Tin recovery and solidification of sludge from mirror grinding

Barbora VACHOVÁ, Štěpán VINTER, Vratislav BEDNAŘÍK, Martina KOPOVÁ

Department of Environmental Protection Engineering, Tomas Bata University in Zlin, Faculty of Technology, Vavreckova 5669, 760 01, Zlin, Czech Republic, e-mail: vinter@utb.cz , bednarik@utb.cz

Abstract

This study aims on tin recovery and solidification of mirror-grinding sludge. To extract tin from sludge, different hydroxide solutions (0.1 – 10M) are used. The sludge is also treated using the stabilization and solidification technique using ordinary Portland cement as a binder. Samples were evaluated using x-ray fluorescence analysis, leaching tests and compressive strength in the case of solidified samples. The results showed that nearly 57 % of tin was recovered as a precipitate in case of extraction in 10M sodium hydroxide. The 50 % of ordinary Portland cement was the optimal content for the solidification of sludge. The influence of active carbon addition into solidification mixtures was also evaluated. In conclusion, the mirror-grinding sludge was suitable for tin recovery, and its solidification resulted in non-hazardous waste.

Keywords: *tin recovery, solidification, sludge, mirror grinding, x-ray fluorescence, compressive strength, active carbon*

1. Introduction

In 2019, the production of tin was 306,000 tonnes [1]. This source also indicates that at the end of 2019, tin reserves of about 15.4 million tons were calculated, which means that these reserves should be sufficient for about 50 years. However, mining is expected to be more expensive in the future, and the price of the metal will rise. For this reason, it is appropriate to consider recycling tin from wastes that contain it, even in small quantities, such as sludge from mirror grinding. Although the content of tin in some wastes is low, in tin ores, its content is even lower, ranging from 0.01 to 5%.[1]

The possibilities of tin regeneration from various materials are wide. Particular attention is paid to the recovery of tin from printed circuits in electronics, where metallic tin is used in the form of alloys for soldering. Tin can be recovered by pyrometallurgy, where the waste material is heated in a vacuum to temperatures around 400 °C, for example, studies Zhou, 2010[2] and Park, 2015[3]. Tin can also be regenerated from printed circuits using hydrometallurgical methods, in which tin is released from the waste in the form of insoluble SnO_2 [4,5]. In addition, hydrometallurgical methods possess high recovery rates, up to 100% [1–3]. Another suitable material for tin regeneration can be LCD displays, where tin is used in colour-filters and thin-film transistors in the form of iridium-tin oxides (ITO). The ITO is first regenerated from the display, for example, by dry methods such as grinding and separation [6]. The tin can then be obtained, for example, by super-critical water treatment [7] or by acid leaching [8].

Some authors stabilized and solidified industrial sludges containing amphoteric elements such as zinc, lead, and tin[9–11]. One utilization of solidified industrial waste sludge from the production of mirrors can be manufacturing building materials such as blocks or tiles [12,13]. Zinc-containing wastes are stabilized mainly by the addition of phosphates [14], and hydroxyapatite [15]. However, other binders such as fly ash, bauxite or red mud are very common in treatment, too [9,16]. Lead-containing wastes are stabilized mainly by the addition of cement [17,18] or hardened slag [19]. The toxicity of tin and its common compounds is low; therefore, tin is not among the parameters commonly observed in hazardous waste[20].

The aim of this study is to obtain tin by extraction from mirror-grinding sludge and solidify this waste using ordinary Portland cement. Similar types of wastes were treated using clay or lime with recycled glass[12,13].

2. Experimental part

2.1 Materials

The sample of waste was obtained from a factory that produces various types of glasses and mirrors. The waste is collected from the cleaning of wastewater produced during the manufacturing process. The amount of inorganic sludge is 30 tonnes annually. The preliminary analysis revealed that the amount of tin in waste was 16 – 21% in dry mass. In this study, ordinary Portland cement (OPC) was used as a binder with a specification CEM III/A 32,5 R, and it is produced by Turňa cement company (Slovak Republic). The elemental characterization of all materials was carried out using X-ray fluorescence (XRF).

