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Stabilization/solidification of munition destruction waste by asphalt emulsion

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Abstract

Destruction of discarded military munitions in an explosion chamber produces two fractions of hazardous solid waste. The first one is scrap waste that remains in the chamber after explosion; the second one is fine dust waste, which is trapped on filters of gas products that are exhausted from the chamber after explosion. The technique of stabilization/solidification of the scrap waste by asphalt emulsion is described in this paper. The technique consists of simple mixing of the waste with anionic asphalt emulsion, or two-step mixing of the waste with cationic asphalt emulsion. These techniques are easy to use and the stabilized scrap waste proves low leachability of contained heavy metals assessed by TCLP test. Hence, it is possible to landfill the scrap waste stabilized by asphalt emulsion. If the dust waste, which has large specific surface, is stabilized by asphalt emulsion, it is not fully encapsulated; the results of the leaching tests do not meet the regulatory levels. However, the dust waste solidified by asphalt emulsion can be deposited into an asphalted disposal site of the landfill. The asphalt walls of the disposal site represent an efficient secondary barrier against pollutant release.

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1. Introduction

Discarded military munitions represent extremely hazardous material. If the possibility of their misusage for terrorists' activities is ignored, there is a potential danger of the environment damage. In former times, the discarded munitions were liquidated by explosion in open-air space, which is quite unacceptable nowadays. The disposal of discarded military munitions is becoming a new industrial branch. The disposal comprises of munitions disassembly and destruction of explosive in an explosion chamber. However, this procedure produces hazardous waste containing mainly Pb, eventually Hg, Ba, Cd, Sb and other toxic metals. Schematic illustration of production of wastes is shown in Fig. 1. The compositions of these wastes are variable, of course, and depend directly on the kind of munitions being

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destructed. This fact requires application of a highly universal stabilization/solidification technology for these wastes.

Regulations in most countries allow only physically, chemically or biologically modified hazardous waste to be deposited in the landfills; the wastes have to meet the regulatory levels of pollutants release into the environment. This situation brings the necessity of finding new technologies for the waste disposal. Lately, an increasing interest in the technology of stabilization/solidification (S/S) can be observed. Asphalt appears to be an ideal S/S binder due to its exceptional properties: it is highly hydrophobic, chemically and biologically extraordinarily stable, it has favorable properties such as creep, inertness, stability in the environment and it is widely produced [1]. Furthermore, it is possible to recover the waste from asphalt matrix relatively easily in the future.

The S/S procedure by asphalt emulsion (AE) produces stabilized/solidified waste that can be deposited in a landfill. Solid wastes of different structure and composition can be treated by asphalt emulsions [2]. Even wet waste [3] or sludge after solidification [4] can also be treated by this technique. The facts

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Fig. 1. Production of wastes by explosive destruction of discarded munitions.

that asphalt emulsions are produced in a large-scale for road construction, techniques of asphalt cement processing are commonly used and devices for processing of this material are widely available, are also very significant for implementation of this S/S technique in practice.

Arocha et al. [5] and Meegoda et al. [6] presented asphalt S/S of soils contaminated by heavy metals. Meegoda [7] dealt also with wastes contaminated by petroleum. Petroleum contaminated soils stabilized either by hot mixed asphalt or by asphalt emulsion were suggested for construction purposes. Li et al. [8] suggested that a cement-asphalt emulsion composite (CAEC) might be an alternative to the base course material in pavements. They concluded that the CAEC possesses most of the characteristics and advantages of both cement and asphalt. Asphalt emulsions were also used for S/S of wastes containing heavy metals [3,9]. In these both papers, a technique of secondary asphalt barrier was used to prevent leaching of pollutants.

The principle of S/S using AE consists in the waste encapsulation by the asphalt binder. Thus, it is evident, that the S/S by AE is highly universal. The waste is mixed with the asphalt emulsion and the asphalt emulsion breaks gradually into water and pure asphalt binder. As a result, the particles of waste are coated with an asphalt layer.

