Stabilization/solidification of galvanic sludges by asphalt emulsions

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Abstract

A combination of two-aqueous asphalt emulsions was proposed for stabilization/solidification treatment of galvanic sludges prior to landfilling. The presented procedure comprises mixing the galvanic sludge with a slow setting nonionic asphalt emulsion and subsequently forming a secondary asphalt barrier by means of a rapid setting anionic asphalt emulsion. The method was tested on four samples of galvanic sludge from various galvanizing plants, with various water and pollutant contents. Stabilization efficiency was assessed by water-leaching test, TCLP test and by determining ecotoxicity of leachates. Leachate parameters exhibited very low values and favorable results of ecotoxicological tests indicate high efficiency of the developed procedure for galvanic sludge disposal.
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1. Introduction

An inherent constituent of the majority of products, from petty consumer goods up to complex technological devices, is that their surface is treated for corrosion-resistance as well as for cosmetic reasons. Electroplating, as one of the most widely expanded technologies particularly for treatment of metal surfaces, is at present an entirely commonplace ingredient in a number of manufacturing processes. The principle of electroplating, put in a greatly simplified manner, is electrochemically forming a thin layer of metal on an object being plated through the action of direct current on an electrolyte solution containing cations of the metal used for plating (so-called galvanic bath). The metal plated object forms a negative electrode and the positive electrode usually (but not necessarily) being of a metal employed for plating. The metals usually applied to produce electroplated coating are Cr, Sn, Cu, Zn, Ni, Cd, Pb and Fe, for special purposes, Ag, Au or Pt. Besides, galvanic treatments also include anodic

oxidation of aluminum, so-called eloxal process. Galvanic baths may be either acidic or basic. The acid baths mostly contain sulfates, but also chlorides, nitrates, oxides or carbonates of the mentioned metals, while cyanides have an absolute majority for basic baths. After a certain period of use the galvanic bath becomes so exhausted and/or inadmissibly contaminated that its replacement becomes necessary and it thus becomes waste, wastewater. Apart from that, the galvanizing plant wastewaters also contain waters from rinsing of finished metal plated products and also wastes produced in necessary processes of mechanical and chemical surface treatment carried out prior to actual metal plating (degreasing, derusting, pickling, grinding, polishing).

It is obvious from above that electroplating represents a significant potential source of environmental pollution. Treatment of wastewaters from galvanizing processes results in producing so-called galvanic sludge. Cyanides contained in basic baths are oxidized by means of chlorinated lime or chlorine dioxide [1] or even Fe(VI) [2]. Acidic and basic waters are subsequently mixed together. Present metals are then precipitated with lime in the form of oxides or hydroxides and low-soluble calcium sulfate is simultaneously formed. The galvanic sludge originates from the precipitate

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by its dewatering. It represents hazardous waste and must be stabilized prior to landfilling in order to prevent releasing of present pollutants into the environment.

Herein, it must be emphasized that composition of galvanic sludge is given in the first place by currently used electroplating technology, and not only differs from the galvanic sludges from various galvanizing plants, but naturally also from sludges from the same plant depending on the particular type of plating performed.

Metal recovery from galvanic sludges has been under study [3–7], but it is not being realized at present and will probably not be easily implemented on a technical scale in the case of a galvanizing plant carrying out a wide range of electroplating treatment owing to the mentioned presence of a number of metals and employed chemicals.

Common stabilization/solidification (S/S) of galvanic sludges with cement or pozzolanic materials in specific cases leads to markedly reduced leachability of pollutants [8–10], but it is encumbered by two-adverse facts: amphoteric metals (Cr, Pb, Zn) can easily leach from solidified waste at high pH value given by CaO content in cement [11], and the concrete matrix does not resist an acidic leaching medium attack or other environmental influences [12]. An acidic leaching medium has to be taken into consideration with respect to organic acids originating in the body of landfill and to the reality of acid rains.