2.2 Analytical methods

Dry matter content and loss on ignition were determined by heating to a constant weight at 105 or 1000 °C, respectively, in accordance with the European standard BS EN 15935:2021[21]. The elemental composition of the waste was characterized by XRF analysis using an energy dispersive ElvaX spectrometer (Elvatech, Ukraine). The samples were measured as untreated powders in special sample containers made from polypropylene with a diameter of 30 mm and a height of 20 mm.

2.3 Tin extraction procedure

The tin concentration in the leachates of untreated waste and test solids was determined using atomic absorption spectroscopy (AAS). The instrument GBC 933 AA (GBC Scientific Equipment Australia) with a graphite furnace for electrothermal atomization was used (GBC Scientific Equipment Australia), and the settings were the following: pyrolysis temperature 800 °C and atomization temperature 2400 °C. The calibration standards were prepared from a stock solution of 1 g/l in the range from 0 to 100 ug/L.

The regeneration of tin from the inorganic sludge involved the following steps:

- The amount of 10 g of wet inorganic sludge was leached in the 40 mL of solutions of potassium hydroxide (0.1 – 5M) or sodium hydroxide (5-10M) for 24 hours.
- These suspensions were then filtered (50 µm glass-fibre filter). The tin content in extracts was determined by AAS.
- Tin was precipitated from 50 ml of extracts by neutralization using 5M hydrochloric acid.
- The obtained suspensions were centrifuged at 4600 RPM for 20 minutes and washed with distilled water four times. The obtained precipitates were dried at 105 °C, and elemental composition was measured using XRF.

2.4 Solidification using ordinary Portland cement

Wet sludge and cement binder were mixed in different ratios (see **Table 1**), and no additional water was added to the mixture. In some cases, a small amount of activated carbon was added to sorb organic compounds (samples 9-12). Then the mixtures were homogenized for 10 minutes using an overhead stirrer in a plastic cup with a height of 80 and a base diameter of 70 mm. Then the mixtures were poured into cylindrical plastic moulds (30 x 50 mm). To remove air bubbles from the mixtures, the mixtures were shaken on the vibrating table for 5 minutes. The prepared samples were left at ambient conditions for 28 days without cover from day 7. After that, the compressive strength (CS) of solidified waste specimens was measured according to European standard EN 196-1[22]. As a result, 12 samples were prepared with different water to solid ratios.

Table 1: Stabilization/solidification mixtures prepared using OPC

Mixture	Binder/dry waste ratio	Water/solid ratio	Sorbent/dry waste ratio
1	15:85	1.13	-
2	20:80	1.06	-
3	25:75	0.99	-
4	30:70	0.93	-
5	40:60	0.80	-
6	45:55	0.73	-
7	50:50	0.66	-
8	60:40	0.53	-
9	50:50	0.66	0.5:50
10	50:50	0.66	1:50
11	45:55	0.73	0.5:45
12	45:55	0.73	1:45

2.5 Leaching tests

In addition, the samples were leached in distilled water according to European standards 12457-4 at the liquid to solid ratio of 10:1, using the vibration shaker at the shaking frequency of 120 rpm for 24 hours [16]. The leachates were filtered through the glass-fibre filter (paper glass microfiber type Z, ø = 50 mm, pore size 5 µm, manufacturer Papirna Pernstejn Ltd., Czech Republic) and the following parameters: tin concentration, pH, and conductivity were measured. Furthermore, the dissolved organic carbon (DOC) was measured in selected samples, which were adjusted to pH =7 using 2M or 0.2M HCl. Triplicate specimens were used at each ratio.

