ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 16, No. 2. 2010

Hazardous Wastes Recycling by Solidification/Stabilization Method

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Received 04 January 2010; accepted 05 May 2010

The solidification/stabilization (S/S) method is used for treatment of various types of wastes. This paper deals with S/S of the selected type of hazardous waste – sludge from biological industrial waste water treatment with the content of hazardous substances. The aim of this research is to develop the technology for this type of industrial hazardous wastes disposal using S/S method on qualitatively new technological level. The classic fly ash, fluid fly ash (secondary raw materials) and cement were chosen as suitable solidification agents. The efficiency of these solidification binders was improved by the specific surface increasing. Leaching tests were used for verifying the efficiency of solidification formulas.

Keywords: solidification/stabilization, hazardous waste, leaching tests, waste disposal, waste treatment.

1. INTRODUCTION

Stabilization and solidification 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 the alteration of waste contaminants to a more chemically stable form, thereby resulting in the more environmentally acceptable waste form. Typically, the stabilization processes also involve some form of the physical solidification [1 – 3].

Land disposal restrictions are becoming ever increasingly stringent, driven by the technical, regulatory, and political considerations. To the largest extent practicable, alternatives to land disposal are desirable, such as waste minimization, recycling, and destruction. In many instances, however, these alternatives are unrealistic due to the physical nature or location of the waste, the type and concentration of contaminants that it contains, or technical and economic issues [4]. In such cases, S/S technology is viable technical option, which has historically proven to be cost effective [5].

Waste producer's costs for hazardous wastes disposal are very high at the present time in case of using other way then hazardous waste depositing on waste disposal site [6]. Causes of high financial expenses are first of all high investment expenses and operating expenses of these disposal technologies. Disposal of hazardous wastes by its S/S is much more efficient alternative because we provide its deposition on the landfill with markedly lower fee for waste depositing. By finding suitable S/S way for definite hazardous waste we can achieve not only successful disposal of hazardous waste, but also we can provide the possibility of its next utilization in building industry by its proper modification [7, 8]. Idea of next utilization of S/S products from hazardous wastes can ensure considerable economical savings.

The aim of this research is to develop a technology for hazardous industrial wastes disposal using S/S method on qualitatively new technological level. Other partial project targets include research of suitable solidification binders and selection of suitable hazardous industrial wastes. Next stage of the research deals with technological S/S processes and final stage of project is the design of suitable S/S line including also final verification of laboratory developed procedures on the prototype of new S/S line.

2. EXPERIMENTAL

2.1 Selection of suitable hazardous waste

The first step was to choose a suitable hazardous waste whose S/S appears to be successful and profitable in term of technical, economic and ecological aspects. All hazardous wastes that are mentioned in list of hazardous waste according to valid Czech legislation were listed for the selection of suitable hazardous waste. There are listed 402 different types of hazardous wastes in this document. Most suitable wastes from theoretical point of view were chosen from the list of hazardous wastes. Finally 8 different types of hazardous wastes with the help of subsequent optimization calculation were selected. This paper describes process and results from the laboratory research of solidification possibilities of one chosen hazardous waste – sludge from biological industrial waste water treatment with content of hazardous substances.

The waste water treatment plant in city Pardubice – Rybitvi (Czech Republic) was chosen as a source of selected hazardous waste. The waste provided by waste producer contained 81 % of dry residue because waste producer makes a preliminary treatment of sludge mediated by its drying. Table 1 shows leaching tests (TCLP) results provided by waste producer on sample of hazardous waste.

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Table 1. Initial hazardous waste leaching test results

	[mg/l]	Indicatator	[mg/l]
pH	7.33	Hg	0.0045
Dissolved solid substances	4110	Mo	<0.50
Cl^-	76	Ni	0.081
Fl^-	0.2	Pb	<0.05
SO_4^{2-}	452	Sb	<0.05
As	<0.05	Se	<0.02
Ba	0.14	Zn	0.02
Cd	<0.003	DOC	1099
Cr	0.011	Phenols	0.38
Cu	0.07		

2.2. The selection of solidification/stabilization agents

The selection of S/S is a complex problem. Above all it is necessary to consider the type of solidified hazardous waste and its properties to accomplish successful results of S/S process. Different S/S binders are being used for the S/S of various types of hazardous wastes at present times. These various types of S/S binders have different S/S effect on various types of hazardous wastes. Both inorganic and organic binders are being used for S/S and the most common and most often used of them is cement [9 – 11].

