CZASOPISMO TECHNICZNE Ch
WYDAWNICTWO POLITECHNIKI KRAKOWSKIEJ

z. 2-Ch/2008
ISSN 0011-4561
ISSN 1897-6298

KAMIL P. BANASZKIEWICZ, TADEUSZ A. MARCINKOWSKI*

APPLICATION OF HYDRATED LIME AND FLY ASHES IN THE PROCESS OF NEUTRALIZATION OF WASTES FROM ELECTROCOATING WITH PORTLAND CEMENT

ZASTOSOWANIE WAPNA HYDRATYZOWANEGO ORAZ POPIOŁÓW LOTNYCH W PROCESIE UNIESZKODLIWIANIA ODPADÓW GALWANICZNYCH CEMENTEM PORTLANDZKIM

A b s t r a c t

Results of neutralizing galvanic sludges (GS) using the technology of stabilization/solidification are presented. Two solidifying/binding mixtures (B) were applied: B1 (a compilation of fly ashes, mortar sand, hydrated lime and Portland cement) and B2 (hydrated lime was eliminated, instead an equivalent dose of sand was applied). To solidifying mixtures sludges were being dosed in proportion B/GS of 1:3 and 1:5. The monolithic structures obtained were subjected to the pollutants leaching test (TCLP) and the test of axial compressive strength. The results were used as a base for evaluation of the effect of hydrated lime and fly ashes on the course and effectivity of the stabilization/solidification of electrocoating waste.

Keywords: stabilization, solidification, industrial waste, safe depositing

S t r e s z c z e n i e

Przedstawiono wyniki badań unieszkodliwiania osadów galwanicznych (GS) w technologii stabilizacji/zestalania. Zastosowano dwie mieszaniny zestalająco-wiążące (B): B1 (będącą mieszaniną popiołów lotnych, piasku do zapraw budowlanych, wapna hydratyzowanego i cementu portlandzkiego) oraz B2 (w której wyeliminowano wapno hydratyzowane, zwiększając jednocześnie o adekwatną ilość dawkę piasku). Do mieszanin zestalających dozowano osady w stosunku B/GS = 1/3 i 1/5. Uzyskane monolity poddano testowi na wymywanie zanieczyszczeń (TCLP) oraz badaniu wytrzymałości mechanicznej na ściskanie jednoosiowe. Na podstawie uzyskanych wyników badań określono wpływ wapna hydratyzowanego oraz popiołów lotnych na przebieg i skuteczność procesu stabilizacji/zestalania odpadów galwanicznych.

Słowa kluczowe: stabilizacja, zestalanie, odpady przemysłowe, bezpieczne składowanie

* Mgr inż. Kamil P. Banaszkiewicz, dr hab. inż. Tadeusz A. Marcinkowski, Instytut Inżynierii Ochrony Środowiska, Wydział Inyżnierii Środowiska, Politechnika Wrocławska.

1. Introduction

Stabilization of industrial waste is a process that should guarantee such a treatment causing that waste would not be arduous and hazardous in further treatment, i.e. should enable safe transportation (from the healthy and environmental point of view), and then safe and permanent deposition in properly prepared landfill. This last condition can be met if wastes are transformed into homogenous solid structures, having form of blocks or pellets – and this process is called solidification.

As a result of stabilization/solidification processes pollutants contained in waste are transformed into forms that are hardly soluble and distinguished by reduced toxicity. The product obtained has also definite compressive strength that enables its safe transportation and subsequent deposition [1–5].

The best solution is when stabilization of chemical composition of waste, as well as its solidification occurs in a single technological operation, i.e. during mixing hazardous waste with neutralizing chemicals and solidifying components.

The stabilization/solidification process proceeds in mixtures of chemically active components, that combined with water and hazardous agents of waste form stable solid substances [6, 7]. Stabilizing/solidifying materials can also significantly reduce solubility, and therefore mobility of pollutants by their sorption and encapsulation, as well as by their destruction [8, 9]. As a result of stabilization/solidification process a product in solid form is obtained, not revealing features of hazardous waste, or at most revealing such characteristic at significantly lower level than raw waste [10, 11]. Processes of stabilization/ /solidification are commonly utilized across the world and are described by the American Environmental Protection Agency (U.S. EPA) as the Best Available Technology for neutralizing 57 types of hazardous waste. Described method is most often used for stabilizing and neutralizing hazardous mineral waste, mainly soils, slurries and sludges contaminated with toxic metals [3, 12, 13].