3. Results and discussion

3.1 Basic characterization of sludge

The basic analytical procedures were carried out to characterize essential parameters of dry sludge. The dry mass analysis determined that the solid content in the sample was 43.4 %. Furthermore, the value of a loss on ignition (LOI) of dried sludge at 1000 °C was 17 %. The XRF analysis of dry sludge showed that the main elements were tin (Sn), silicon (Si), aluminium (Al), calcium (Ca), iron (Fe), sulphur (S), and titanium (Ti), as is shown in **Figure 1**. As a result, the approximate composition of dry sludge was evaluated, which is shown in **Table 2**. The tin content expressed as SnO_2 in the dry mass of sludge was near 19%, which is much higher than the normal presence of tin in ores.

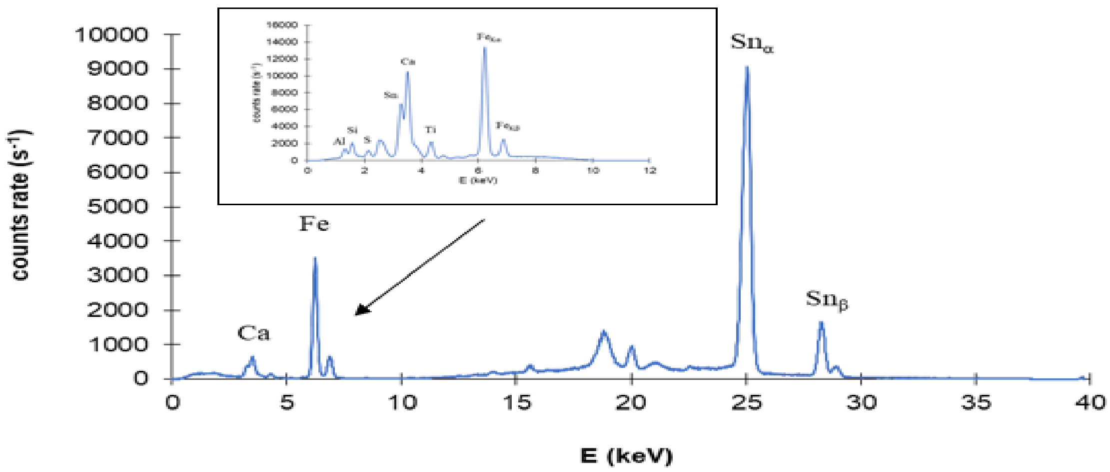

Figure 1: XRF spectrum of dried sludge

Table 2: The XRF analysis of dry sludge

Waste composition	%wt.
Al_2O_3	20.25
SiO_2	23.61
SO_3	2.99
SnO_2	18.78
CaO	7.39
TiO_2	1.37
Fe_2O_3	8.60
LOI_{1000}	17.01

3.2 Hydroxide leaching of sludge

Because tin is an amphoteric metal, it is favourable to extract it in an alkaline environment. Extraction in an acid environment would release unwanted elements such as iron. Thus, the sludge was leached in the different potassium hydroxide solutions (from 0.1 to 5M) to obtain the maximum tin amount. Potassium hydroxide was used because it is a stronger base than sodium hydroxide. The tin concentrations and weight of leached tin from the sludge are summarized in **Table 3**. From the results, it is obvious that the tin concentration was the highest in the most concentrated potassium hydroxide solution (5M). It was also confirmed by the amount of tin leached from 100 g waste, which was near 18 % in the 5M solution from 19 % as part of untreated waste. In fact, the tin concentration was the highest of all leaching mediums tested.

Table 3: Tin concentrations in the different hydroxide leachates

c_{KOH} [mol/L]	c_{Sn} [mg/L]	%wt. Sn [%]
0.1	535	0.18
0.5	1363	0.45
1	3996	1.33
2	8998	3.00
5	53511	17.84

Sodium hydroxide is less expensive than potassium hydroxide for technical use, so the leaching experiment was also repeated with sodium hydroxide. However, higher hydroxide concentrations had to be used to obtain similar results (5-10M). The colour obviously changed from brown to grey in solutions with the highest hydroxide concentrations after 24 hours of leaching, which might be caused by iron leaching. Tin compounds were separated from solutions by precipitation by adding 5M hydrochloric acid. The precipitates were dried out and weighted to estimate the recovery value of the process. Nearly 57 % of tin contained in sludge was recovered by this procedure in 10M NaOH.

