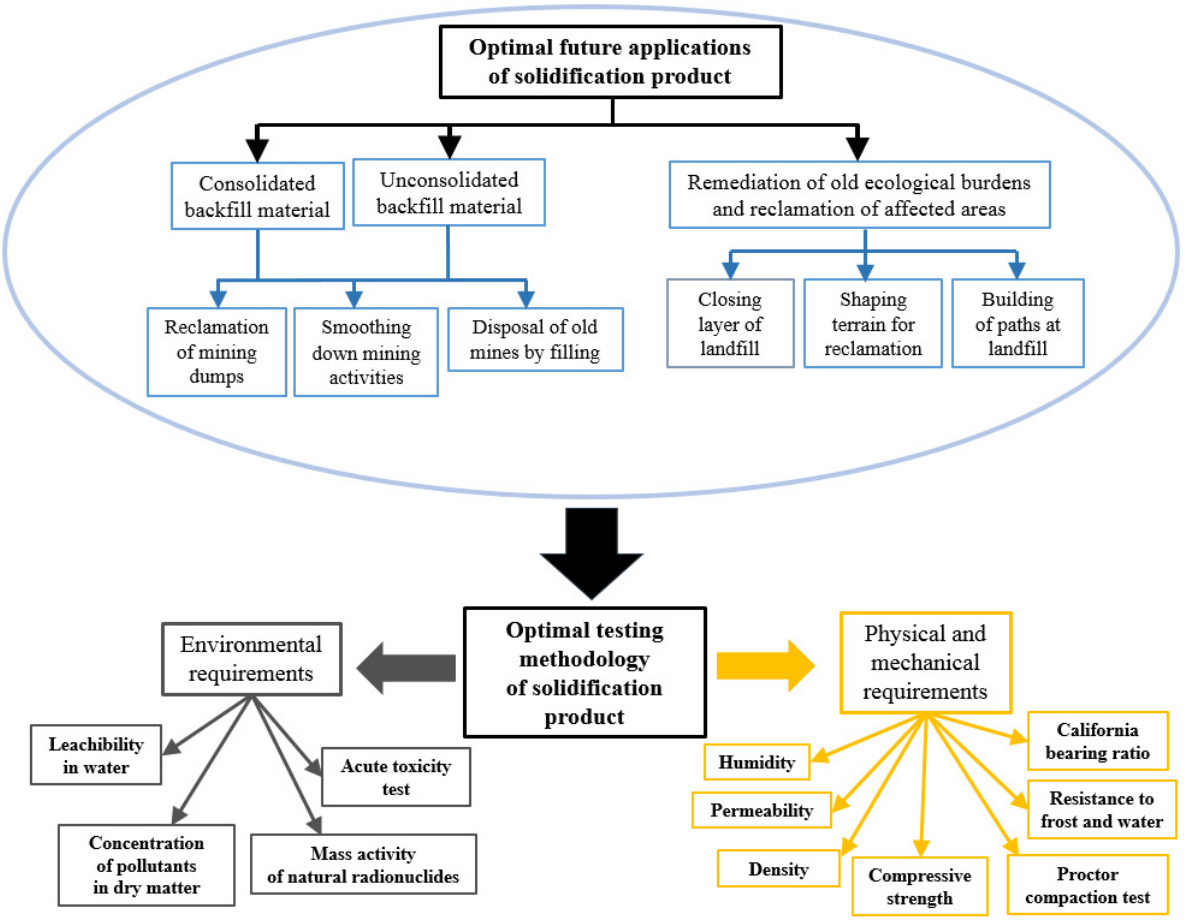

Fig. 1. Optimal testing methodology of solidification product resulting from optimal future applications of solidification product.

