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INACTIVATION OF TOXIC METALS FROM WASTE GALVANIC SLUDGE BY OTHER HAZARDOUS WASTE

Abstract: *The paper presents the process of inactivation of toxic metals from waste galvanic sludge by other waste materials such as waste sludge from the technological process of iron production, waste ash from thermal power plants, zeolite and waste cathode glass. Inactivation is performed by the sintering process at high temperatures. The obtained sintered product has such a structure that where toxic metals present in it can not be started even under critical conditions. Furthermore, such a product can have a use-value and the risk of environmental pollution is reduced to a minimum.*

Key words: galvanic sludge, slag, ash, zeolite, cathode glass.

INTRODUCTION

Galvanic sludge is declared as hazardous waste. If it is not processed or improperly disposed of, the easily mobile fraction of metal elutes with atmospheric precipitation and pollutes the environment by infiltration. In that case, the paper will present the characteristics of incorporated waste materials and the flow diagram of the inactivation of waste galvanic sludge.

Figure 1. *Ingredient of hazardous waste*

Stabilization of toxic metals from the technological process of galvanization will be performed by other waste industrial materials, such as waste slag from the technological process of iron production, waste ash from the thermal power plant, zeolite and waste cathode glass, Figure 1.

SLAG AS AN INGREDIENT OF SINTERED MATTER

The technological process of iron production creates a large amount of by-products in the form of waste slag, which is most often disposed of in landfills. In order to reduce the risk of environmental pollution, research on the possibilities of using slag for various purposes has been intensified. Slag can be used as an aggregate for filling and making embankments, filling roads, making lower layers of roads, making dams, as an aggregate for making concrete and asphalt, a raw material for making stone wool, as bedding under concrete blocks, as raw material for ceramics, etc. [1]. It is also used in agriculture as a substitute for limestone, i.e. to reduce soil acidity [2].

Figure 2. *Slag in road construction*

Slag is a complex system consisting of a number of components, most commonly of melting of various oxides with very high melting temperatures [3]. In relation to appearance, mode of cooling and mineralogy, slag is similar to magma. The type of slag that is formed during the technological process of iron production (crystal, granular, expanded) depends on the ore used, as well as the method of cooling [4]. The way the slag is cooled affects the appearance and granulation of the aggregate. Air-cooled slag is formed into a solid aggregate, while water-cooled slag is formed into a light fine-grained aggregate suitable for the preparation of mortar and concrete. Air-cooled slag will be used to stabilize the galvanic sludge due to its melting properties.

In air-cooled slag, the present CaO binds moisture from the surrounding, creating hydroxide, and reacting with CO_2 from the atmosphere, it turns into carbonate, which has a larger volume, which causes the slag to "swell". The same happens if free MgO is present which is converted to $MgCO_3$ in the same way. This transformation of free oxides into carbonates takes place during the "aging of slag", which usually takes place in landfills where the slag is exposed to atmospheric conditions with certain mechanical (swelling, cracking, crushing) and chemical (carbonization) changes. Carbonates have proved to be good glass melters and for this reason, this slag is used to obtain sintered glassy matter.

ASH AS AN INGREDIENT OF SINTERED MATTER

"Flying ash" will be used as an ingredient of the sintered material as a waste product of the coal combustion process in thermal power plants. The amount of ash deposited from thermal power plants is estimated to be several million tons per year. This is a huge economic and environmental problem of countries around the world, far ahead of other industrial wastes, such as phospho-gypsum, fluoro-gypsum and various types of industrial sludge [5].

Figure 3. *Ash dump*

The chemical composition of the ash and the share of the glassy phase contribute to its use in the production of glass-ceramic materials.

According to the American standard ASTM C618, ash produced in the process of coal combustion is classified into two groups: type F and type C. Type F (acidic) is formed during the combustion of anthracite and bituminous coal with low calcium oxide content (<7%) and with increased content of silicon dioxide, aluminum oxide and iron oxide. Type C (alkaline) is formed during the combustion of lignite and contains a larger amount of calcium oxide (from 15 to 30%). Class C ash has self-binding properties. Class F ash has pozzolan characteristics, and due to its low calcium content (less than 10% CaO), it does not have self-binding properties [6].

The ash characteristics depend on the type of coal and the method of collecting ash from electrostatic precipitators. It is generally a fine-grained and powdery material. The color of the ash is usually gray and depends on the Fe_2O_3 content and the amount of incombustible coal residues in the ash. The ash particles are of different sizes, mostly spherical in shape. The ash particle size is 0.01 to 100 μm in diameter, with the largest grain size being about 20 mm [7].