To evaluate the effectiveness of hydroxide leaching, a comparison of XRF spectra between an untreated sample of waste and precipitate which emerged during leaching in 10M NaOH was carried out. The aim was to observe if the tin is leachable in this medium. As a result, a decrease in tin and aluminium counts rate was observed, as shown in **Figure 2**. It is obvious that mainly amphoteric metals such as tin and aluminium were transferred from sludge to the precipitate in the alkaline solution. Iron, sulphur, and titanium remained predominately in the sludge, which is favourable from the point of view of tin recycling.

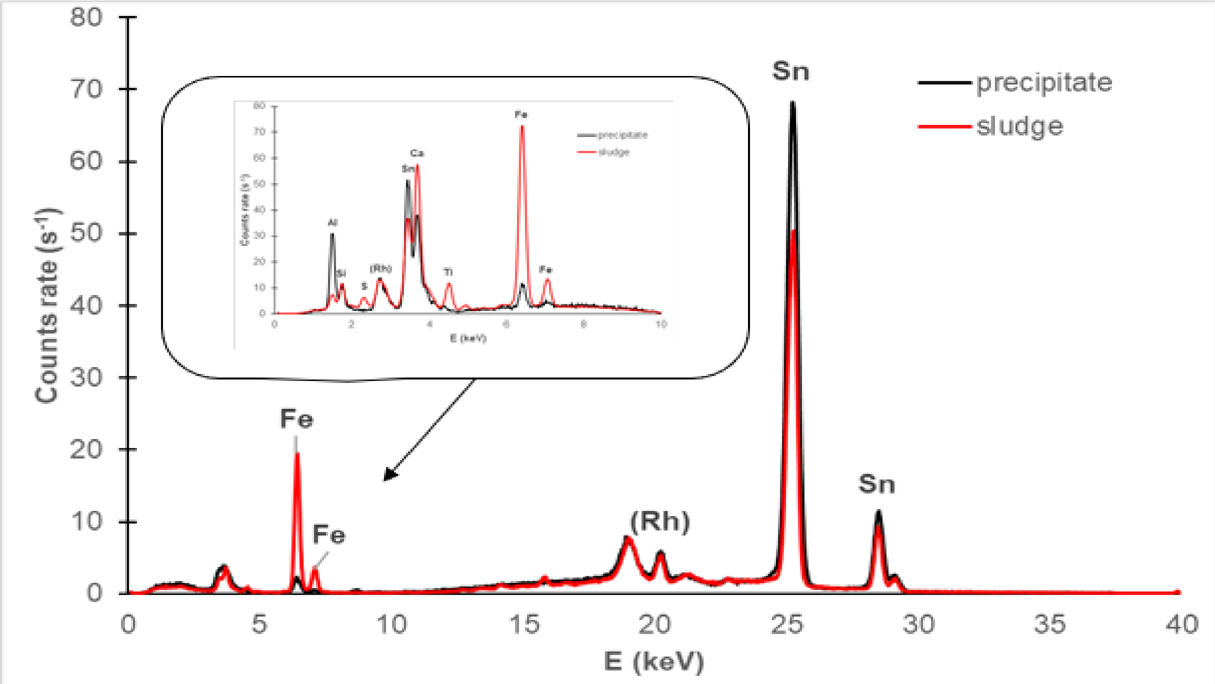

Figure 2: The normalized (rhodium peak) XRF spectra of untreated sludge and precipitate

3.3 Stabilization and solidification using ordinary Portland cement

A different approach of treating tin sludge was solidification using ordinary Portland cement. Generally, the tested solids showed grey or dark grey (the addition of active carbon) colour except for the ratio (dry sludge to waste 40:60), in which the colour was white. The CS was measurable from the ratio of 65:35. Other test solids containing a large percent of dry sludge were crushed immediately or slowly crumbled during the time. Another common characteristic of test solids was the softness, which was not required. The results of solidified sludge testing are shown in **Table 4**, which presents measured values of tin concentration, pH, and dissolved carbon content. Samples 1-5 and 8 did not solidify sufficiently, so they were not tested. The values were marginal, and, in some cases, the test solids have broken themselves without using force.