3. Identification of input raw materials and design of appropriate ratios of mixing

The selected input neutralization sludge (NS) belonged to hazardous waste (HW) with designation A, B and C. Hodul [3] characterized NS as a waste arising after neutralization of waste acids from various industrial processes that contain hazardous substances. These selected NS are produced because of the process of the surface treatment of steel materials as by-products. Al-Tabbaa and Perera [2] and Hodul [3] reported that for purposes of the classification of their negative effects on the environment the leaching test, the determination of the concentration of pollutants in the dry and also determination the dry matter content must be carried out. NS-A (Fig. 2 (a)) showed high concentrations of dissolved solids in an aqueous extract (5250 mg/l) and aqueous extracts of NS-B and NS-C contained about 3000 mg/l dissolved solids (Table 1). Leachate pH of all the NS ranged from 9 to 11. None of the NS have exceeded the parameters corresponding to the leachability class IIa according to Regulation

No. 294/2005. All NS are shown in Fig. 2 below and they are characterized by increased lead and chromium content in the dry matter (Table 2). NS-B and NS-C also contained large amounts of chromium and hydrocarbons C_{10} - C_{40} (NS-B (5360 mg/kg of dry matter)). Limits for the use of waste on the terrain in the Czech Republic according to Regulation No. 294/2005 were exceeded in all NS.

Fig. 2. (a) NS-A, (b) NS-B, (c) NS-C.

Table 1. Results of leaching tests of NS.

Parameter	NS-A	NS-B	NS-C	Limits (leachability class IIa)
pH of the leachate	11.4	9.2	9.9	≥6
Dissolved solid substances [mg/l]	5250	3170	2810	8000
Chlorides [mg/l]	2760	121	935	1500
Sulfates [mg/l]	15.9	1820	221	3000
Dissolved organic carbon (DOC) [mg/l]	11.9	57	91.2	80
Cadmium (Cd) [mg/l]	<0.005	<0.005	<0.005	0.5
Arsenic (As) [mg/l]	<0.001	<0.001	<0.001	2.5
Barium (Ba) [mg/l]	0.0457	<0,010	0.12	30
Copper (Cu) [mg/l]	0.152	<0.005	0.082	10
Selenium (Se) [mg/l]	<0.025	<0.025	<0.025	0.7
Nickel (Ni) [mg/l]	0.0328	<0.02	<0.02	4
Lead (Pb) [mg/l]	<0.005	<0.001	0.0013	5
Chromium (Cr) [mg/l]	<0.03	<0.03	0.162	7

Table 2. Results of concentration of pollutants in dry matter of NS.

Parameter	NS-A	NS-B	NS-C	Limits for use of waste on the terrain
Dry matter [%]	42.89	44.11	24.19	-
Cadmium (Cd) [mg/kg dry]	0,38	0.15	146	1
Arsenic (As) [mg/kg dry]	1.49	6.41	3.14	10
Chromium (Cr) [mg/kg dry]	159	574	3990	200
Nickel (Ni) [mg/kg dry]	77.8	55.2	30.5	80
Lead (Pb) [mg/kg dry]	1870	240	108	100
Hydrocarbons C_{10} - C_{40} [mg/kg dry]	23.1	2330	949	300

As suitable solidification agents cement, fly ash (from high temperature combustion (Classic fly ash – CA) and from fluid combustion (Fluid fly ash – FA), dusts from the ladle furnace and carbide lime were selected. The selection of their specific resources took place with regard to the economic and environmental points of view and accessibility. FA came from the thermal power plant situated in the city Hodonín (the Czech Republic) and CA came from the thermal power plant in the town Chvaletice (the Czech Republic). The chemical composition of these fly ashes are shown in the Table 3 below. Suitability of listed solidification agents was examined by experimental testing properties of the solidification products prepared in accordance with the proposed basic recipes.

Table 3. Chemical composition of used fly ashes.

Fly ash	SiO_2	Al_2O_3	Fe_2O_3	SO_3	CaO	MgO	K_2O	Na_2O	P_2O_5
Classic (CA)	50.16	27.54	13.08	0.07	2.51	1.46	1.35	0.35	0.19
Fluid (FA)	36.90	13.60	4.92	6.12	20.10	1.31	4.92	0.65	0.66

From the selected input materials 12 basic solidification formulas were proposed for three selected NS and each formula contained 50 % wt. NS amount. The amount of water was added to obtain the required consistency of solidification mixtures and it was approximately 30 – 50 % of solidification agents. When designing formulas, emphasis was placed on the use of secondary raw materials, mainly two kinds of fly ash (CA, FA). The optimum mixing ratio of inputs was determined on the basis of experimental testing of the properties of solidification products.