The purpose of the research presented here was to develop a technological procedure for S/S of the wastes produced by destruction of discarded military munitions in the explosion chamber. The procedure should consist in simple mixing of the waste with commercially available AE and it should be easily applicable in practice.

2. Materials and methods

2.1. Waste

The waste comes from industrial destruction of discarded military munitions in the explosion chamber. The original explosive contained mainly lead azide, lead trinitroresorcinate, lead fulminate, potassium chlorate, barium nitrate, trinitrotoluene, pentaerythritetranitrate and trinitrophenylmethylnitramine. The explosion in the chamber produces gas products with initial temperature approximately 2000 °C, which are cooled down to exit temperature 50 °C and the contained solid particles are trapped

Table	1
Basic	characteristics of wastes

Waste	Dry matter (%)	Bulk density (g cm ⁻³)	Density (g cm ⁻³)	Loss on ignition at 800 °C (%)
Scrap	99.95	3.1	7.1	0.7
Dust	98.56	5.6	7.4	3.3

in cyclone and on textile filters. The coarse fraction of solid products of the explosion destruction remains in the chamber. Thus, two separate fractions of the waste are produced:

- scraps (scrap waste),
- dust (dust waste).

Large pieces of metal – residues of the explosive containers – are removed from the scrap waste by the operator. Basic characteristics of both wastes can be found in Table 1. The scrap waste contained particles of 0.1–1.0 cm; particle size distribution of the dust waste is shown in Fig. 2 (measured by CILAS 920 Liquid, CILAS US Inc.).

Leachates of the waste samples used in this research contained beside Pb following metals: Hg, Ba, Sb, Cd, Cu and Ni (see Table 2). A qualitative analysis of the waste samples by X-



Fig. 2. Particle size distribution of the dust waste measured by CILAS 920 liquid.

Table 2	
TCLP leaching results of untreated munition destruction wastes	

	Scrap waste	Dust waste	Regulatory level ^a
Pb (mg/L)	1278	3708	5
Hg (mg/L)	$< 1 \times 10^{-4}$	0.26	0.2
Sb (mg/L)	1.23	3.40	_b
Ba (mg/L)	5.87	23.69	100
Cd (mg/L)	0.03	32.61	1
Ni (mg/L)	7.27	166.6	_b
Cu (mg/L)	2.70	224.7	_b
pH	5.36	5.17	_b

TCLP, toxicity characteristic leaching procedure, extraction liquid 1 was used for scrap waste, extraction liquid 2 was used for dust waste.

^a Regulatory level for the untreated waste according US regulations (40CFR261.24).

^b Regulatory level is not specified; the highlighted values exceed the regulatory levels.

ray fluorescence spectroscopy also showed presence of Fe, Zn, S, Mn and Sn (see Fig. 3 as an example).

2.2. Asphalt emulsions

Two different asphalt emulsions (AE) were used for stabilization/solidification of the waste

- Anionic AE "Latexfalt" (Latexfalt b.v., Koudekerk a/d Rijn, The Netherlands); this emulsion is aqueous anionic slowsetting asphalt emulsion with pH 11; contains approximately 64% of asphalt binder. AE "Latexfalt" was chosen from several anionic commercially produced emulsions due to its best encapsulating effect.
- Cationic AE "L03/05" (Stavby silnic a zeleznic, a.s., Kolin, Czech Republic); this emulsion is aqueous cationic slowsetting asphalt emulsion with neutral pH and contains approximately 54% of asphalt binder. This AE was specially designed for S/S purposes.

These emulsions were selected on the basis of our experiences [2,3,9,10].

2.3. S/S of the waste

For preparation of stabilized waste, 50 ± 0.1 g of the scrap waste or 20 ± 0.1 g of the dust waste was used in each S/S experiment. Two techniques were used for mixing the waste with AE:

- Technique of one-step addition of AE: the waste was mixed with the whole dose of AE in a kneader for 5 min, the mixture was left to dry on a polyethylene (PE) foil for 5 days and then the stabilized waste together with the foil were subjected to leaching tests.
- Technique of two-step addition of AE: the first portion of AE (weighted with accuracy ± 0.1 g) was added to the waste; the mixture was mixed with the laboratory kneader for 5 min; clots resulting from this step were placed on the PE foil and left to dry for 3 days; then the second portion of AE was added, the mixture was mixed in the kneader for 5 min and then it was left to dry on the PE foil for 3 days; resulting stabilized waste was subjected to the leaching tests together with the foil (see Section 2.4). Compositions of stabilized wastes (weight ratios) are presented in Tables 3 and 4.