In the case when the sample contained 45 % of cement, the CS was negligible. This effect was also valid for all additions of activated carbon. The test solids which contain 50 % of cement showed low CS value, which was not the goal of our study because the cement manufacturer declares that after 28 days of curing, the minimal value of CS is 32.5 MPa according to the European norm 197-1[23]. Therefore, the CS of test solids was significantly influenced by the addition of dry sludge to the mixtures, which was characterized by strong adhesion.

As can be seen in **Table 4**, the negligible CS was measured for samples which contained 55 % of dry sludge, 11, 12, and 6. The samples with a dry mass content of 50 % showed CS around 1.9. Moreover, the addition of activated carbon to the mixture resulted in increasing the CS to 3.8 and 4.4 MPa for mixtures 9 and 10. Furthermore, leaching tests were carried out according to chapter 1.5. All leachates were pure and transparent. The tin concentration ranged from 16 µg/L to 70 µg/L with pH from 11.27 to 11.68, which is a significant decrease in tin leachability compared with untreated waste.

Table 4: The measured values of tin concentration, pH, DOC, and CS for the selected samples

Mixture	pH [1]	c_{Sn} [μg/l]	DOC [mg/l]	σ [MPa]
6	11.68	16.9	4.67	-
7	11.38	70.4	4.74	1.9
9	11.66	32.0	3.84	3.8
10	11.55	43.4	5.08	4.4
11	11.61	18.6	4.64	-
12	11.27	17.3	4.22	-
sludge	3.7	95.0	-	-

The addition of activated carbon seemed to be effective for the test solids with a content of 50 % dry mass of sludge. The tin concentration without addition was only 70 μg/l, whereas the tin concentration with addition decreased to 32 μg/L (0.5 grams) respective 43 ug/L (1 gram). The presence of activated carbon also influenced the concentration of dissolved organic carbon in the samples. A decrease was noticed. This phenomenon showed that the AC absorbed some amount of organic mass in the samples, which was observable for sample 9[24,25]. Overall, the tin concentration was marginal for the samples containing 45 % dry mass of sludge (17 μg/L), which significantly improved the binding of tin into cementitious matric. Moreover, the DOC concentrations were around 4 mg/L in the prepared samples. Due to the Czech law about waste (541/2020 Coll.) and decree 273/2021 Coll., the landfill limit for IIa leachate class is set to 80 mg/L[26,27]. This criterion was met by all prepared tested solids. This was also valid for pH limit values (≥6). In fact, no limit values for tin concentrations are presented in landfill restrictions due to the low toxicity of tin and its compounds. The cementation procedure showed that the enhanced fixation of pollutants was observed for the samples prepared with cement as a binder, which also correlated with the pH of leachates.

4. Conclusions

The results showed that the sludge contained mainly compounds of Al, S, Si, Ti, Ca, Fe, and Sn. The tin content was determined to be close to 19 % (%wt.) of the dry mass of sludge. The most effective solution for the tin extraction from sludge was 5M KOH. It is easy to separate tin as a solid compound from alkaline solution using neutralization by hydrochloric acid. The tin recovery was above 50 % of the total tin content in the sludge.

The solidification using Portland cement proved as an acceptable option. The compressive strength was only measurable for three tests of solidified solids with 50 % of Portland cement. The addition of activated carbon showed the capability of organic mass absorption and CS improvement. Tin concentrations were very low in the leachates of solidified samples (in the order of micrograms per litre). The solidified sludge can be disposed of as non-hazardous waste.