In research on effectivity of stabilization/solidification processes physical, chemical and microstructural methods are used [4, 14]. As indicators in tests of stabilization/ /solidification the most often used are: evaluation of hardening and gaining mechanical compressive axial strength by the material, as well as the course of pollutants leaching after 28-days period of maturation. According to the methodology used by U.S. EPA, solidified/stabilized material can be acknowledged as satisfying the minimum requirements with reference to compressive strength, if its unconfined compressive strength is equal or higher than 0.35 MPa. This minimum is recommended to use in making decision of depositing such materials on landfills, what is connected with necessity of appropriate compressive strength for materials being deposited in upper layers of the landfill bowl. In Great Britain the acceptable compressive strength, measured 28 days after solidification, is 0.7 MPa, although (depending on parameters of the sample tested) it is possible to accept a material having compressive strength as small as 0.35 MPa [15]. In Poland, required compressive strength [16] is only 0.05 MPa.

With reference to pollutants leaching procedures, a wide variety of tests can be applied to determine pollutants leaching characteristics from waste materials. They differ in type of test, orientation towards different aspects of leaching and methodology of interpreting results in aspect of diversified research objects. However, quite common method is elaborated by U.S. EPA and used also in Europe, including Poland, procedure of determining leachate toxicity characteristics (TCLP) [17]. This method was drawn up as a simulation of leaching process that occurs in waste deposited in non-gasketed sanitary landfill. It is based on the assumption of co-disposal of material containing 95% of municipal and 5% of industrial wastes. The method consists in extraction shaking test using leaching liquid reflecting alkalinity of solid phase in the waste. In practical applications buffering solutions are used in tests: sodium acetate solution of pH 4.93 ± 0.05 or acetic acid solution of 2.88 ± 0.05 pH. The procedure requires reduction of particles size of tested material to a diameter below 9,5 mm. TCLP procedure was designed for evaluating mobility of 40 compounds that determine toxicity characteristics in solid, liquid and multiphase waste. The toxicity characteristics is determined by both organic, as well as inorganic compounds. Leachability of volatile organic compounds is determined using ZHE (Zero-Headspace Extractor) and buffering solution of sodium acetate.

TCLP procedure was drawn up in the year 1984 on account of amendments concerning hazardous and solid waste introduced into the Resource Conservation and Recovery Act [18] and is accepted by EPA as a standard in classifying waste as hazardous or non--hazardous, on the base of its toxicity. If the TCLP extract contains any of the components determining toxicity characteristics in amount equal to or higher than amount defined by the Directive 40 CFR 26.1.24 [19], waste has toxic features and therefore is classified as a hazardous material.

In stabilization/solidification processes wastes are mixed with appropriately compiled solidifying/binding mixture (B), based on mineral building materials, such as: various types of cement, fly ashes, furnace slag, water glass, mortar sand, hydrated lime, etc. The composition of B applied is determined by its purpose. Effective solidifying mixture is compiled depending on kind of waste being neutralized. The most commonly used are stabilization/solidification processes based on Portland cement and its mixtures with other hydraulic materials mentioned above.

The stabilization/solidification process using cement consists in hydratation reaction of cement and pozzolanic reactions, or in reactions between cement, ashes and lime. Usage of hydrated lime (HL) or flying ashes (FA) as components of the solidifying mixture has a beneficial effect on the course of cement hydratation process and final mechanical properties of the monolith after 28 days of hardening. Addition of FA to cement reduces shrinkage and creep, as well as the heat of hardening [20].

The aim of research reported here was evaluation of the effect of hydrated lime and fly ashes on the course of the process of solidifying galvanic sludges (GS). In research two solidifying/binding mixtures were applied, based on Portland cement, fly ashes, hydrated lime and mortar sand.

2. Materials and methods

2.1. Galvanic sludges

Due to its high content of toxic metals, sludge from electrocoating is classified as hazardous waste that can not be deposited on the landfills in its primary form [21]. Composition of sludge from galvanization plant is closely related to the technological process used as well as the method of neutralizing wastewaters it was derived from [22].