So the next step of laboratory work was to choose suitable S/S agents for selected hazardous waste that will give birth to quality of solidificate. The background research of possible S/S agents was made for selection of suitable S/S agents and then on the basis of this research and with the help of optimization calculation these S/S binders were chosen: fluid fly ash, classic fly ash and as S/S additive – cement. One of the important aims of this project is also to find the utilization for secondary raw materials that will act as S/S binder for hazardous waste solidification.

2.3. The solidification/stabilization process

In the next step S/S formulas were work out for selected hazardous waste with the use of selected solidification agents. These S/S formulas are presented in Table 2.

Table 2. Composition of solidification formulas

Compounds		Formula		
		1	2	3
Fluid fly ash	[%]	60	40	20
Classic fly ash		0	20	40
Cement		10	10	10
Hazardous waste		30	30	30

Ensued the efficiency of S/S formulas was examined. Test specimens were made following S/S formulas with dimensions 40, 40, 160 mm and 100, 100, 100 mm. S/S agents were grinded in the ball grinder in order to increase the S/S efficiency of S/S formulas and test specimens were made again according to defined S/S formulas, but with the use of grinded S/S agents. Sample specimens were put out of forms after three days and they matured for 28 days in laboratory conditions.

Table 3 shows original specific surfaces and after grinding specific surfaces that were determined using Blaine method according to Czech version of European Standard CSN EN 196-6 Determination of fineness; Methods of testing cement.

Table 3. Specific surface of S/S agents with original and increased specific surfaces

Compound	Specific surface [$m^2 \cdot kg^{-1}$]	
	Initial	Increased
Fluid fly ash (FA)	590	1510
Classic fly ash (CA)	190	580
Cement	310	630

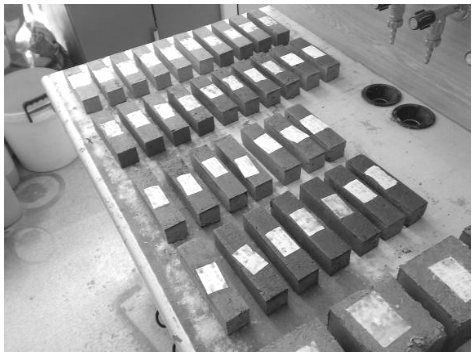

Fig. 1. Test specimens after removal of forms

2.4. The quality evaluation of solidification/ /stabilization process

The most important part of analytical methods represents leaching tests. These tests are based on extraction processes and they define the solidificates`s possibility to release contaminants to environment [12]. Their principle is to expose solidificates to action of leaching medium and after defined time interval follows determination of contaminants content in this medium.

The valid legislation doesn't set any minimum compressive strength; nevertheless solidificate has to keep definite minimum compressive strength to ensure its safe disposal [5]. In the place of solidificate disposal can occur definite mechanical load, during which solidificate can be damaged. It is assumed, that generally higher compressive strength provides better physical barriers that conduce to risk depression of leaching hazardous substances to environment.

3. EXPERIMENTAL AND DISCUSSION

3.1. Leaching test results

The aim of performed S/S was to lower the content of contaminants in aqua leach of solidificates to minimum value. We can find out the ability of S/S formulas to immobilize hazardous components that are present at treated wastes by comparing aqua leaches before and after S/S process. Exact procedures for leaching tests are laid down by Czech version of European Standard CSN EN 12457-4: Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction).

After 28 day-long solidificate`s maturing leaching tests were carried out to find out efficiency of investigated S/S formulas. In aqua leaches of solidificates values of these contaminants: dissolved solid substances, Cl^{-}, Fl^{-}, SO_4^{2-}, As, Ba, Cd, Cr, Cu, Hg, Mo, NI, Pb, Sb, Se, Zn, DOC, Phenols, were defined. Figures 2 – 6 show the dependence of contaminants content in leach of solidificates on composition of the S/S formula. These graphs also show values of chosen contaminants, which were the most critical in original sample of hazardous waste.

Higher S/S efficiency was reached by S/S formulas that contained S/S agents with higher specific surface. Solidificates with using of higher specific surface S/S agents proved lower content of all contaminants in aqua leach then solidificates without using of S/S agents, that were grind in ball mill (Fig. 2 – Fig. 6).