Some other procedures for disposal of galvanic sludges were found in literature, e.g. incorporation in ceramic materials [13,14] or thermal treatment [15–17].

However, due to the mentioned variability in composition of galvanic sludge, a more suitable method of galvanic sludges disposal seems to be that one which is universal and independent on current pollutant content. This requirement can be met in the case of S/S by asphalt binders because asphalt, as a highly hydrophobic substance, is capable of forming an immobilizing barrier efficiently preventing any pollutant from leaching out from stabilized waste into the environment [18,19]. At the same time, asphalt is exceptionally resistant to chemical and biological influences [20,21] so that long-term stability of asphalt-solidified wastes in a landfill environment may rightfully be anticipated, as opposed to wastes stabilized by hydraulic binders. Nevertheless, melted asphalt technology, beside well-known complications concerning asphalt melting (energy requirements, demanding handling, gaseous emissions), is applicable with difficulty in the case of galvanic sludge S/S also due to a large quantity of water (20–70%) present in the sludge. On the contrary, S/S of wastes employing aqueous asphalt emulsions does not suffer from these drawbacks. Asphalt binder produced by emulsion breaking retains all of the adhesion, durability and water-resistance of the asphalt binder from which the emulsion was produced [22]. Furthermore, choice of suitable asphalt emulsions with respect to surface charge of waste particles achieves better compatibility of the waste–asphalt mixture [23], and thus also achieve potentially better results to those attained applying melted asphalt binder.

2. Experimental

2.1. Asphalt emulsions

Two-aqueous asphalt emulsions employed were as follows:

- slow setting, nonionic, clay-stabilized asphalt emulsion, commercial product designated Gumoasfalt SA-7, asphalt content 50–55%, asphalt softening point 42 °C, pH 11–12, emulsifier—alkalized vinsol resin (approximately 1.5%), stabilizer—bentonite (approximately 2.5%);
- rapid setting, anionic asphalt emulsion, commercial product designated Silembit S-60, asphalt content 60%, asphalt softening point 37–44 °C, pH 12–13, emulsifier—salts of higher saturated organic acids.

Both emulsions are produced by Paramo Co., Pardubice (Czech Republic) and are used in road construction and building industry.

2.2. Galvanic sludges

Tests were run on four samples of galvanic sludges from four different galvanizing plants. The sludges in question were obtained by precipitation from galvanic wastewaters by means of lime and subsequent dehydration of precipitate in filter press (sample 1, sludge dry matter approximately 80%; metals content in dry matter: Ca 3.6%, Cr 2.6%, Fe 18%, Ni 1.6%, Cu 1.5%, Zn 13.8%—determined by X-ray fluorescence spectroscopy) or centrifuging and drying (samples 2–4, sludge dry matter 30–35%; metal content in sample 3: Ca 13.4%, Cr 0.2%, Fe 8.2%, Ni 0.2%, Cu 0.7%, Zn 8.4%, Cd 2.0%—determined by X-ray fluorescence spectroscopy). Sample 2 came from a galvanizing plant, where merely chrome and zinc plating and eloxal process were carried out; samples 1, 3 and 4 came from galvanizing plants carrying out any type of electroplating. Approximately, 20 kg of each sludge was sampled, homogenized by mixing in a laboratory kneader and stored in airtight closed container until used.

2.3. Procedure of S/S and specimen preparation

The S/S procedure was based on empiric findings gained in S/S of ash and salt from a waste incinerator [23] and of noncombustible industrial waste [24].