Sludges used in our research came from one of Lower Silesian galvanizing plants, they were characterized by very high concentrations of chromium, copper, zinc and nickel that amounted to, respectively, 115,334 mg/kg; 99,228 mg/kg; 79,374 mg/kg; 6,056 mg/kg (Tab. 1). Their hydratation levels were from 66,49 to 66,19% H_2O (average 66.34% H_2O). They had semi-solid consistency and were dark-green in colour, that confirmed domination of chrome-plating and nickel-plating processes. Test of TCLP (Toxicity Characteristic Leaching Procedure) [17, 23] performed on raw material showed that normatively acceptable concentrations of chromium in eluate (5 mg/dm^3) was exceeded 28-fold (140 mg/dm^3) – Tab. 1. Value of pH for fluid from extraction according to the TCLP procedure was 4.34.

Table 1

Concentrations of metals in galvanic sludge tested and in eluate from the TCLP test

Parameter	Concentration in raw sludge	Concentration in eluate from the TCLP test	Normative value acc. to the TCLP procedure
	[mg/kg]	[mg/dm^3]	[mg/dm^3]
Chromium (Cr)	115,334	140	5
Copper (Cu)	99,228	770	–
Zinc (Zn)	79,374	944	–
Nickel (Ni)	6,056	16.6	–

2.2. Fly ashes

Solid fuels are among the most commonly used source of energy in Poland. Over 60% of power in energetic system come from combustion of pit coal. Usage of solid fuels leads to generation of combustion products in solid form (ashes and slags). The amount of hearth waste is closely connected with the quality and caloricity of coal, as well as its ash content. Annually, about 20 mln tons of energetic waste is generated, of which as much as 20% is deposited in landfills [24].

Fly ashes applied in our research as components of solidifying/binding mixtures came from electrofilter of the Wrocław heat and power generating plant, combusting pit coal (Tab. 2). Their hydration was 0.45% H_2O at an average. Pollutants leaching test showed that none of indicators established in the TCLP standard was exceeded. The pH value of the eluate obtained was 4.61.

Table 2

Concentrations of metals in fly ashes and in eluate from the TCLP test

Parameter	Concentration in raw sludge	Concentration in eluate from the TCLP test	Normative value acc. to the TCLP procedure
	[mg/kg]	[mg/dm^3]	[mg/dm^3]
Chromium (Cr)	103.83	0.20	5
Copper (Cu)	197.68	1.97	–
Zinc (Zn)	375.20	3.69	–
Nickel (Ni)	155.75	0.87	–

2.3. Portland cement

The main binding agent applied in solidifying/binding mixtures was Portland cement CEM I 32,5 R, commonly used in construction industry, among others for ground stabilization and road underbuildings, as well as for cement and cement-lime mortars (for brickworks and plasters). This material is easily available on the market and realatively cheap, and these features can be directly related to costs of waste solidification technology.

Table 3

Concentrations of metals in Portland cement and in eluate from the TCLP test

Parameter	Concentration in raw sludge	Concentration in eluate from the TCLP test	Normative value acc. to the TCLP procedure
	[mg/kg]	[mg/dm^3]	[mg/dm^3]
Chromium (Cr)	39.42	0.15	5
Copper (Cu)	22.82	0.02	–
Zinc (Zn)	107.88	0.01	–
Nickel (Ni)	838.17	2.39	–

Table 3 presents analysis of composition of cement used. The pH value of eluate obtained from extraction TCLP method was 11.99; concentrations of evaluated metals were quite low and did not exceed acceptable values [17].

Hydration level of used cement was 1.58%, whereas the content of silica was 25.79% of entire mass.

2.4. Other materials

In research on stabilization/solidification of galvanic sludge mortar sand of type I was used (utilized as an aggregate improving the silicatization process); it was also a typical material, commonly available at the market [25].

Hydrated lime used as a component of one of solidifying/binding mixtures was a typical construcion material, up to the standard PN-EN 459-1:2003 [26]. Application of lime as a component of solidifying mixture was aimed at enforced activation of pozzolanic agents contained in fly ashes.

2.5. Methodology of research

Two solidifying/binding mixtures were used in presented experiment of solidifying galvanic sludge:

- Mixture I – B1: (Portland cement, hydrated lime, mortar sand, fly ashes),
- Mixture II – B2: (Portland cement, mortar sand, fly ashes).

