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## EVALUATION OF USEFULNESS OF HYDRATED LIME IN PROCESS OF STABILIZATION OF SLUDGES FROM ELECTROCOATING

The effect of hydrated lime on the course of neutralization of sludges from electrocoating (GS) is determined. For our experiment two solidifying-binding mixtures (B) were prepared: B1 and B2. The mixture B1 was the combination of Portland cement, hydrated lime, mortar sand and fly ashes from hard coal burning used in various proportions. From the matrix of the second mixture, B2, hydrated lime was removed; instead a double dose of mortar sand was applied. In both mixtures, the content of Portland cement CEM I 32.5R did not exceed 40% of their entire mass. In the stabilizers obtained, galvanic sludges constituted 75 to 87.5% of their mass. The efficiency of the process of toxic pollutants immobilization was assessed after 28 days of sludge maturation. Monolithic structures of stabilized sludge were subjected to the tests of mechanical axial compression strength and to the tests of heavy metals leaching, according to the standard PN-EN 12457-4: 2006 [1].

### 1. INTRODUCTION

Mineral binding construction materials, such as cement, lime or fly ashes, can be used for treating industrial wastes of various kinds, both organic and mineral [2], [3]. It is possible to stabilize/solidify (S/S) waste containing toxic metals [4], [5], but it is just easy to carry out the S/S process of waste containing alkanes and polycyclic aromatic compounds from petroleum refinery [6] or of typically organic waste, e.g., from tannery [7]. Stabilization takes place when pollutants, especially organic, are being transformed from liquid (mobile) phase to solid (immobile) one as a result of such reactions as precipitation, sorption or exchange (substitution) [8]. Organic pollutants, e.g., proteins or lipids, are also stabilized due to hydrolysis and saponification (fats or oils) or denaturation (proteins) [9].

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Reaction course, in the case of both mineral and organic wastes, depends to a large extent on pH, therefore the presence of components affecting pH value can be of the vital importance for the course of stabilization [8], [10]. This especially concerns alkaline reaction caused by presence of cement, lime or fly ashes. Addition of lime to cement or fly ashes can improve – or quite the opposite – worsen the conditions of binding pollutants contained in waste being treated. The aim of this research was to evaluate the usefulness of  $\text{Ca}(\text{OH})_2$  in the process of stabilizing/solidifying waste from electrocoating. The treatment efficiency is a result of interactions between stabilizing/solidifying factors and the components of the waste being treated. Neutralization of waste with the use of stabilization/solidification techniques combines two interconnected processes that take place at the same time and generate product whose capability for affecting environment is limited [11]. This concerns both the option of final removal of waste (deposition in the landfill) and its re-utilization (recycling). Stabilization process consists in transforming pollutants to the forms that are less toxic (less mobile), whereas due to solidification the stabilized waste additionally becomes the product of improved physical properties (high mechanical axial strength) which enables their safe and convenient transport to the places of their utilization or deposition [12].

The subject of the present paper was, among others, to evaluate the process of waste stabilization on the basis of pollutants-leaching test and mechanical strength test.

## 2. MATERIALS

### 2.1. SLUDGE FROM ELECTROPLATING

Sludge subjected to neutralization came from one of the Lower Silesian electroplating plants. It was semi-solid and dark-green in colour. The main processes taking place in the plant were galvanic chromium and copper coating as well as bethanizing, which was confirmed by the analysis of particular metal concentration in sludge (table 1). In untreated material, the content of chromium, copper and zinc was very high and amounted to 115334 mg/kg<sub>d.m.</sub>, 99228 mg/kg<sub>d.m.</sub>, 79374 mg/kg<sub>d.m.</sub>, respectively. Due to high concentration of toxic metals, galvanic sludges are classified in Polish legislation as hazardous [13]. Hydration of stabilized sludge was on an average 66.34%. Pollutant leaching test, performed in accordance with the standard PN-EN 12457-4, showed that three of the four metals exceeded permissible values of concentration [14], [15], i.e., the concentration of copper in the eluates obtained was over twofold, of zinc over 81-fold and of nickel over 40-fold higher (table 1). pH of the extract was 5.11 and it did not meet the minimum allowable pH 6, determined by the Directive of Economy Min-

istry [15]. The minimum pH that does not comply with the requirements and normatively acceptable values of toxic metals' concentration does not allow the sludge to be deposited in its primary form [14], [15].