The first step involved mixing galvanic sludge with slow setting asphalt emulsion in the chosen ratio and homogenizing the produced mixture for approximately 15 min. The mixture, in a quantity of 100–130 g, was subsequently put into a duralumin cylindrical mold of 40-mm i.d., compacted under pressure about 0.4 MPa and then pushed out, producing thus a cylinder-shaped test specimen of height about 100 and 40 mm in diameter. This test specimen was kept freely in air for 48 h to ensure complete breaking of the asphalt emulsion. It was then hung on polyamide

thread, sprayed with the rapid setting asphalt emulsion and left for additional 24 h so that excess emulsion could drip off creating a stiff asphalt coating. In order to ensure that a continuous, nonporous asphalt coating was formed on its surface, the specimen was briefly dipped into the rapid setting asphalt emulsion, and subsequently left hanging again for another 48 h till the asphalt coating completely dried up. Based on dimensions and weights of test specimens, measured prior to and after formation of asphalt coating, the thickness of the coating was estimated at 0.2–0.8 mm.

2.4. Leaching tests

Leachability of untreated galvanic sludges was evaluated using two-standard leaching methods: TCLP test (EPA method no.1311) with extraction liquid #2 (aqueous solution of acetic acid, pH 2.88 ± 0.05, liquid/solid ratio 20:1, leaching time 18 h) and leaching test with deionized water (DIN 38414 S-4, liquid/solid ratio 10:1, leaching time 24 h).

Evaluating stabilization/solidification of galvanic sludges utilized the same leaching tests; however, disintegration of the test specimens prior to leaching down to the particle size specified by the leaching tests instructions was not carried out. Tests were run on monolithic test specimens provided with the asphalt coating, preparation of which is described in Section 2.3.

2.5. Analysis of leachates

- Metals were determined by atom absorption spectrophotometer (AAS) (GBC 933 AA, GBC Scientific Equipment Pty. Ltd., Australia).
- Specific conductivity was measured with microprocessor conductometer LF 3000 with automatic temperature correction to 25 °C (Wissenschaftlich Technische Werkstatten GMBH, Germany).
- Determination of DOC (dissolved organic carbon) was performed employing carbon analyzer TOC 5000A (Shimadzu Corp., Japan).
- F^- anions were determined by potentiometry applying a fluoride ion-selective electrode.
- CN^- were determined by spectrophotometry in accordance with ISO 6703-1; absence of cyanides was proved through highly selective qualitative test based on the Konig–Zincke reaction.
- Determination of other inorganic anions was performed by the ion chromatography method (LC Module I, Waters, USA) with conductance detection (Cl^-, SO_4^{2-}, HPO_4^{2-}) and UV detection at 230 nm (NO_3^-, NO_2^-).

2.6. Ecotoxicity tests

Ecotoxicity of leachates of untreated wastes and leachates of prepared test specimens was assessed it tests with:

- bacterium *Pseudomonas putida* (ISO 10712:1995, growth inhibition test);
- higher plant *Latuca sativa* (OECD 208/1984, terrestrial plants, growth test);
- freshwater alga *Scendesmus subspicatus* (ISO 8692:1989, growth inhibition test);
- crustacea *Artemia salina*.

In the test with crustacea, the percentage of immobilized organism was evaluated in media containing various leachate contents during a 72-h exposure. The basic medium employed was synthetic seawater (ISO 10253:1995).

3. Results and discussion

3.1. Characterization of tested galvanic sludges

All four samples of galvanic sludges were subjected to the mentioned leaching tests (Tables 1 and 2). Table 1 summarizes contents of relevant metals and values of selected parameters in aqueous leachates. Despite the fact that galvanic sludges contain considerable quantities of metals, it is obvious from results that aqueous leachates contain these metals in relatively low concentrations. This contradiction is merely apparent because metals are present in the form of low-soluble oxides and/or hydroxides or carbonates. This chemical form yields leachability values, which as the table indicates, meets limit values II/CZ (see Table 1), which would signify the given waste is not hazardous when viewed from the standpoint of toxic metals leachability by water. Values of other determined parameters are variable, which corresponds to the already mentioned fact that galvanic sludge composition is given in the first place by electroplating technology in actual use (see high nitrite content with sample 3, e.g. or high chloride content with sample 2 and the like). Negligible concentrations of cyanides prove efficiency of their removal in galvanizing plants. According to Sharma et al. [2], nitrites can be formed during oxidation of cyanides. Their noticeable presence was detected in leachate of the sample 3. Organic matter, presented in the table as the parameter DOC, was found in leachates of all four samples of galvanic sludges only in negligible concentrations.