4. Laboratory testing

In the first phase laboratory experimental testing of properties solidification products (SPs) prepared according to basic solidification formulas was carried out. Based on the results of this experimental testing three best formulas (3A, 3B and 7B) were selected, which were then further tested for purpose to their further certification according to Government Directive No. 163/2002. The composition of three chosen solidification formulas is shown in the Table 4 below. The demonstration of physical and mechanical requirements was based on the following tests: Cube compression strength, Bulk density, Laboratory reference density and water content – Proctor compaction, California bearing ratio (CBR), Permeability - filter coefficient. Ecological requirements that are specified in the relevant legislation, were assessed by the leachability test, determining the concentration of pollutants in dry matter, acute toxicity tests and determination of the activity concentration of ^{226}Ra and activity concentration index.

Table 4. Composition of chosen solidification formulas.

Component	3A	3B	7B
Neutralization sludge (NS)	50	50	50
Classic fly ash (CA)	20	20	15
Fluid fly ash (FA)	25	25	25
Cement CEM II/B-M (S-LL) 32,5R	5	5	-
Carbide lime	-	-	10

Compressive strength. The compressive strength of SPs was performed on the test specimens - cubes 100 x 100 x 100 mm according to ČSN EN 12390-3. The results of the compressive strength of SPs (in different ages) prepared according to three chosen recipes are shown in Fig.2. Each of the test specimens was until the mechanical loading on the test press stored in a laboratory environment and the resulting strength is average value of three specimens. The highest compressive strength was achieved in solidification formula 3B (the sample of the age of 28 days – 1.4 MPa). Compressive strengths of solidification products were declining in time, however with formulas 3A and 3B occurred after 180 days maturation of samples a slight increase. Asavapisit et al. [4] and Antemir [5] state that failing to achieve sufficient strength is an indicator of poor microstructure and imperfect hydration of solidification product that can result in increased leachability of contaminants. The requirements for the compressive strength vary depending on the end use of solidification product and in some developed countries also on local legislation. To determine the density of solidification products the same specimens as in the test of compressive strength were used. The highest density had specimens in the time of their filling to the forms (fresh state).

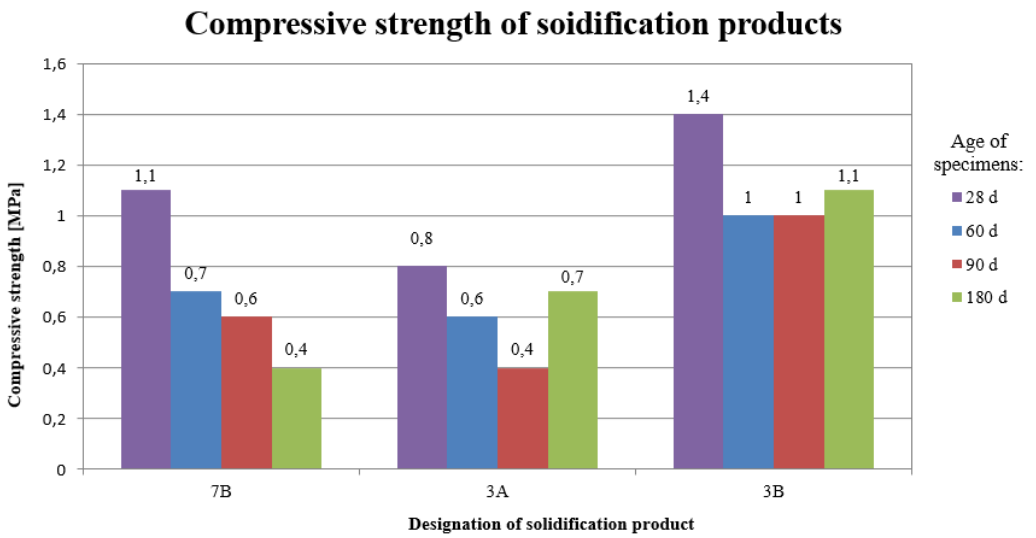

Fig. 2. Results of compressive strength (cubes) of solidification products prepared according to chosen recipes in different ages.