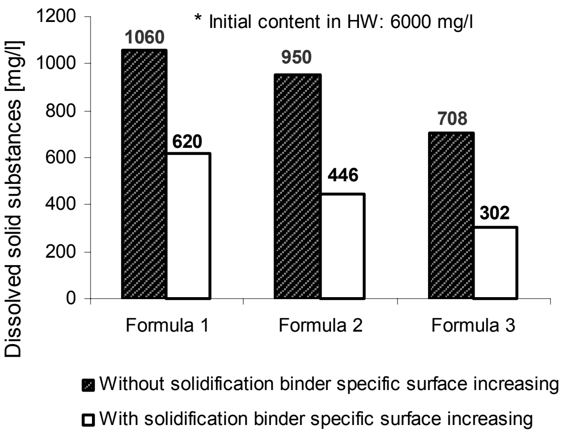

Fig. 2. Dissolved solid substances content in water leaches of solidificates

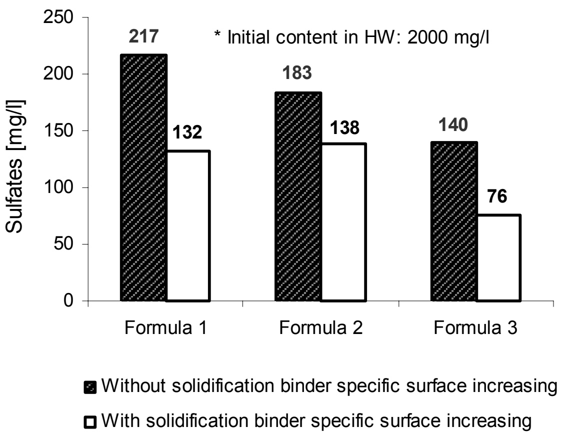

Fig. 3. Sulfates content in water leaches of solidificates

If we consider the dependence of aqua leach contaminants content on the composition of S/S formulas, we can find out, that growing content of classic fly ash in S/S formula (with lowering content of fluid fly ash) lowers the content of contaminants in solidificate`s aqua leaches.

The lowest values of contaminants content (except Fig. 4) were reached in Formula 3 that consisted of 20 % fluid fly ash, 40 % of classic fly ash, 10 % cement and 30 % of hazardous waste.

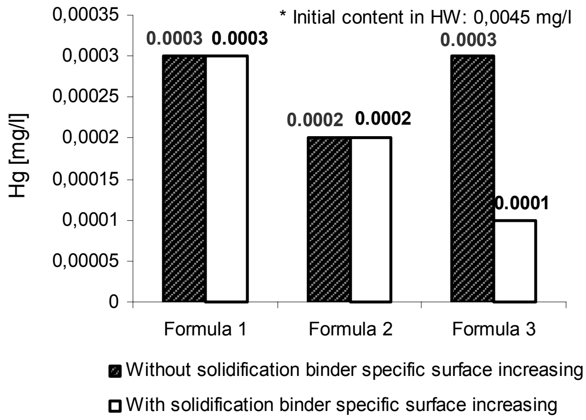

Fig. 4. Hg content in water leaches of solidificates

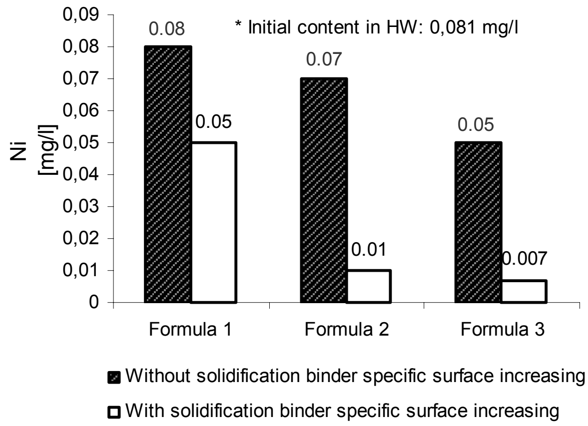

Fig. 5. Ni content in water leaches of solidificates

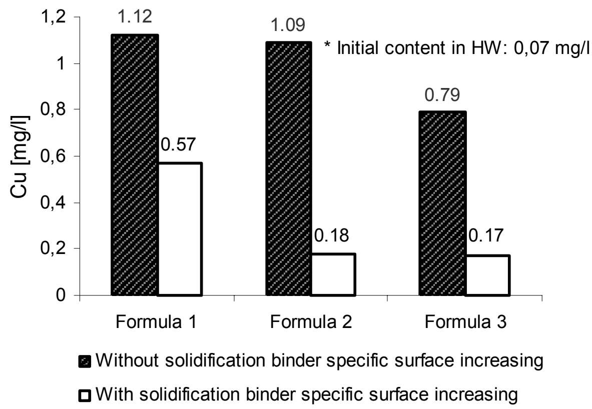

Fig. 6. Cu content in water leaches of solidificates

Special exception was indicator Cu. Cu was the only one contaminant, whose values were higher after the solidification process then in original sample of waste (Fig. 6).