Table 2 summarizes determined contents of relevant metals in TCLP leachates. Appreciable dissolving of metals obviously takes place during acid leaching, as opposed to leaching by water. Concentrations of metals under observation attain high levels from which it follows that simple landfilling of galvanic sludges is unacceptable. Comparing test results of leachability by water and by acidic leaching medium indicates that water leachability alone is an insufficient criterion for assessing leachability of metals from the waste.

3.2. S/S by asphalt emulsions

As noted previously in Section 2.3, the applied procedure for S/S of galvanic sludges was based on the process

Table 1
Determination of relevant metals contents and selected parameters in aqueous leachates of untreated galvanic sludges

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	II/CZ	DWS/CZ
Cd (mg L^{-1})	<0.005	0.010	<0.005	<0.005	0.05	0.005
Cr (mg L^{-1})	<0.1	<0.1	<0.1	<0.1	1.0	0.05
Pb (mg L^{-1})	<0.1	<0.1	<0.1	<0.1	0.5	0.01
Ni (mg L^{-1})	<0.05	<0.05	<0.05	0.10	0.5	0.02
Ag (mg L^{-1})	–	<0.05	<0.05	<0.05	0.1	0.05
Zn (mg L^{-1})	<0.1	0.854	<0.1	0.105	5.0	N/A
Cu (mg L^{-1})	0.082	0.055	<0.05	0.184	1.0	1.0
Fe (mg L^{-1})	<0.1	<0.1	<0.1	<0.1	N/A	0.2
Al (mg L^{-1})	–	<0.2	2.63	0.19	10.0	0.2
pH value	9.16	8.01	9.08	8.08	5.5–12	6.5–9.5
Specific conductivity (mS m^{-1})	132.3	312	251.3	226.6	600	250
Dissolved substances (mg L^{-1})	665	**2450**	**2150**	**1725**	N/A	1000
DOC (mg L^{-1})	9.62	4.57	3.03	5.01	30.0	5.0
F$^-$ (mg L^{-1})	0.88	0.4	<0.3	0.35	5.0	1.5
Cl$^-$ (mg L^{-1})	**186**	**1211**	**139**	42.8	N/A	100
NO$_2$$^-$ (mg L^{-1})	<0.05	<0.05	9.0	<0.05	1.0	0.5
NO$_3$$^-$ (mg L^{-1})	<1.0	<1.0	4.4	<1.0	N/A	50
SO$_4$$^{2-}$ (mg L^{-1})	203	**918**	**1085**	**865**	N/A	250
HPO$_4$$^{2-}$ (mg L^{-1})	<1.0	<1.0	<1.0	<1.0	N/A	N/A
CN$^-$ (mg L^{-1})	0.38	<0.1	<0.1	0.1	0.5	0.05

II/CZ, limit value of leachability class II for aqueous leachates of wastes according to Czech regulations; DWS/CZ, drinking water standard valid in Czech Republic; –, parameter was not determined; <, determined value of parameter was below given detection limit of analytical method used; N/A, limit value is not prescribed. Bold values exceeded limit II/CZ or DSW/CZ, where II/CZ is not prescribed.

developed for S/S of dry loose wastes. Nevertheless, completely dry wastes rather pose a complication in S/S by asphalt emulsions: the dry waste can take water out of asphalt emulsion, which causes its premature breaking, and consequently makes waste–emulsion mixing more difficult. This problem was solved in the two-mentioned studies by adding water to the blended waste–asphalt emulsion mixture. In the case of galvanic sludges, which already contain a certain quantity of water, mixing is easy and no additional water is needed. For this reason, galvanic sludges containing up to 70% water were deliberately used, in a condition in which they usually leave the galvanizing plants if they are not dried. In this case, mixing galvanic sludge with asphalt emulsion is quite easy, as it comprises mixing liquid (asphalt emulsion) with a pasty form of galvanic sludge. Excess water spontaneously evaporates from the mix.

