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STABILIZATION OF POST-GALVANIC SLUDGE USING PORTLAND CEMENT AND SILICA FUME

MAŁGORZATA OSIŃSKA[1*], AGNIESZKA ŚLOSARCZYK[2]

[1] Poznan University of Technology, Faculty of Chemical Technology, Institute of Chemistry and Technical Electrochemistry
ul. Piotrowo 3, 60-965 Poznań, Poland
[2] Poznan University of Technology, Faculty of Civil Engineering, Institute of Structural Engineering
ul. Piotrowo 3, 60-965 Poznań, Poland
*Corresponding author e-mail: malgorzata.osinska@put.poznan.pl

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Abstract: Solidification in mineral binders is one of the useful methods of neutralizing hazardous materials. In this work some waste created after neutralization of used etching baths, obtained in the process of wire galvanizing and copper plating were solidified by cement mortar with and without silica fume. The researches showed that the addition of waste to cement mortar in the amount of up to 5% is safe in respect of ecology. At such an amount of waste addition to cement, metals are permanently immobilized in a matrix. While the addition of 10% of silica fume to cement improved the strength properties of products, it had no influence on the enhancement of immobilization of metals in cement mortars.

INTRODUCTION

Solid waste and by-products obtained from industrial plants are one of the basic causes of environmental degradation. Bigger and bigger amounts of waste lead to the need of expansion of existing waste dumps and limitation of soil area. Therefore, it is essential to eliminate the results of dump storing and to find a proper way of coping with unavoidable.

Post-galvanic waste materials, containing heavy metals, are classified as hazardous substances, so they must be neutralized. The solid part of such waste consists mainly of insoluble metal hydroxides, carbonates or sulphides, which, with lowered pH, can undergo leaching and endanger the environment.

One of the popular methods of waste neutralization used on a large scale in the USA is solidification in mineral binders, especially by means of cement [2]. This way of isolating hazardous materials is interesting because of beneficial for the environment immobilization of ingredients, lowered percolation of materials, and reduced leaching of the stabilized substances [1, 10, 11]. This method does not require huge expenses and can be introduced in any plant which produces construction components, such as setts, pavement plates, openwork pavements and kerbs. To improve features of products applied in construction or highway engineering, various types of additives, such as pozzolans enhancing physicomechanical parameters of cement materials, can be used. Pozzolan additions, when they take part in the process of hydration of cement, are conductive to the microstructure forming and beneficially influence keeping metals in a matrix [3, 12, 14].

The waste that was put to the processes of stabilization and solidification needs some assessment with respect to its influence on environment, among others, by means of the evaluation of toxic substances leaching and physicomechanical properties of admixed cement materials. The way of immobilization of particular components can influence leaching in utilization conditions, which was confirmed by the trials of introducing mixed sludge after fluorborate leading [17], copper hydroxide [15], nickel [9, 18], or lead chromate [16] to ceramics.

In this work the influence of the addition of post-galvanic waste to cement mortar, with and without silica fume, on physicomechanical properties of received mortars was studied. Furthermore, the researchers tested, by means of leaching tests according to TVA. AS. 1991 [8] and TCLP [6] methods, whether the stabilized waste was bound firmly enough with a cement matrix so that it did not endanger the environment.

METHODS

Waste

Post-galvanic sludge from "Galmar" galvanizing plant in Poznan was used. This sludge is created in the neutralization processes of used etching baths diluted with washings, obtained from the process of zinc and copper plating of wire. The sludge was in the form of brown powder – humidity 10% and bulk density 1.24 kg/dm^3. A sample of waste was taken once in the quantity of about 10 kg, dried and homogenized by means of sieving (with sieve meshes d = 1 mm).

The waste was poured with concentrated hydrochloric acid solution as well as *aqua regia* and boiled for a few hours in order to analyze the post-galvanic sludge composition. After cooling, the solutions with the rest of suspended matter were diluted and filtered. Some analysis aimed at checking if any heavy metals and sulphates were present in the solution. Metals, the presence of which was most important and most probable because of the conducted technological processes, were determined taking into consideration their toxicity.

The main component of sludge was iron which constituted about 15% of dry weight (DW). The composition of sludge is presented in Table 1.