Table 1

The concentrations of selected pollutants' indicators in raw sludge and in eluate from the test performed according to the standard PN-EN 12457-4: 2006 [1]

| Indicator | Unit                     | Boundary value* | Concentration in raw sludge | Concentration in eluate from the test performed according to the standard PN-EN 12457-4: 2006 |
|-----------|--------------------------|-----------------|-----------------------------|---|
| Chromium  | [mg/kg <sub>d.m.</sub> ] | 10              | 115334                      | 0.41  |
| Copper    | [mg/kg <sub>d.m.</sub> ] | 50              | 99228                       | 118   |
| Zinc      | [mg/kg <sub>d.m.</sub> ] | 50              | 79374                       | 4094  |
| Nickel    | [mg/kg <sub>d.m.</sub> ] | 10              | 6056                        | 41.60   |
| pH        | –                        | min. 6          | –                           | 5.11  |

\* European Community Council Decision, 2003 [14]; Dziennik Ustaw, 2005 [15].

## 2.2. FLY ASHES

Chemical and mineralogical composition of fly ashes depends mainly on the chemical composition of coal being burnt, the type of furnace and the conditions of combustion and can be significantly diverse. We should also take into account the heavy metals' content which quite often limits the possibilities of fly ashes utilization [16]. Fly ashes used as a component of solidifying–binding mixture left after combustion of hard coal in one of the Lower Silesian heat and power generating plants. Their chemical composition, taking account of the selected toxic metal content (Cr, Cu, Zn and Ni), is presented in table 2. The hydration of the ashes tested was very low and amounted on an average to 0.45%.

Table 2

The concentration of selected pollutants' indicators in fly ashes and in eluates from the test performed in accordance with the standard PN-EN 12457-4: 2006 [1]

| Indicator | Unit                     | Boundary value* | Concentration in raw sludge | Concentration in eluate from the test performed according to the standard PN-EN 12457-4: 2006 |
|-----------|--------------------------|-----------------|-----------------------------|---|
| Chromium  | [mg/kg <sub>d.m.</sub> ] | 10              | 103.83                      | 2.80  |
| Copper    | [mg/kg <sub>d.m.</sub> ] | 50              | 197.68                      | <0.001  |
| Zinc      | [mg/kg <sub>d.m.</sub> ] | 50              | 375.20                      | 1.70  |
| Nickel    | [mg/kg <sub>d.m.</sub> ] | 10              | 155.75                      | 3.20  |
| pH        | –                        | min. 6          | –                           | 11.40   |

\* European Community Council Decision, 2003 [14]; Dziennik Ustaw, 2005 [15].

### 2.3. PORTLAND CEMENT

In our research, a commonly used Portland cement CEM I 32.5 R satisfies the requirements of the standard PN-EN: 197-1:2002 [17]. This material is used in construction, among others, for the production of concretes, prefabricated units, masonry mortars and plasters [18]. Table 3 presents the concentration of selected toxic metals in the cement and in the eluate obtained as a result of their extraction with distilled water, in accordance with the standard PN-EN 12457-4. pH of post-extraction liquid was 10.84; the concentration of the metals of interest was quite low and did not exceed the permissible values [14], [15].

Table 3

The concentration of selected pollutants' indicators in fly ashes and in eluates from the test performed in accordance with the standard PN-EN 12457-4: 2006 [1]

| Indicator | Unit                     | Boundary value* | Concentration in raw sludge | Concentration in eluate from the test performed according to the standard PN-EN 12457-4: 2006 |
|-----------|--------------------------|-----------------|-----------------------------|---|
| Chromium  | [mg/kg <sub>d.m.</sub> ] | 10              | 39.42                       | 2.10  |
| Copper    | [mg/kg <sub>d.m.</sub> ] | 50              | 22.82                       | 0.05  |
| Zinc      | [mg/kg <sub>d.m.</sub> ] | 50              | 107.88                      | 0.41  |
| Nickel    | [mg/kg <sub>d.m.</sub> ] | 10              | 838.17                      | 0.10  |
| pH        | –                        | min. 6          | –                           | 10.84   |

\* European Community Council Decision, 2003 [14]; Dziennik Ustaw, 2005 [15].

### 2.4. OTHER MATERIALS

The mortar sand used was a typical material, commonly employed in all kinds of constructive works, masonry mortars, plasters or underlayments.

Another cementing agent of the two solidifying-cementing mixtures was hydrated lime prepared according to Polish standard PN-EN: 459-1:2003 [19]. The aim of using lime was to activate the pozzolanic properties of fly ashes.

## 3. PREPARATION OF SAMPLES

A detailed description of raw materials used is presented in item 2 of this paper. For our research two solidifying-binding mixtures (B) were prepared, i.e., B1 and B2.