Due to slightly basic pH of galvanic sludges (Table 1) and also to presence of heavy metal ions in galvanic sludges, it was not considered to employ acidic cationic asphalt emulsions, which are used more frequently in road construction, and are thus commercially more available. Cationic emulsifiers used in cationic emulsions require an acid environment, which would naturally lead to increased solubility of metals contained in galvanic sludges and that would be inconsistent with the purpose of S/S. Therefore, a basic, nonionic, clay-stabilized, slow setting asphalt emulsion was used. Mixtures of individual samples of galvanic sludges with this slow setting asphalt emulsion were prepared in such manner that asphalt content in mixtures was 5–20 wt.%. This quantity of asphalt is too small for complete encapsulation (i.e. for complete coating of all waste particles with asphalt binder), nevertheless is enough to form a coherent, relatively firm matrix of solidified waste. The formed matrix; however, is quite porous and does not significantly prevent pollutant leaching. Consequently, a compact asphalt coating was produced on test specimens prepared from the mentioned mixtures,

Table 2
Relevant metals contents in TCLP leachates of untreated galvanic sludges

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	UTS	RL
Cd (mg L^{-1})	0.267	0.758	17.75	0.529	0.11	1.0
Cr (mg L^{-1})	0.62	1.36	0.16	2.52	0.60	5.0
Pb (mg L^{-1})	<0.05	<0.1	<0.1	<0.1	0.75	5.0
Ni (mg L^{-1})	39.6	<0.05	2.98	43.7	11	N/A
Ag (mg L^{-1})	–	<0.05	<0.05	<0.05	0.14	5.0
Zn (mg L^{-1})	549	889	166	147	4.3	N/A
Cu (mg L^{-1})	8.64	2.57	2.80	14.0	N/A	N/A
Fe (mg L^{-1})	0.10	30.7	0.15	2.55	N/A	N/A
Al (mg L^{-1})	–	3.91	3.21	437	N/A	N/A

UTS, Universal Treatment Standards (USA, Code of Federal Regulations, 40CFR268.48); RL, Regulatory Level (USA, Code of Federal Regulations, 40CFR261.24); –, parameter was not determined; <, determined value of parameter was below given detection limit of analytical method used; N/A, limit value is not prescribed.

Table 3
Aqueous leachate conductivities of asphalt coated specimens of solidified galvanic sludges

Asphalt binder content (wt.%)	Specific conductivity (mS m^{-1})			
	Sample 1	Sample 2	Sample 3	Sample 4
5	1.47	0.68	0.56	1.69
10	1.46	0.44	0.53	0.47
15	1.32	2.66	1.04	0.49
20	1.34	2.02	1.07	1.46

Specific conductivity of pure leaching medium was 0.11 mS m^{-1}; blank test specific conductivity (glass body of dimensions corresponding to test specimens, provided with asphalt coating and leached by the same procedure as test specimens) was 0.30 mS m^{-1}.

representing a secondary barrier against leaching, an efficiency of which had already been proved in studies mentioned earlier. Its formation involved use of a rapid setting, basic anionic asphalt emulsion. Choice of an anionic emulsion for formation of the secondary barrier was again based on the same criteria as in the case of an emulsion for primary mixing with waste (i.e. preventing dissolution of metals in emulsion and suitable surface polarity to ensure asphalt breaking).

Test specimens of solidified galvanic sludges provided with secondary barrier were subjected to the water-leaching test in which the only studied parameter was specific conductivity of leachate, as a highly sensitive and easily measurable variable informing on ion leaching. Results of this test are summarized in Table 3, and as it is apparent from these values, they do not indicate any obvious trend. This means that leachability is independent on asphalt binder content in the

solidified waste matrix, but dependent on quality of the created asphalt coating, i.e. on the secondary barrier. Concerning absolute values of the obtained conductivities, they may be said to attain low values in all cases which means that performed S/S was efficient. Some results are even of the same order of magnitude as the results of blank test (asphalt coated glass body, conductivity 0.30 mS m^{-1}).