To mixtures described above galvanic sludge (GS) was dosed in proportion B/GS = 1:3 and 1:5. All components were mixed together in a special reactor Tecnotest B205/X5 until uniform consistency was achieved, then water was added and entire mixture was mixed for about 180 s. In the next stage the obtained mass was poured into cylindrical steel forms of a diameter of 80 mm and height 80 mm and then thickened on a vibration table for 300 s.

Samples obtained after 3 days of hardening were taken out of forms and left for next 25 days for maturation in temperature 23°C and humidity of 60%. On the 28th day the effectivity of stabilization/solidification process was evaluated on the base of mechanical compressive strength and analysis of eluates from pollutants leaching test according to the standards of the TCLP procedure.

3. Analysis of results

3.1. Measurements of mechanical axial compression strength

Figure 1 presents experimental results of measuring axial compression strength on the 28th day of hardening. In each case 3 identical samples were examined, and the presented results are average values from measurements. In accordance with the requirements determined by the American Environmental Protection Agency (U.S. EPA), that have to be fulfilled by solidified waste, the minimum compression strength is 0.345 MPa [1, 2, 15].

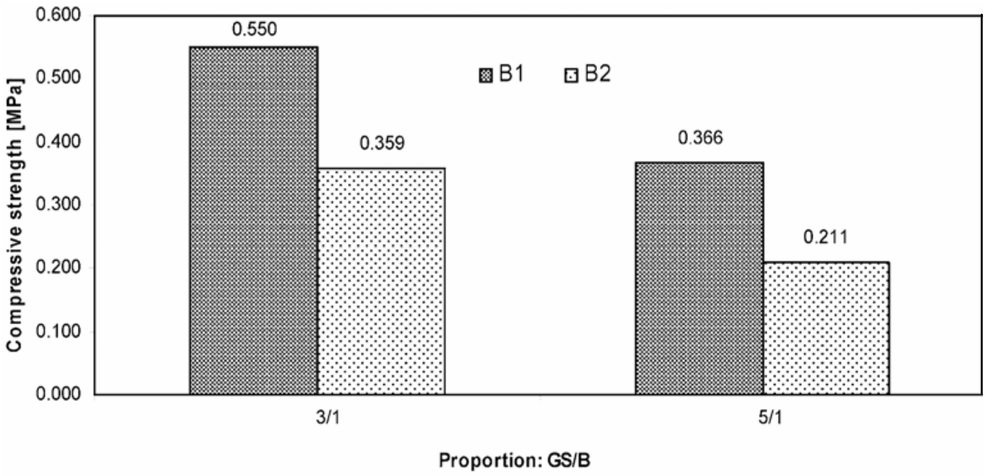

Fig. 1. Results of compression strength test on solidified samples of waste

Rys. 1. Wytrzymałość mechaniczna na ściskanie zestalonych prób odpadów

Monolithic structures in which the solidifying/binding mixture based on Portland cement, hydrated lime, sand and fly ash (B1) was applied had significantly higher compression strength compared with samples solidified with a mixture without addition of lime (B2). All samples solidified with B1 mixture met requirements defined by U.S. EPA. Addition of hydrated lime activated pozzolanic properties of fly ashes, what produced a beneficial effect on mechanical properties of the products obtained. The sample of proportion B/GS = 1:3 – GS/B1 (3) had compression strength at the level of 0.550 MPa, and in the monolith with the proportion B/GS = 1:5 – GS/B1 (5) it was lowered by 33.5% (0.366 MPa). Samples solidified with B in which hydrated lime was replaced with double amount of mortar sand revealed significantly worse mechanical properties. Compression axial strength for the sample having the composition of B/GS = 1:3 – GS/B2 (3) was 0.359 MPa, whereas the monolith of proportion B/GS = 1:5 – GS/B2 (5) had a mechanical strength of only 0.211 MPa – and did not met the requirement of minimum compression strength defined by U.S. EPA.

3.2. Test for solubility of pollutants contained in solidified waste

The second criterium for evaluating effectivity of the process of stabilizing/solidifying galvanic sludges was the effectivity of immobilizing pollutants contained in waste. Monolithic structures obtained was crumbled to a granulation below 1 cm and leached with solution of 2.88 pH, according to the TCLP procedure [17, 23]. Results of chemical analysis of concentrations of selected pollutants in eluates are presented in Tab. 4 and on Fig. 2.