Leaching test results. Hodul [6] reported that leachability tests are one of the basic tests by which the individual national legislation created and create criteria for further utilization of industrial waste. When exceeding certain legislative the waste cannot be treated as secondary raw material, but as hazardous waste. During the preliminary treatment of the solidification products (SPs) sample and following preparation of a water leachate, the procedure according to ČSN EN 12457-4 (83 8005) is applied. The preliminary treatment of sample of waste modified by solidification is contained in Appendix No. 7 of Regulation No. 294/2005. Technical standards were used for chemical analyses for the analytical determination mentioned in Appendix No. 12 of Regulation No. 294/2005. The determination was carried out by accredited testing laboratory LABTECH, located in Brno. Results of leaching tests of the chosen solidification products are listed in Table 5. In the table are listed only major parameters, but the determination was carried out for all elements listed in Regulation No. 294/2005. None of the (SPs) have exceeded the parameters corresponding to the leachability class IIb. Conductivity is an approximate degree of concentration of electrolytes (ionic dissolved solids) in aqueous solutions. Indirectly, it indicates mineral content ("salt" dissolved solids) in the water. There is the relation between the conductivity and the volume of dissolved substances in the leachate. Recent results from Bone et al. [7] and Li et al. [8] showed that monitoring of pH values is also important because influence the dissolubility of metals, i.e. their extraction capacity from the solidification product matrix. From Table 5 it is obvious that aqueous leachates of all the SPs were alkaline.

Table 5. Results of leaching tests of the SPs.

Parameter	3A	3B	7B	Limits (leachability class IIb)
pH of the leachate	11.3	9.8	9.7	≥6
Dissolved solid substances [mg/l]	2450	2980	2990	6000
Conductivity [mS/m]	496	272	259	-
Chlorides [mg/l]	904	45.9	27.8	1500
Sulfates [mg/l]	122	1760	1430	2000
Dissolved organic carbon (DOC) [mg/l]	23	54	65	80
Cadmium (Cd) [mg/l]	0.00017	0.00013	0.0105	0.1
Arsenic (As) [mg/l]	<0.001	0.0041	0.0067	0.2
Barium (Ba) [mg/l]	0.152	0.127	0.081	10
Copper (Cu) [mg/l]	0.025	0.111	0.374	5
Selenium (Se) [mg/l]	0.0019	0.0067	0.0069	0.05
Lead (Pb) [mg/l]	<0.001	<0.001	<0.001	1
Chromium (Cr) [mg/l]	<0.03	<0.03	<0.03	1

Ecotoxicological tests. Table 6 shows the results of acute toxicity tests carried out by accredited testing laboratory ALS, the Czech Republic (ALS Group). Ecotoxicological tests are one of the most expensive and time consuming tests. Within the requirements for the use of waste on surface, Regulation No. 294/2005 sets out the requirements for ecotoxicological tests results, according to which waste can be classified as category I or II. Based on the assessment results with the requirements specified in the relevant regulation it can be concluded that all three SPs prepared according chosen solidification formulas met these requirements.

Table 6. Acute toxicity test results.

Parameter (Tested organism)	Requirements (Regulation No. 294/2005)		Results		
	I	II	3A	3B	7B
Acute lethal toxicity of substances to a freshwater fish (Poecilia reticulate)	No mortality (0) and no changes in behavior	No mortality (0) and no changes in behavior	0	0	0
Inhibition of the mobility of Daphnia magna Straus	Max. immobilization 30 %	Max. immobilization 30 %	0	0	0
Inhibition of the growth of freshwater green algae (Scenedesmus subspicatus)	Max. inhibition of growth 30 %	Max. inhibition/stimulation of growth 30 %	5.4	7.0	5.5
Root growth inhibition of mustard (seeds of Sinapsis Alba)	Max. inhibition of growth 30 %	Max. inhibition/stimulation of growth 30 %	17.7	10.2	21.7

5. Conclusion

In this paper the test results were presented through which some physical and mechanical and also environmental properties were identified. The presented results are just a part of number of the tests which were carried out in order to certificate the solidification products and its future use as technological material to landfill. All tested solidification products were prepared on the basis of chosen solidification formulas while each formula contained 50 wt. % NS, two types of fly ash (FA, CA), cement and the solidification product (SP) with designation 7B contained carbide lime instead of the cement.