Due to the fact that the higher content of asphalt binder in a specimen of solidified galvanic sludge does not bring about the smaller ion leachability in the presented S/S procedure, higher dosage of asphalt emulsion appears to be useless and economically inconvenient. Accordingly, such dosage of asphalt emulsion was selected that entailed 5% content of asphalt binder in the solidified galvanic sludge. Several test specimens of the solidified galvanic sludge containing 5% of asphalt binder were prepared from each sample of galvanic sludge, all specimens were provided with the secondary asphalt barrier, and three test specimens of each sample were subjected to the leaching tests in both aqueous as well as acidic leaching medium. In the prepared leachates, those parameters and metals were determined which had been found in leachates of untreated galvanic sludges. Results are presented in Tables 4 and 5. Values of all observed parameters may be stated to be very low. Primarily, a positive result is the fact that no present metals leach even by acid leaching medium. This reality confirms again the universality of asphalt barrier against leaching of any ions. All is quite obvious when these results are compared to limit values for drinking water (Czech and EPA drinking water standards). Values of

Table 4
Determination of selected parameters in aqueous leachates of test specimens provided with secondary asphalt barrier, asphalt content in specimens 5%

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Limit value		
					II/CZ	DWS/CZ	DWS/EPA
pH	7.31	6.02	5.33	5.77	5.5–12	6.5–9.5	6.5–8.5
Specific conductivity (mS m^{-1})	1.47	1.04	0.21	0.56	600	250	N/A
Cl$^-$ (mg L^{-1})	<0.3	2.1	<0.3	<0.3	N/A	100	250
NO$_2^-$ (mg L^{-1})	<0.05	<0.05	0.17	<0.05	1.0	0.5	1.0
NO$_3^-$ (mg L^{-1})	<1.0	<1.0	<1.0	<1.0	N/A	50	10
SO$_4^{2-}$ (mg L^{-1})	<0.1	4.4	<0.1	1.8	N/A	250	250

II/CZ, limit value of leachability class II for aqueous leachates of wastes according to Czech regulations; DWS/CZ, drinking water standard valid in Czech Republic; DWS/EPA, drinking water standard according to US-EPA; <, determined value of parameter was below the given detection limit of the analytical method used; N/A, limit value is not prescribed. Values are averages of measured leachate parameters of three test specimens.

Table 5
Determination of relevant metals in TCLP leachates of test specimens provided with secondary asphalt barrier, asphalt content in specimens 5%

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Limit value		
					UTS	DWS-CZ	DWS-EPA
Cd (mg L^{-1})	<0.01	0.017	<0.01	<0.01	0.11	0.005	0.005
Cr (mg L^{-1})	<0.05	<0.05	<0.05	<0.05	0.60	0.05	0.1
Ni (mg L^{-1})	<0.05	<0.05	<0.05	<0.05	11	0.02	N/A
Zn (mg L^{-1})	<0.05	0.45	0.75	0.12	4.3	N/A	5
Cu (mg L^{-1})	<0.05	<0.05	<0.05	<0.05	N/A	N/A	1.0
Fe (mg L^{-1})	<0.1	<0.1	<0.1	<0.1	N/A	0.2	0.3
Al (mg L^{-1})	–	<0.2	<0.2	<0.2	N/A	0.2	0.05–0.2

UTS, Universal Treatment Standards (according to 40CFR268.48); DWS-CZ, drinking water standard valid in Czech Republic; DWS-EPA, drinking water standard according to US-EPA; –, parameter was not determined; <, determined value of parameter was below given detection limit of analytical method used; N/A, limit value is not prescribed. Values are averages of measured leachate parameters of three test specimens.