Table 4

Results of analysis of concentrations of observed pollutants indicators in eluates from tests according to the TCLP procedure

Sample	GS/B1 (3)	GS/B2 (3)	GS/B1 (5)	GS/B2 (5)
Parameter	[mg/dm^3]	[mg/dm^3]	[mg/dm^3]	[mg/dm^3]
Chromium (Cr)	20.5	2.71	16.8	9.7
Copper (Cu)	67.2	32.8	175	100.6
Zinc (Zn)	149.6	227.5	249	365.9
Nickel (Ni)	3.14	2.42	2.4	3.57
pH	4.92	5.11	4.45	4.66

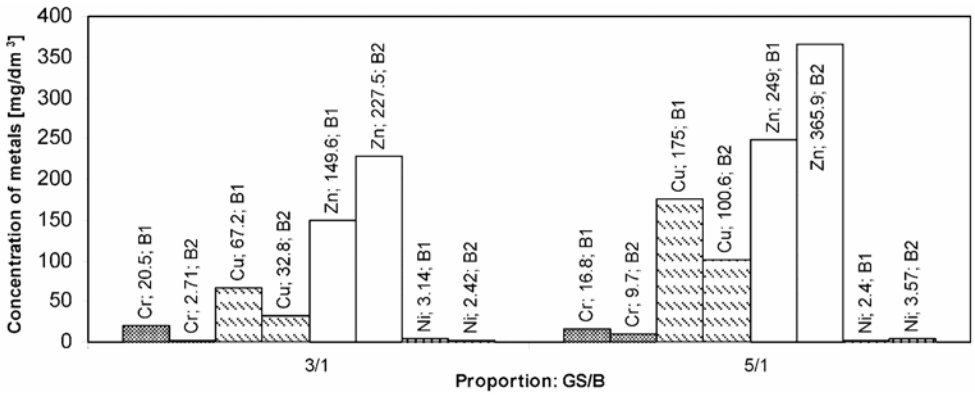

Fig. 2. Concentrations of selected pollutants indicators in eluates after TCLP test

Rys. 2. Stężenia wybranych wskaźników zanieczyszczeń w eluatach po przeprowadzeniu testu TCLP

Values of pH in solutions after 18 hours of extraction increased from 2.88 to 4.92 and 4.45 in samples GS/B1 (3) and GS/B1 (5) as well as to 5.11 and 4.66 in samples GS/B2 (3) and GS/B2 (5). It was observed that concentration of Cr and Ni in leachates was significantly lower than concentrations of Cu and Zn. Emissions of particular metals from monoliths were determined by the concentration of given indicator in galvanic sludge, as well as solubilities of these metals. The difference between obtained pH values of eluates and such pH value, at which chromium hydroxide is hardly soluble (about 7.5), was smaller than in case of zinc (its hydroxide is hardly soluble at pH 9.5), what was confirmed by other results obtained [5]. Solidifying mixture B2 showed better ability for immobilizing Cr, Cu and Ni, unfortunately it was less effective in case of Zn. However, this indicator is not standarized in the TCLP procedure. Performed test for pollutants leaching showed that the concentration of Cr standarized by the U.S. EPA (5 mg/dm^3) was not exceeded only in sample GS/B2 (3).

4. Conclusions

It was confirmed that application of hydrated lime may have a beneficial effect on mechanical properties of the product. Samples of solidified waste, in which a solidifying/ /binding mixture based on cement, lime, sand and fly ashes (B1) was used, had greater axial compression strength than samples solidified with B2 mixture. Both samples GS/B1 (3) and GS/B1 (5) met standards established by U.S. EPA in relation to the minimum axial compression strength (0.345 MPa). However, this mixture turned out to be ineffective from the point of view of pollutants immobilization. None of the samples that were solidified with B1 mixture met requirements with reference to acceptable concentration of chromium in eluate from the TCLP test (5 mg/dm^3) [17].

The only sample that met the chemical criterium and criterium of minimum strength after 25 days od maturation was the sample GS/B2 (3), that had the axial compression strength at the level of 0.359 MPa and concentration of chromium in eluate amounting to 2.71 mg/dm^3.