Table 1. Approximate percentage constitution of post-galvanic sludge

Components	Content of component in waste (in DW) [%]
Fe	14.672
Zn	2.915
Cu	1.874
Ni	1.263
SO_4^{2-}	1.152
Ca	1.000
Pb	0.253
Cr	0.199
Mn	0.094
Co	0.002
Cd	0.002
Insoluble substances	67.79

Portland cement

In order to prepare cement mortar with waste addition, ordinary Portland cement (CEM I 42.5 R, Górażdże EN 197-1) and norm sand for cement strength tests (PN EN 196-1, Certificate IMMD o. Krakow KWARCMIX Tomaszów Mazowiecki) were used. Concrete additive containing micro-silica SikaFume®HR (Poland Sika Company) with the bulk density of 0.65 ± 0.1 kg/dm^3 was introduced to some part of prisms.

Preparation of specimens

The cement mortar was made of 450 g of cement, 1350 g of sand, 225 cm^3 of water and post-galvanic sludge added in the amounts of 2.5, 5 and 10%. A batch of prisms with 10% additive of silica fume as well as 2.5, 5 and 10% additive of waste was also prepared. Reference prisms, i.e. without sludge addition, were also made. All amounts of additives are given in mass fractions in relation to cement. The determination of particular cement samples with additives used in this work are presented in Table 2.

Table 2. Kinds of additions added to cement

Kind of additives	Amount of additives [%] and the samples' symbols							
	C	C2.5	C5	C10	CP	CP2.5	CP5	CP10
Pozzolans	0	0	0	0	10	10	10	10
Waste	0	2.5	5	10	0	2.5	5	10

40 x 40 x 160 mm prisms were prepared in order to determine the compression and flexural strength of cement mortar and for freeze-thaw resistance tests. Roller-shaped specimens with diameter of 30 mm and height 50 mm were made for leaching tests by means of TVA. AS. method. 24 hours after the preparation of the mortar, the prisms were demoulded and placed in water bath for 4 weeks. After this period they were ready for tests of physicomechanical properties and leaching tests.

Physicomechanical properties

Physicomechanical features were determined according to EN 196-1:1994 [5], EN 196-3:1994 [4] and PN-88/B-4500 [13] Norms.

Testing the setting time was conducted by means of the Vicata apparatus. The Vicata ring was filled with cement paste of norm consistence and placed under the needle of the apparatus. The movable parts were quickly released in order to make the needle sink vertically into cement paste. The period of time between the moment when cement was poured into mixer and the moment when the needle was 4 ± 1 mm distant from glass plate was treated as the beginning of cement setting.

Six cement prisms with all kinds of additives after 28 days of hardening and all prisms after freeze-thaw resistance tests underwent the compressive strength tests. Louis Schopper Staafl – a press for testing strength – was used, with the maximum acceptable load 100 kN. A prism was put into the apparatus with its lateral surface on support rollers so that its oblong axis would be perpendicular to the rollers. The load was vertically transferred to the opposite lateral surface of the prism by means of the loading roller, while pressure was gradually increased until the prism was broken. The halves of prisms broken during the flexural strength tests were analyzed in compression strength tests (on lateral surfaces 40 x 40 mm). The halves were placed with their lateral surfaces in the centre of the plate while the load was gradually increased (with pressure increase 2400 ± 200 N/s), until the prisms were destroyed.

Determining the absorbability consists in finding the mass of water that can be absorbed by a cement specimen dipped in water under standard atmospheric pressure. For the test 6 cement prisms with all kinds of additive were used. All samples were dried at 105°C, and then, after precise weighing and measuring, they were placed in a bath and poured with water at 20°C to ¼ of height. After 3 hours the next portion of water was added – to ½ of height, and after next 3 hours – to ¾ of height. After 24 hours the samples were completely poured with water in order to have the upper surfaces of the prisms 2 cm under the water level. When 24 hours passed the samples were taken out of the water, dried, and weighed. Then, the prisms were again immersed in water and weighed after 24 hours. Weighing was repeated till the mass was steady.

After soaking 4 prisms their freeze – thaw resistance was tested (while the tests were conducted, the two remaining prisms were conditioned in water as reference prisms). After taking out of water and drying the prisms were put in to a freezer at minus 20 ± 2°C, where they were kept for 4 hours, then taken out and placed in water for the next 4 hours in order to defrost them. 25 cycles of freezing and thawing were conducted.