The demonstration of physical and mechanical requirements was specified by demonstration of compressive strength using cubes as test specimens. The value of compressive strength ranged around 1 MPa in all SPs after 28 days curing. The decrease of the strength over time may be caused by the chemical reaction between unreacted components of the NS and the matrix causing gradual degradation of the SPs.

Among the performed tests for the assessment of the impact on the environment the leaching test and acute toxicity tests were carried out. Both tests are included in the relevant legislation for the use of treated waste on the surface. All the tested solidification products (SPs) meet the requirements for the classification in leachability class IIa according Regulation No. 294/2005. The obtainment of minimum leachability of contaminants at maximum strength and also the provision of its long-term durability are basic requirements expected from SPs. Even after the solidification is carried out, contaminants (etc. lead, cadmium, hydrocarbons C_{10} - C_{40}) will still occur in the SPs but by the effective solidification there will be no release into the environment, as these contaminates will be firmly incorporated in the matrix of SPs.

From the mentioned results it can be concluded that the use of the technology of solidification process for reducing the toxicity of selected neutralization sludge proved to be successful. However, to ensure the requirements for the certification of this product and its future safe use in the reclamation or building industry it is necessary to perform a number of other important tests and mainly the pilot plant operation of solidification technology.

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References

[1] Vacenovska B, Cerny V, Drochytka R, Urbanek B, Vodickova E, Pavlikova J, Valko V. Verification of the possibilty of polidification product made of neutralization sludge use in the building industry. Procedia Engineering 57. Vilnius Gediminas Technical University: 11th International Conference on Modern Building Materials; 2013, p. 1192-1197.

[2] Al-Tabbaa A, Perera ASR. Stabilisation/solidification treatment and remediation. Part V: Long termperformance and environmental impact. Cambridge: Proceedings of the International Conference on Stabilisation/ Solidification; 2005, p. 437-457

[3] Hodul J. Solidifikát z nebezpečného odpadu a možnosti jeho uvedení na trh [Solidification product made of hazardous waste and possibilities of its launch to the market]. Brno: University of technology, Institute of Technology of Building Materials and Components, Faculty of Civil Engineering. Diploma Thesis; 2015.

[4] Asavapisit S, Naksrichum S, Harnwajanawong N. Strength, leachability and microstructure characteristics of cement-based solidified plating sludge, In: Scrivener K, editors. Cement and Concrete Research 35, Lausanne; 2005, p. 1042-1049.

[5] Antemir A. Performance Assessment of Stabilised/Solidified Waste-Forms. University of Greenwich: Environmetal Science. Degree of Doctor of Philosophy; 2010.

[6] Hodul J. Vývoj nové metodiky pro hodnocení trvanlivosti solidifikátů připravených z nebezpečných odpadů [Development of a new methodology for the evaluation durability of solidification products prepared from hazardous waste]. Brno: University of technology, Institute of Technology of Building Materials and Components, Faculty of Civil Engineering. Bachelor Thesis; 2015.

[7] Bone BD, Bernard LH, Boardman DI, Carey PJ, Hills CD, Jones HM, MacLeod CL, Tyrer M. Review of scientific literature on the use of stabilisation/solidification for the treatment of contamined soil, solid waste and sludges. Bristol: Environment Agency; 2004.

[8] Li XD, Poon CS, Sun H, Lo IMC, Kirk DW. Heavy metal speciation and leaching behaviours in cement based solidified/stabilized waste materials. Journal of Hazardous Materials A 82; 2001, p. 215-230.