The first mixture was the combination of all the materials mentioned earlier used in various proportions, i.e., Portland cement, hydrated lime, mortar sand and fly ashes from hard coal burning. From the matrix of the second mixture (B2) hydrated lime was removed; instead a double dose of mortar sand was applied. In both mixtures, the content of Portland cement CEM I 32.5R did not exceed 40% of their entire mass.



Fig. 1. Mixer for cement mortars, Tecnotest B205/X5

To the mixtures prepared the galvanic sludges (GS) of the granulation below 4 mm were added in the proportions  $B/GS = 1/3$ ;  $1/5$  and  $1/7$ . All the reagents were mixed together for 3 minutes in cement mortar reactor, Tecnotest B205/X5. A homogeneous paste obtained was poured into forms of cylindrical shape, with the height and diameter equal to 8 cm. Then the samples were vibrated on a vibrating table for about 5 minutes and left to harden. After 3 days the samples were taken out of forms and left for the next 25 days (maturation period). In order to avoid the effect of changing conditions of environment (humidity, temperature) on the properties of stabilizers, the samples in maturation period were placed in thermostat (ST-5B60) at the temperature of  $20\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ . Qualitative examinations aimed at evaluating the effectiveness of pollutants immobilization were performed on 28-day samples.

## 4. DISCUSSION OF RESULTS

### 4.1. MECHANICAL AXIAL STRENGTH

According to the Directive of the Economy Ministry, solidified hazardous waste must have the minimum axial compression strength on the level of  $\geq 50 \text{ kN/m}^2$  [15]. The tests were performed on 3 identical samples on the 28th day of maturation and the results presented in table 4 and in figure 2 are mean values of all readings.

Table 4

| Mechanical strength of solidified waste samples in axial tension system |                      |                 |                                 |
|---|----------------------|-----------------|---------------------------------|
| Sample  | Unit                 | Boundary value* | Mechanical compression strength |
| GS/B1 (3)   | [kN/m <sup>2</sup> ] | $\geq 50$       | 550                             |
| GS/B2 (3)   | [kN/m <sup>2</sup> ] | $\geq 50$       | 359                             |
| GS/B1 (5)   | [kN/m <sup>2</sup> ] | $\geq 50$       | 366                             |
| GS/B2 (5)   | [kN/m <sup>2</sup> ] | $\geq 50$       | 211                             |
| GS/B1 (7)   | [kN/m <sup>2</sup> ] | $\geq 50$       | 269                             |
| GS/B2 (7)   | [kN/m <sup>2</sup> ] | $\geq 50$       | 178                             |

\* Dziennik Ustaw, 2005 [15].

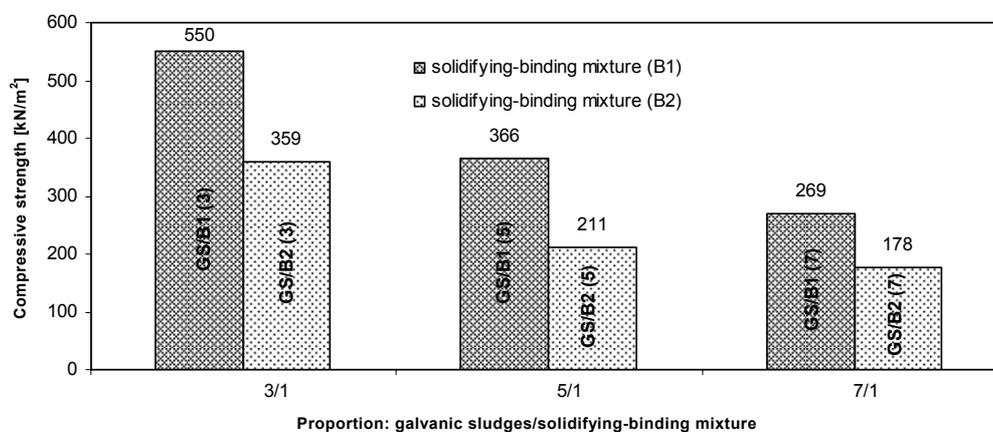


Fig. 2. Axial compression strength of the stabilizates obtained

All of the monolithic structures obtained satisfied the requirements for minimum compression strength imposed by Polish legislation. Sludge solidified with B1 (based on Portland cement, hydrated lime, fly ash and mortar sand) had significantly better mechanical properties than that solidified with B2 (without addition of lime). The

monolithic structure GS/B1 (3) with the proportion of GS/B = 3/1 had the strength of 550 kN/m<sup>2</sup>, which is 11 times higher than the permissible value. The mechanical strength of the sample with identical proportion of GS/B solidified with GS/B2 (2) mixture (without addition of lime) was only 359 kN/m<sup>2</sup>.