Leaching tests

The tests of leaching hazardous substances from waste were conducted by means of Swiss method TVA. AS. 1991. A test according to this method was conducted in two 24-hour leaching phases with water saturated with carbon dioxide in water mass proportion to a prism 10:1, while the tested material was not crumbled. Each phase of leaching was conducted with a fresh portion of water saturated with CO_2. After filtering, hazardous substances in the leachates were analyzed. Average normalized concentration was counted according a formula:

$$\left[\mathrm{mg/dm^3}\right] = \frac{(C_1 + C_2)M_1}{2M_2},$$

where:

$(C_1 + C_2)$ – sum of measured concentrations of eluats after 24 and 48 hours in [mg/dm³],
M_1 – mass of a sample [g],
M_2 – dry mass of a sample after leaching [g].

For leaching tests by means of TCLP method, crumbled samples, separated with a sieve (with sieve meshes of 10 mm) were used. After the introductory test, for the right leaching, solution with pH = 2.88 ± 0.5 was used. After leaching and filtering the solution was analyzed by means of absorptive atomic spectrometry method to see whether any metals were present.

Analytical methods

The determination of the concentration of metals was done according to analytical curves with appropriate lengths of waves using atomic absorption spectroscopy (AAS) Carl Zeiss Jena.

RESULTS AND DISCUSSION

Tests of physicomechanical parameters

The tests of the initial setting time showed that in the case of cement with additives more water was necessary in order to get the norm consistence than in the case of ordinary cement. The initial setting time was various depending on the kind of cement additive (Fig. 1). Cement with the waste addition had longer setting time and the bigger amount of additive was, the longer the setting time was (by 42 minutes for 10% of addition in comparison to the reference sample).

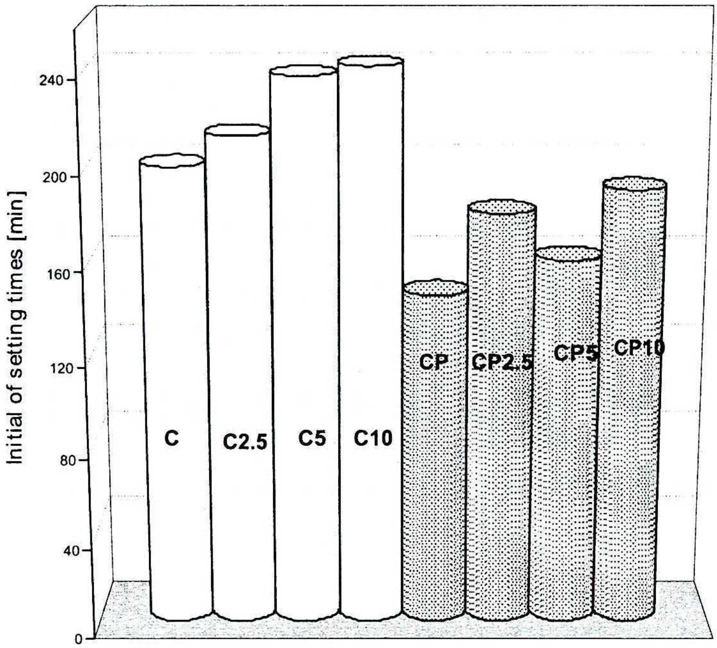

Fig. 1. Setting times of prisms with various sludge additions

The setting time in the case of cement with silica fume addition started 55 minutes earlier than in the case of ordinary cement. Additions of waste to cement with pozzolans retarded this moment and made it close to setting times reached for cement without pozzolans.

The results of absorbability, as well as compression and flexural strength determination are presented in Table 3. The highest absorbability was noted for prisms made of cement without additives (5.22%). The absorbability of remaining samples was between 2.19 and 4.14%.