2.4. Leaching test

Toxicity characteristic leaching procedure (TCLP, EPA method 1311) according to US Environmental Protection Agency was used for assessment of the S/S efficiency.

For leaching of the scrap waste (both untreated and stabilized), extraction fluid 1 (acetic buffer, pH 4.93) was used. For leaching of the dust waste (both untreated and stabilized), extraction fluid 2 (acetic acid, pH 2.88) was used. The liquid/solid ratio in TCLP is 20:1. The selection of extraction fluids was made according to the TCLP instructions.

As it has been mentioned, no stabilized waste specimens were prepared specially for the leaching tests—the waste encapsulated by asphalt binder placed on PE foil was subjected to the leaching test directly, without any mechanical finishing procedure. The leachates of untreated wastes were filtered through a glass–fibre filter with an effective pore size of $0.7-1.3 \,\mu\text{m}$.



Fig. 3. X-ray fluorescence spectrum of the dust waste sample.

Table 3 Compositions of stabilized scrap waste and leaching test results

S/S technique	Composition				TCLP ^a	
	$\overline{m_{AE1}^{b}(g)}$	$m_{AE2}{}^{c}(g)$	$m_{A}{}^{d}\left(g\right)$	A/W ^e	Pb ^f (mg/L)	pН
Anionic AE, one-step	30.0	0	19.2	0.384	0.55	4.94
Anionic AE, two-step	7.5	12.5	12.8	0.256	0.35	4.89
Cationic AE, one-step	25.0	0	13.5	0.270	6.36	4.87
Cationic AE, two-step	10.0	15.0	13.5	0.270	0.58	4.91

All values in the table are average of three parallel experiments; weight of waste was 50 g in all cases;

^a Leaching results of the toxicity characteristic leaching procedure; extraction liquid 1 was used.

^b Weight of asphalt emulsion added in the first step.

^c Weight of asphalt emulsion added in the second step.

^d Total amount of asphalt binder contained in the stabilized waste.

^e Asphalt binder/waste weight ratio of the stabilized waste.

^f Concentration of Pb in the TCLP leachate; regulatory level of Pb for treated waste is 0.75 mg/L (according 40CFR268.48); the highlighted values exceed the regulatory levels.

The filtration of stabilized waste leachates was not carried out, because the leachates were quite clear.

In the leachates of the untreated wastes, concentrations of all relevant metals were determined. Concentration of Pb in these leachates exceeded the regulatory level significantly (see Table 2) and therefore the concentrations of Pb in the stabilized waste leachates were monitored as a demonstrative criterion for the S/S procedure efficiency assessment. Concentrations of Hg were determined by a mercury analyzer (AMA 254, Altec Ltd.), other metals were determined by atomic absorption spectrometry (GBC 933AA, GBC Scientific Equipment Pty Ltd.).

The leaching test with distilled water as the extraction medium is commonly used for assessment of waste stabilization/solidification. However, if the leaching of metal ions is evaluated, the water-leaching test brings about misguided results. Anyway, these results depend on the pH value of the leachate, which is given by chemical character of the waste. In addition, the evaluation is complicated in the case of amphoteric metals.

 Table 4

 Compositions of stabilized dust waste and leaching test results

S/S technique	Composition				TCLP	
	m _{AE1} (g)	m _{AE2} (g)	m _A (g)	A/W	Pb (mg/L)	pН
Anionic AE, one-step	25.0	0	16.0	0.80	3.45	2.88
Anionic AE, two-step	15.0	20.0	22.4	1.12	3.23	2.93
Cationic AE, one-step	60.0	0	32.4	1.62	16.04	2.91
Cationic AE, two-step	25.0	35.0	32.4	1.62	10.57	2.95

Weight of waste was 20 g in all cases; extraction liquid 2 was used for TCLP. The symbols correspond to the notation in Table 3.