#### 4.2. POLLUTANTS LEACHING FROM STABILIZERS

The effectivity of pollutants immobilization was evaluated based on the analysis of heavy metal content in the eluates from pollutants leaching test, performed according to the standard PN-EN 12457-4:2006 on the 28th day of maturation. The results of the analysis carried out after 24 hours of leaching are presented in table 5 and in figures 3 and 4. pH of all the post-extraction liquids ranged from 7.66 to 10.37 and met the requirements of Polish legislation (min. 6) [15]. The analyses of the eluates for copper, zinc and nickel showed that the concentration of any of the metal was not exceeded [14], [15].

Table 5

The content of heavy metals in the eluates from pollutants leaching test performed according to the standard PN-EN 12457-4: 2006 [1]

| Indicator | Unit                     | Boundary value* | GS/B1 (3) | GS/B2 (3) | GS/B1 (5) | GS/B2 (5) | GS/B1 (7) | GS/B2 (7) |
|-----------|--------------------------|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Chromium  | [mg/kg <sub>d.m.</sub> ] | 10              | 64.00     | 19.6      | 30.30     | 6.20      | 19.60     | 5.60      |
| Copper    | [mg/kg <sub>d.m.</sub> ] | 50              | 14.40     | 7.50      | 10.10     | 7.80      | 10.50     | 6.40      |
| Zinc      | [mg/kg <sub>d.m.</sub> ] | 50              | 0.15      | 1.30      | <0.001    | 1.80      | 0.14      | 1.69      |
| Nickel    | [mg/kg <sub>d.m.</sub> ] | 10              | 2.30      | 3.80      | 2.60      | <0.001    | 3.90      | 0.10      |
| pH        | -                        | min. 6          | 10.37     | 10.08     | 9.42      | 8.93      | 8.59      | 7.66      |

\* European Community Council Decision, 2003; Dziennik Ustaw, 2005.

The only indicator whose concentration in the eluates obtained exceeded the permissible value was chromium (10 mg/kg<sub>d.m.</sub>). It was also observed that in post-extraction liquids from the samples solidified with B1 mixture based on cement, hydrated lime, ashes and sand (B1), the concentration of chromium was significantly higher. Its content in eluate from the sample with the proportion of sludge to solidifying-binding mixture = 3/1, where B2 mixture being applied, was over three times lower than that in the eluate from the sample of the same proportions, but solidified with B1 mixture. The chromium concentration in the extracts from the samples solidified with B1 mixture ranged from 19.6 mg/kg<sub>d.m.</sub> in sample GS/B1 (7) to 64.0 mg/kg<sub>d.m.</sub> in sample GS/B1 (3). This can be explained by the relationship between the solubility of each metal and pH. At pH of about 7.5 the solubility of

chromium hydroxide is low. The difference between pH value of the eluates obtained from samples solidified with B2 mixtures and pH at which chromium is poorly soluble was in all cases smaller than the same difference in the eluates from the samples solidified with the B1 mixture [20]. This also explains the reason why from the samples, where less amount of sludge being dosed, high concentration of chromium was leached. The use of larger amount of binding agent was directly connected with alkalizing the medium and an increase in the difference between pH of eluates obtained and pH at which solubility of chromium hydroxide reached its minimum (figure 3).

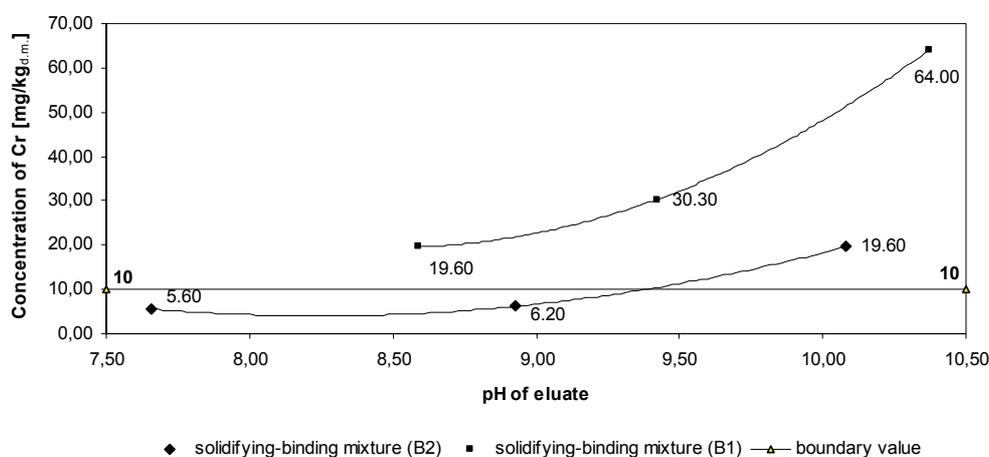


Fig. 3. The concentration of chromium in leachates from pollutants leaching test versus pH