List of symbols

XRF X-ray fluorescence
DOC Dissolved organic carbon
OPC Ordinary Portland cement
CS Compressive strength
AAS Atomic absorption spectrometry
ITO iridium-tin oxides

Acknowledgement

This research was supported by an internal grant from Tomas Bata University in Zlin, no. IGA/FT/2022/006

References

1. ITA. Global Resources & Reserves. *Int Tin Assoc*., https://www.internationaltin.org/
2. Zhou Y, Wu W, Qiu K. Recovery of materials from waste printed circuit boards by vacuum pyrolysis and vacuum centrifugal separation. *Waste Manag*. 2010;30(11):2299 – 2304. doi:10.1016/j.wasman.2010.06.012
3. Park S, Kim S, Han Y, Park J. Apparatus for electronic component disassembly from printed circuit board assembly in e-wastes. *Int J Miner Process*. 2015;144:11 – 15. doi:10.1016/j.minpro.2015.09.013
4. Mecucci A, Scott K. Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards. *J Chem Technol Biotechnol*. 2002;77(4):449 – 457. doi:10.1002/jctb.575
5. Jha MK, Kumari A, Choubey PK, Lee JC, Kumar V, Jeong J. Leaching of lead from solder material of waste printed circuit boards (PCBs). *Hydrometallurgy*. 2012;121 – 124:28 – 34. doi:10.1016/j.hydromet.2012.04.010
6. Wang Y, Liu B, Sun H, Huang Y, Han G. Selective extraction and recovery of tin from hazardous zinc-leaching residue by oxalic acid/sulfuric acid mixture leaching and hydrolytic precipitation. *J Clean Prod*. 2022;342(January):130955. doi:10.1016/j.jclepro.2022.130955
7. Yoshida H, Izhar S, Nishio E, Utsumi Y, Kakimori N, Feridoun SA. Application of sub-critical water for recovery of tin and glass substrates from LCD panel E-waste. *Detritus*. 2018;4(December):98 – 103. doi:10.31025/2611-4135/2018.13738
8. Li Y, Liu Z, Li Q, Liu Z, Zeng L. Recovery of indium from used indium-tin oxide (ITO) targets. *Hydrometallurgy*. 2011;105(3 – 4):207 – 212. doi:10.1016/j.hydromet.2010.09.006
9. Erdem M, Özverdi A. Environmental risk assessment and stabilization/solidification of zinc extraction residue: II. Stabilization/solidification. *Hydrometallurgy*. 2011;105(3 – 4):270 – 276. doi:10.1016/J.HYDROMET.2010.10.014
10. Sukandar, Padmi T, Tanaka M, Aoyama I. Chemical stabilization of medical waste fly ash using chelating agent and phosphates: Heavy metals and ecotoxicity evaluation. *Waste Manag*. 2009;29(7):2065 – 2070. doi:10.1016/j.wasman.2009.03.005
11. Jung CH, Matsuto T, Tanaka N, Okada T. Metal distribution in incineration residues of municipal solid waste (MSW) in Japan. *Waste Manag*. 2004;24(4):381 – 391. doi:10.1016/S0956-053X(03)00137-5
12. Kazmi SMS, Abbas S, Nehdi ML, Saleem MA, Munir MJ. Feasibility of Using Waste Glass Sludge in Production of Ecofriendly Clay Bricks. *J Mater Civ Eng*. 2017;29(8):04017056. doi:10.1061/(asce)mt.1943-5533.0001928
13. Nandi VS, Raupp-Pereira F, Montedo ORK, Oliveira APN. The use of ceramic sludge and recycled glass to obtain engobes for manufacturing ceramic tiles. *J Clean Prod*. 2015;86:461 – 470. doi:10.1016/j.jclepro.2014.08.091
14. Cao X, Wahbi A, Ma L, Li B, Yang Y. Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid. *J Hazard Mater*. 2009;164(2 – 3):555 – 564. doi:10.1016/j.jhazmat.2008.08.034
15. Song YC, Sivakumar S, Nguyen TT, Kim SH, Kim BG. The immobilization of heavy metals in biosolids using phosphate amendments-Comparison of EPA (6010 and 3051) and selective sequential extraction methods. *J Hazard Mater*. 2009;167(1 – 3):1033 – 1037. doi:10.1016/j.jhazmat.2009.01.089
16. Çoruh S, Ergun ON. Use of fly ash, phosphogypsum and red mud as a liner material for the disposal of hazardous zinc leach residue waste. *J Hazard Mater*. 2010;173(1 – 3):468 – 473. doi:10.1016/j.jhazmat.2009.08.108
17. Lin SL, Cross WH, Chian ESK, Lai JS, Giabbai M, Hung CH. Stabilization and solidification of lead in contaminated soils. *J Hazard Mater*. 1996;48(1 – 3):95 – 110. doi:10.1016/0304-3894(95)00143-3
18. Gollmann MAC, da Silva MM, Masuero AB, dos Santos JHZ. Stabilization and solidification of Pb