Values of indicator DOC (dissolved organic carbon), which describes summary concentration of organic substances, were especially high. The value of DOC in original untreated waste was 1099 mg/l. With use of S/S method were its values successfully and significantly lowered (Fig. 7).

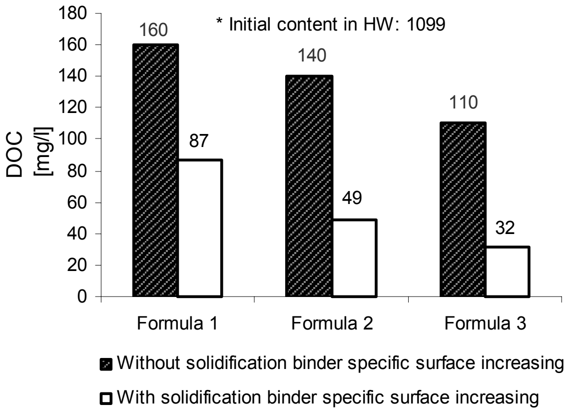

Fig. 7. DOC content in water leaches of solidificates

3.2. The compressive strength

The valid legislation doesn't set any minimum compressive strength; nevertheless solidificate has to keep definite minimum compressive strength to ensure its safe disposal [5]. For these reasons compressive strength was investigated according to standard that is Czech version of European standard CSN EN 12390-3 Testing hardened concrete – Part 3: Compressive strength. Compressive strength was tested on sample specimens with proportions 100 mm, 100 mm, 100 mm after 28 day-long maturing in compression-testing machine. The sample cube is put between pressure platens of press in vertical direction to mixture compaction. Then compressive strength is calculated from failure load divided by cross-sectional area resisting the load.

Fig. 8 shows results of the compressive strength testing.

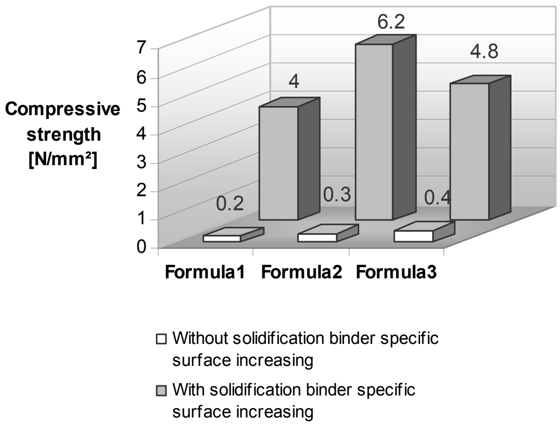

Fig. 8. Compressive strength of solidificates produced

It is obvious from the last graph (Fig. 8) that compressive strength achieved by solidificates without using of S/S agents with higher specific surface is very low. Whereas solidificates with using of ground S/S agents reach compressive strength about twenty times higher. The highest compressive strength was achieved by Formula 2, which consists of 40 % of fluid fly ash, 20 % of classic fly ash, 10 % of cement and 30 % of hazardous waste.

One of the research stages was also project and realization of S/S line pilot plant prototype, which at present serves for laboratory results verification (see Figs. 9, 10 and 11).

In future the project will expand for increasing the effectivity of outputs, this new part of research will deal with development of solidificates that by their prosperous properties will ensure use of solidificates as the recultivation material. This will provide not just minimization of unfavourable hazardous waste, but also its material using.

Fig. 9. S/S line pilot plant prototype

Fig. 10. First solidificates produced by S/S line prototype

Fig. 11. First solidificates produced by S/S line pilot plant prototype

4. CONCLUSIONS

1. The possibility of secondary raw material utilization as S/S agents was proved for solved type of hazardous waste. Classic fly ash and fluid fly ash were chosen for laboratory research as secondary raw material. Lowering the quantity of fluid fly ash in S/S formula caused inreasing of S/S effectivity. Classic fly ash was proven as more effective S/S binder.
2. Lower content of contaminants in aqua leach of solidificates was achieved by the formulas with use of ground S/S agent. Dramatically higher compressive strength was accomplished by S/S formulas with content of S/S agents, whose specific surfaces were increased by grinding in ball mill.
3. As the most effective formula was proved Formula 3 (that consisted of 20 % of fluid fly ash, 40 % of classic fly ash, 10 % of cement and 30 % of hazardous waste) with using ground S/S agents. Values of all contaminants (except Hg) in aqua leach of solidificates were the lowest for this formula.

Acknowledgments

This paper has been developed under the support of the project MSM 0021630511 "Advanced building materials with use of secondary raw materials and its impact on life span of constructions" and project FT-TA3/137 "Advanced technology of disposal of industrial waste by solidification".

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DOI: 10.5755/j02.ms.26063