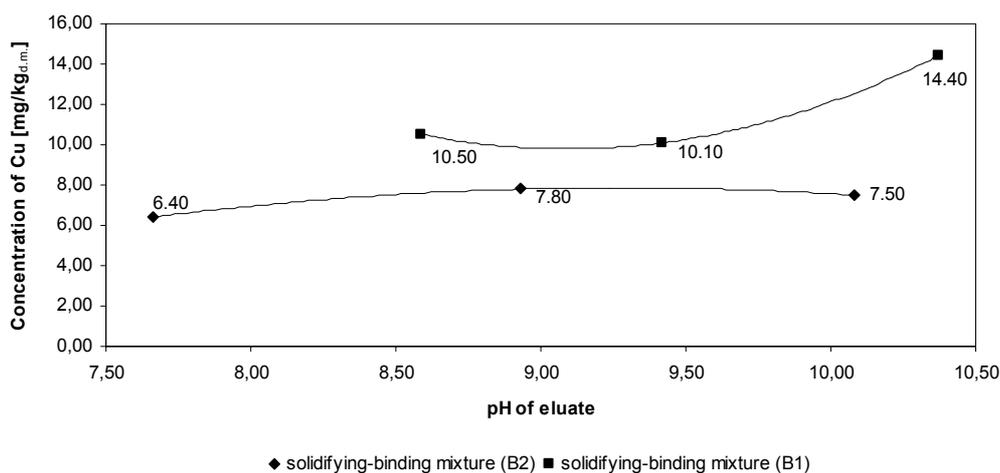


Fig. 4. The concentration of copper in leachates from pollutants leaching test versus pH

The samples GS/B2 (5) and GS/B2 (7) solidified with the mixture lacking in hydrated lime [14], [15] satisfied the requirements of Polish and European permissible concentration of toxic metals in eluates from pollutants leaching test carried out according to the standard PN-EN 12457-4:2006.

## 5. CONCLUSIONS

The results presented allow us to state that the use of hydrated lime in the process of stabilizing sludges from electroplating does not bring about any satisfactory effects. The samples solidified with B1 mixture that contained hydrated lime were characterized by significantly better mechanical properties compared with the monoliths being solidified with B2, where instead of lime a double dose of mortar sand was used. Regrettably, the improvement of the sample physical (mechanical) properties was not in a direct way tantamount to the improvement in the effectiveness of the immobilization of toxic pollutants. None of B1-based stabilizers obtained met chemical requirements determined by Polish and European Union legal acts [14], [15].

The samples GS/B2 (5) and GS/B2 (7) satisfied the criterion of minimum compression strength as well as the criterion of permissible concentration of pollutants in eluates after 28 days of maturation. In the monolith, GS/B2 (7) waste (fly ashes + sludge) constituted 90% of its mass.

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#### OCENA PRZYDATNOŚCI WAPNA HYDRATYZOWANEGO W PROCESIE STABILIZACJI OSADÓW GALWANICZNYCH

Przedstawiono wpływ wapna hydratyzowanego na przebieg procesu neutralizacji osadów galwanicznych (GS). Na potrzeby eksperymentu opracowano dwie mieszaniny zestalająco-wiążące (B): B1 i B2. Mieszanina B1 składała się z cementu portlandzkiego, wapna hydratyzowanego, piasku do zapraw budowlanych oraz popiołów lotnych ze spalania węgla kamiennego użytych w różnych proporcjach. W matrycy drugiej mieszaniny (B2) nie było wapna hydratyzowanego, lecz podwójna dawka piasku budowlanego. W obu mieszaninach zawartość cementu portlandzkiego CEM I 32.5 R nie przekraczała 40% ich masy. W otrzymanych stabilizatach osady galwaniczne stanowiły od 75 do 87.5% ich masy. Efektywność procesu immobilizacji zanieczyszczeń toksycznych w technologii stabilizacji oceniano po 28 dniach sezonowania. Uzyskane monolity ustabilizowanych osadów poddano badaniom wytrzymałości mechanicznej na ściskanie w jednoosiowym stanie naprężenia oraz testowi na wypłukiwanie metali ciężkich według normy PN-EN 12457-4: 2006 [1].