Table 6
Ecotoxicity of TCLP leachates of untreated and stabilized/solidified galvanic sludges

Test		EC$_{50}$ (vol.%)			
		Pseudomonas putida	*Latuca sativa*	*Artemia salina*	*Scendesmus subspicatus*
Sample 1	Untreated	0.98	26	25	3.0
	Treated	LT (93)	LT (90)	LT (80)	LT (80)
Sample 2	Untreated	0.12	70	8.1	1.5
	Treated	LT (93)	LT (90)	LT (80)	LT (80)
Sample 3	Untreated	14	52	LT (80)	13
	Treated	LT (80)	LT (90)	LT (80)	LT (80)
Sample 4	Untreated	0.13	23	LT (80)	3.2
	Treated	LT (93)	LT (90)	LT (80)	LT (80)

EC$_{50}$, TCLP leachate content (vol.%) in culture medium producing 50% inhibition of given parameter; LT, low toxicity. EC$_{50}$ value was not attained even with maximum possible content (vol.%) of leachate in culture medium, which is given in brackets.

parameters obviously correspond in almost all cases to requirements for drinking water. This comparison with drinking water standards was carried out to compensate for the fact that no pertinent limits are specified for leaching of monolithic bodies.

3.3. Ecotoxicological assessment of S/S

Although leaching test results showed that galvanic sludges stabilized/solidified by the presented procedure released only negligible quantities of pollutants, this could not been taken as evidence that the stabilized galvanic sludge would not affect negatively in the environment. Hence, a series of ecotoxicological tests were applied for assessing efficiency of proposed S/S process (Table 6). The EC$_{50}$ values given in the table represent a percent content of TCLP leachate in medium inducing 50% inhibition of the observed parameter. The lower is the EC$_{50}$ value, the more toxic is the leachate, and thereby the waste. The results showed while untreated galvanic sludges exhibited some level of toxicity, particularly when tested in the most sensitive test with *P. putida*, after realized stabilization/solidification the determined toxicity in all cases dropped below the detection limit.

4. Conclusions

- A two-stage procedure of S/S by aqueous asphalt emulsions, consisting of a primary mixing of waste with slow setting asphalt emulsion, and subsequent formation of secondary asphalt barrier by means of rapid setting asphalt emulsion, was applied to galvanic sludges representing hazardous, noncombustible wastes of variable composition and of relatively high water and toxic metals content. Water present in sludge facilitates its mixing with asphalt emulsion.
- Leachability of waste treated by the presented method is virtually independent on asphalt binder content in the mixture; quality of asphalt coating forming the secondary barrier appears to be the decisive factor. Quantity of emulsion corresponding to an approximately 5% content of asphalt binder in the blended mixture proves to be adequate for sufficient solidification of galvanic sludges. The quantity of asphalt binder needed to form a secondary barrier depends on dimensions of the block of solidified mixture and on thickness of produced coating. On laboratory scale, it amounts to further approximately 5–10% asphalt binder related to weight of primary mixture, consumption on a technical scale may be expected to be somewhat lower.
- The universal character of asphalt coating as a secondary barrier that prevents leaching of any pollutants was confirmed.
- All tested samples of galvanic sludges, in their untreated form, represent hazardous waste. After treatment by the presented method, leachability of relevant pollutants decreased to a very low level approaching standards for drinking water.
- Ecotoxicity tests showed that toxicity of leachates of stabilized galvanic sludges was negligibly low compared to relatively high toxicity of untreated galvanic sludge leachates.
- Results of S/S of galvanic sludges by means of asphalt emulsions demonstrated advantages of this kind of stabilization: a highly universal character based on ability to produce a immobilizing barrier against pollutant leaching, possible stabilization of wet wastes, highly hydrophobic character of asphalt binder, inertness and extraordinary stability in the environment. Regarding realization, it is positive that asphalt emulsions are commercially produced on a mass scale, their application is wide and sophisticated and has already become current practice in present-day road construction.

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