The compression strength was highest in the case of cement with 10% pozzolan addition (56.1 MPa) – it is resistance that classifies it a class higher than cement without additive, which belongs to II class – 42.5 MPa. Waste additions lowered the compression strength, but did not lower the class of cement. The lowest compression strength was showed in prisms with the highest sludge addition to cement – 10% waste addition to cement without pozzolans caused lowering of the compression strength by about 24% in

Table 3. Results of absorbability tests and tests of compression and flexural strength of cement mortars with various waste additions

Sample	Absorbability [%]	Flexural strength [MPa]	Compression strength [MPa]
C	5.22	9.3	50.4
CP	3.07	9.8	56.1
C2.5	4.14	8.7	38.6
C5	3.33	8.7	39.8
C10	4.51	8.9	38.3
CP2.5	2.19	9.9	42.2
CP5	2.34	9.2	41.9
CP10	3.93	9.1	35.8

comparison to cement without waste addition. Also 10% waste addition to cement with pozzolan addition significantly lowered the strength – to 35.8 MPa. This parameter was reduced by 36% in comparison to the strength of cement-pozzolan samples and by almost 29% in comparison to cement without additives. Anyway, all prisms with waste addition to cement and cement with pozzolans reached compression strength classifying them to 32.5 MPa class.

After 25 cycles of freezing and thawing there were no chips or cracks on the prisms – all samples were resistant to low temperatures. The change of prism mass after these processes was slight. In order to check the influence of freezing and thawing on the strength of samples, strength tests after the conducted cycles of freezing/thawing were performed (Fig. 2).

Tests showed that all prisms conditioned in water had compression strength higher than prisms after 28 days of hardening. The processes of freezing and thawing had some impact on compression strength increase (in comparison to strength after 4 weeks of

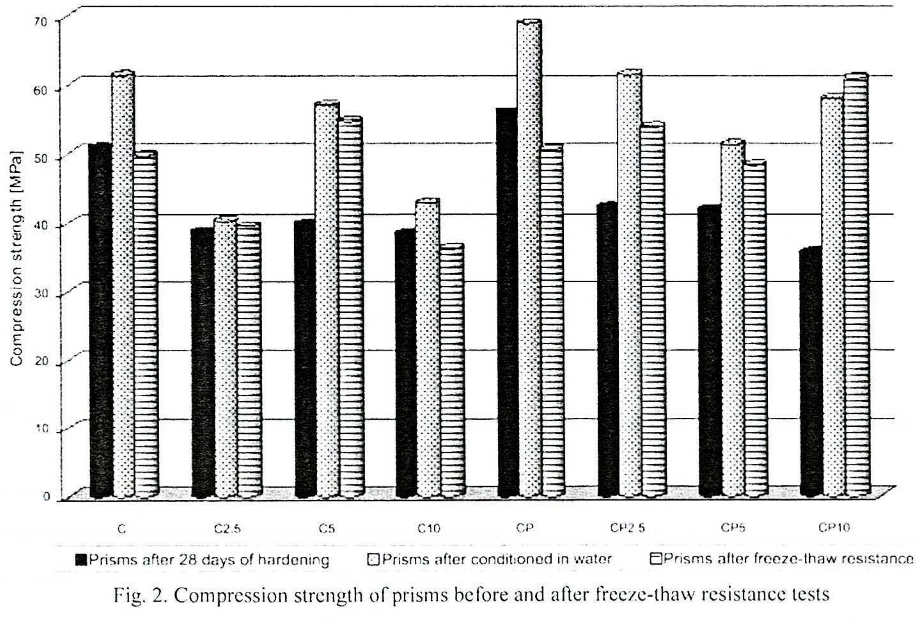

Fig. 2. Compression strength of prisms before and after freeze-thaw resistance tests

hardening) for all prisms with waste addition, apart from the prism with the highest, 10% waste addition to cement mortar without pozzolans.

For all prisms compression strength in relation to reference prisms, i.e. conditioned in water during freeze-thaw resistance tests, was lowered. The biggest strength drop after freeze-thaw resistance tests (in relation to reference prisms) was noted for cement with 10% of waste addition.

Leaching tests

In the respect of the environmental protection it was important to check if the solidified waste in cement mortar is safe for the environment, and whether heavy metals are bound with cement firmly enough and, for example, atmospheric falls will not lead to gradual leaching of metals to the environment. Metal concentrations after leaching of cement and cement-pozzolan prisms by means of TVA. AS. 1991 method are presented in Table 4.