in cement matrices. *J Hazard Mater*. 2010;179(1 – 3):507 – 514. doi:10.1016/j.jhazmat.2010.03.032

19. Rha CY, Kang SK, Kim CE. Investigation of the stability of hardened slag paste for the stabilization/solidification of wastes containing heavy metal ions. *J Hazard Mater*. 2000;73(3): 255 – 267.
20. Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for tin.
21. EN 15935:2001. Soil, waste, treated biowaste and sludge - Determination of loss of ignition. Brussel: European Committee for Standardization, 2021.
22. EN 196-1. Methods of testing cement - Part 1: Determination of strength.
23. EN 197-1:2011. Cement - Part 1: Composition, specifications and conformity criteria for common cements.
24. Yousuf M, Mollah A, Hess TR, Tsai YN, Cocke DL. An FTIR and XPS investigations of the effects of carbonation on the solidification/stabilization of cement based systems-Portland type V with zinc. *Cem Concr Res*. 1993;23(4):773 – 784. doi:10.1016/0008-8846(93)90031-4
25. Zhang H, Wang B, Dong X, Feng L, Fan Z. Leachability of heavy metals from solidified sludge. *Sci China, Ser E Technol Sci*. 2009;52(7):1906 – 1912. doi:10.1007/s11431-009-0124-2
26. Zákon č. 541/2020 Sb., o odpadech, v platném zněni [Czechia, Act No. 541/2020 Coll., on waste, as amended]
27. Vyhláška č. 273/2021 Sb., o podrobnostech nakládání s odpady, v platném znění [Czechia, Proclamation No. 273/2021 Coll., Proclamation on details of waste management, as amended]

Recyklace a solidifikace cínu z odpadního kalu z výroby zrcadel

Barbora VACHOVÁ, Štěpán VINTER, Vratislav BEDNAŘÍK, Martina KOPOVÁ

Ústav inženýrství ochrany životního prostředí, Univerzita Tomáše Bati, Fakulta technologická, Vavrečkova 5669, 760 01 Zlín e-mail: vinter@utb.cz

Souhrn

Tato studie se zaměřuje na získávání cínu a solidifikaci kalu ze zrcadlového broušení. K extrakci cínu z kalu se používají roztoky hydroxidů o různé koncentraci (0,1 – 10M). Kal je dále upravován technikou stabilizace a solidifikace s použitím běžného portlandského cementu jako pojiva. Vzorky byly hodnoceny pomocí rentgenové fluorescenční analýzy, vyluhovacích zkoušek a pevnosti v tlaku v případě solidifikovaných vzorků. Výsledky ukázaly, že v případě extrakce v 10M hydroxidu sodném bylo získáno téměř 57 % cínu jako sraženina. Optimální obsah pro solidifikaci kalu byl obsah 50 % cementu. Dále byl hodnocen vliv přídavku aktivního uhlí do solidifikačních směsí. Závěrem lze říct, že kal ze zrcadlového broušení se ukázal jako vhodný pro získávání cínu a solidifikovaný odpad lze považovat za odpad, který není nebezpečný.

Klíčová slova: *recyklace, cín, solidifikace, rentgenová fluorescence, pevnost v tlaku, aktivované uhlí*