The TCLP test by US EPA has respected all the facts. That is why the water-leaching test was not used in this paper.

3. Results and discussion

3.1. Leaching test results of untreated waste

Each leaching test was carried out three times parallelly; the average results can be seen in Table 2. The highlighted numbers are values of pollutant concentrations that exceeded the regulatory level. It is evident from the table, that the scrap waste leachate exceeded the regulatory level of Pb. The dust waste leachate exceeded regulatory levels of Pb, Hg and Cd. The higher leachability of the dust waste is self-evident result with respect to its much greater surface area.

3.2. S/S of the scrap waste

Different waste/AE weight ratios were tested in a preliminary study [10]. When the optimal ratio was found, the final set of experiments was carried out, results of which can be seen in Table 3. These results are average values obtained in three parallel independent experiments.

It is clear from Table 3, that simple one-step technique of S/S of the scrap waste by anionic AE was successful. In the case of the two-step technique application, the results were even better, in spite of lower total amount of AE (the asphalt/waste weight ratio was 0.384 for one-step technique and 0.256 for two-step technique).

Stabilization by the cationic AE using one-step technique was not successful (concentration of Pb in the leachate 6.36 mg/L exceeded RL, which is 0.75 mg/L: for leaching of stabilized wastes, stricter regulatory levels – Universal Treatment Standards, according US EPA regulation 40 CFR §268.48 – are valid). However, S/S by cationic AE using the two-step technique was successful (concentration of Pb in the leachate was 0.58 mg/L and the regulatory level 0.75 mg/L was met).

The presented results showed convincingly, that application of anionic AE should be preferred. In spite of the fact that the anionic AE Latexfalt gives much better results, the cationic AE was also tested due to its better availability at the Czech market. Availability of AE represents an important factor for implementation of S/S technique in practice.

It is necessary to note that S/S by AE shows a universal character, which is needful for disposing of waste with continuously varying composition. This universal character is given by the mechanism of S/S: encapsulation of waste particles by the asphalt binder, which is hydrophobic, low permeable and chemically and biologically highly stable material.

3.3. S/S of the dust waste

Experiments with the dust waste were analogous to those with the scrap waste. Unfortunately, successful S/S was not accomplished, even when high A/W ratio was applied. The results in Table 4 show that concentrations of Pb in the leachates exceed regulatory level (0.75 mg/L) in all cases. Experiments showed again that anionic AE is markedly better binder than cationic AE.

Unfortunately, the obtained results confirmed our former finding [9] that wastes with small particle size having large specific surface probably cannot be stabilized/solidified using encapsulation by AE. However, the technique of secondary barrier formation can be used to prevent pollutant leaching from the partially stabilized/solidified waste in these cases. In the practice, the secondary barrier can be formed by construction of an asphalted disposal site in the landfill [3,4].

4. Conclusions

Development of S/S technology for disposal of the waste produced by destruction of discarded military munitions can be summarized into following points:

- Destruction of the munitions in the explosion chamber produces two separate fractions of solid waste (1) the scrap waste (scraps remained in the chamber after explosion), (2) the dust waste (fine particles trapped on the filters of gas products that are exhausted from the chamber after explosion).
- S/S technique using simple mixing of the waste with the anionic AE fully meets requirements in the case of scrap waste. The stabilized scrap waste shows low leachability meeting regulatory levels for TCLP leaching test.
- Two-step technique for the waste S/S is more efficient than one-step technique; moreover, it allows decreasing the total amount of AE used and enables usage of cationic AE for S/S of the scrap waste.
- Application of anionic AE (chosen based on experiments with various commercial AE) brings significantly better results than cationic AE application.
- S/S of the dust waste by AE is not sufficient. Thus the solidified dust waste has to be deposited into an asphalted disposal site in the landfill, where the asphalt wall represents secondary barrier against pollutants release.

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