Table 4. Concentration of contaminants in eluats after leaching by means of TVA. AS. method

Sample	Average normalized concentration [mg/dm^3]			
	Cu	Mn	Fe	Zn
C	0.29	ND	0.67	ND
CP	0.21	ND	ND	ND
C2.5	ND	ND	ND	ND
C5	ND	ND	ND	0.30
C10	ND	ND	ND	0.0
CP2.5	0.50	ND	ND	0.37
CP5	0.31	ND	ND	0.62
CP10	1.12	0.08	ND	0.88

ND – not detected

In eluates from leaching rollers with additions of waste to cement mortar, only zinc was present, but in concentration not exceeding the acceptable value. For rollers made with addition of waste to cement with pozzolans, the acceptable concentration of copper ions in leachates for the sample with the highest amount of additive was exceeded. The concentrations of the remaining metals present in the solution did not exceed the acceptable norms. Eluates from leaching tests by means of TCLP method did not contain cobalt, cadmium, or lead. Chromium was present in leachates only at the highest – 10% addition of waste to cement without pozzolans (Tab. 5). However, highest concentrations of iron and zinc in leachates were detected, but the acceptable concentration was not exceeded [6].

Table 5. Concentration of contaminants in eluats after leaching by means of TCLP method

Type of contaminant	Concentration of contaminants in eluats [mg/dm^3]							
	C	CP	C2.5	C5	C10	CP2.5	CP5	CP10
Ni	0	0	0.28	0.28	0.57	0	0	0.22
Fe	20.67	16.20	16.76	13.97	16.76	17.32	9.50	18.43
Cu	0.81	0	0.81	1.41	2.42	0.40	1.61	2.42
Mn	0.15	0.15	0.15	0.31	0.46	0.15	0.31	0.31
Zn	1.30	0.87	2.83	3.91	6.09	2.39	5.43	6.09
Cr	0	0	0	0	0.66	0	0	0

CONCLUSION

The introduction of silica fume addition to cement mortar improved the physicomechanical parameters of cement.

Tests showed that post-galvanic sludge additive, created during the neutralization of used etching baths and diluted with washings from the processes of zinc and copper plating of wire, to cement mortar with and without pozzolans decreased mechanical parameters of mortars, however not to such an extent as to disqualify the received products.

10% of waste addition to cement mortar with pozzolans was not safe from the environmental point of view – copper was not firmly bound in the matrix material. With such an addition of waste in the leachate (from the leaching tests by means of TVA. AS. method), the acceptable concentration of copper was exceeded. In eluates from leaching tests by means of TCLP method the concentration of tested metals was not exceeded. It seems that the stabilization of this kind of waste in cement with pozzolan additive is not safe ecologically. In this case expected effect of the improvement of the immobilization of metals in the cement matrix was not reached. It is possible that some waste components retard cement hydration, which was also observed in the case of the solidification of waste containing Fe, Cu, Ni, Zn in cement with fly ash additions [7].

The tested kind of waste can be safely used as an addition to cement mortar in the amount of 5%. Such an amount of waste in cement does not disqualify received products with respect to tested physicomechanical parameters and is ecologically safe.

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STABILIZACJA SZLAMÓW POGALWANICZNYCH Z UŻYCIEM CEMENTU I PYŁÓW KRZEMIONKOWYCH

Odpady pogalwaniczne zaliczane są do odpadów niebezpiecznych, dlatego muszą być unieszkodliwiane. Jedną z najprostszych metod unieszkodliwiania jest zestalanie w spoiwach mineralnych. W niniejszej pracy przeprowadzono próby zestalania w zaprawie cementowej oraz w zaprawie cementowej z dodatkiem pyłów krzemionkowych odpadu powstałego po neutralizacji zużytych kąpieli do trawienia, rozcieńczonych wodami popłucznymi, pochodzącymi z procesu cynkowania oraz miedziowania drutu. Badania wykazały, że dodatek odpadów w ilości do 5% jest bezpieczny pod względem ekologicznym. Przy takiej ilości dodatku odpadów do cementu następuje nieznaczne obniżenie parametrów fizykomechanicznych, a metale są trwale immobilizowane w matrycy. Dodatek pyłów krzemionkowych w ilości 10% do cementu poprawiał cechy wytrzymałościowe wyrobów, ale wprowadzenie odpadów obniżało te parametry.