References

[1] Anderson W., *Innovative site remediation technology – stabilization/solidificaton*, American Academy of Environmental Engineers, 1994.

[2] Sellers K., *Fundamentals of hazardous waste site remediation*, Lewis Publisher, 1999.

[3] Batchelor B., *Overview of waste stabilization with cement*, Waste Management 26, 2006, 689-698.

[4] Woodard & Curran, Inc., *Industrial Waste Treatment Handbook*, Second Edition, Elselvier, USA, 2006.

[5] Asavapisit S., Naksrichum S., Harnwajanawong N., *Strength, lechability and microstructure characteristics of cement-based solidified plating sludge*, Cement and Concrete Research 35, 2005, 1042-1049.

[6] Corner J.R., *Chemical Fixation and Solidification of Hazardous Waste*, Van Nostrand Reinhold, New York 1990.

[7] Spence R.D., Shi C., *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, CRC PRESS, 2005.

[8] Caldwell R.J., Stegemann J.A., Shi C., *Effect of curring on field – solidified waste properties*, Part 1: *Physical properties*, Waste Management & Research 17, 1999, 37-43.

[9] Caldwell R.J., Stegemann J.A., Shi C., *Effect of curring on field – solidified waste properties*, Part 2: chemical properties, Waste Management & Research 17, 1999, 44-49.

[10] Pichtel, *Waste Management Practices, Municipal, Hazardous, and Industrial*, Taylor & Francis Group, CRC PRESS, USA 2005.

[11] Banaszkiewicz K., Marcinkowski T., *Studies on solidification of wastes from metal coating*, Polish Journal of Chemical Technology, 9, 3, 2007, 51-55.

[12] Shi C., Fernández-Jiménez A., *Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements*, Journal of Hazardous Materials B137, 2006, 1656-1663.

[13] Hester R.E., Harrison R.M., *Issues in Environmental Science and Technology 7, Contaminated Land and its Reclamation*, Royal Society of Chemistry, Cambridge, 1997.

[14] Ojowan M.I., Lee W.E., *An Introduction to Nuclear Waste Immobilisation*, Elsevier Ltd., UK 2005.

[15] Hills C.D., Pollard S.J.T., *Influence of Interferences effect on the mechanical, microstructural and fixation characteristic of cement-solidified hazardous waste forms*, Journal of Hazardous Materials, 52, 1997, 171-191.

[16] Rozporządzenie Ministra Gospodarki i Pracy z dnia 7 września 2005 r. w sprawie kryteriów oraz procedur dopuszczania odpadów do składowania na składowisku odpadów danego typu, Dz. U. Nr 186, poz. 1553, 2005.

[17] U.S. EPA, Toxicity Characteristic Leaching Procedure, Federal Register, Vol. 55, No. 61, Mar., 11798-11877, 1990.

[18] Resource Conservation and Recovery Act, 42; 3001; 6921, 1984.

[19] Code of Federal Regulation, Protection of the Environment, 40 Part 261, Office of the Federal Register, 1992.

[20] Kurdowski W., *Chemia cementu*, Wydawnictwo Naukowe PWN, Warszawa 1991.

[21] Rozporządzenie Ministra Środowiska z dnia 27 września 2001 r. w sprawie katalogu odpadów, Dz. U. Nr 112, poz. 1206, 2001.

[22] Magalhães M.J., Silva E.J., Castro P.F., Labrincha A.J., *Phisical and chemical characterisation of metal finishing industrial wastes*, Journal of Environmental Management 72, 2005, 157-166.

[23] Stefanowicz T., Napieralska-Zagoda S., Osińska M., Szwankowski S., *Test wymywalności zanieczyszczeń jako kryterium oceny szkodliwości składowych odpadów przemysłowych*, Archiwum Ochrony Środowiska, Poznań 1994, 177-194.

[24] GUS, Ochrona środowiska 2005, Warszawa 2005.

[25] Praca zbiorowa, *Budownictwo ogólne, materiały i wyroby budowlane*, t, 1, Wydawnictwo Arkady, Warszawa 2005.

[26] PN-EN 459-1:2003 Wapno budowlane. Część 1: Definicje, wymagania i kryteria zgodności.