The chemical composition of ash is complex, and as characteristic chemical compounds, it contains: SiO_2, Al_2O_3, Fe_2O_3 and CaO and to a lesser extent MgO, MnO, Na_2O, K_2O, SO_3, N, C. In some ashes, TiO_2 and Pb_2O_5 can be found to a lesser extent.

The mineral composition of "flying ash" in a broader sense includes the following components: inorganic components, crystal and amorphous, organic substances derived from coal and liquid, gaseous and gaseous-liquid inclusions in inorganic and organic components [8].

Trace elements Ag, As, V, Ba, Be, Cd, Cr, Cs, Su, Ga, Ge, Li, Mn, Mo, Nb, Ni, Pb, Rb can be detected in the ashes of lignite as well as bituminous coals, Sb, Sc, Sn, Sr, U, Tl, V, Y, Zn and Zr. Many of these elements are extremely toxic, while some can be useful, so they are extracted [9].

ZEOLITE AS AN INGREDIENT OF SINTERED MATTER

Zeolite is a natural mineral formed by mixing volcanic lava with alkaline groundwater. It consists of microporous crystals of aluminosilicate origin whose structure is composed of pores, interconnected by channels in which cations and water molecules are located.

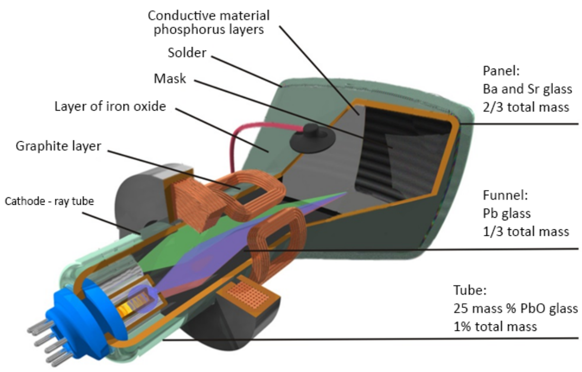
Zeolite has multiple applications in construction, medicine, wastewater treatment, etc. The addition of natural zeolites can improve the properties of concrete, various building materials and create new products. Mihajlov 's paper presents the results of the application of natural zeolites as components of ceramic masses for the production of ceramic tiles, new forms of porous ceramics [10]. Natural zeolites are used for making glazes, as well as for the production of refractory and thermal insulation materials. They are also used to make glass and glass products, such as hollow glass. Thermal treatment of zeolite, ie sintering, takes place in several phases: dehydration of the zeolite and increase of mobility of free ions, amorphization of the sample, crystallization of the new phase and phase transformation. A completely new phase that emerges is stable under certain thermodynamic conditions. When these conditions change, it is transformed into a new phase that is also stable in the new conditions [11].

CATHODE GLASS AS AN INGREDIENT OF SINTERED MATTER

The last waste material that will be used in the inactivation of toxic metals is cathode glass, which appears as a waste material when recycling monitors with a cathode ray tube, the so-called CRT monitor. The total annual production of a waste screen with a cathode ray tube reached 6.3 million tons, and more than half of that weight is cathode glass [12, 13]. In addition, China alone produced about 43.11 million tons of CRT glass in one year [14]. The amount of waste CRT glass will peak between 2015 and 2020 [15].

Depending on the part of the CRT monitor, silicate glass has a very complex chemical composition:

- front of the screen: barium-strontium oxide glass;
- the inner part of the bell: glass with lead oxides;
- combination of screen and bell - frit: easily soluble glass with lead oxides;
- neck: glass with an extremely high content of lead oxides.



Slika 4. *CRT monitor*

The cathode-ray tube of a CRT screen consists of two components: a conical glass and a screen glass. The supporting (conical) glass is coated on the inside with barium oxide and contains a large percentage of lead. The screen glass is of similar composition, large thickness with a photosensitive layer to create an image on the inside. It also contains a significant amount of lead to protect the user from possible radiation.

During the technological process of recycling such electronic waste, it is very important to separate hazardous and non-hazardous glass contained in CRT monitors, as well as safely remove fluorescent dust, which contains many carcinogenic substances, one of which is hexavalent chromium.

The selection of the composition of the initial materials used in the technological process of obtaining glass-ceramics by sintering is based on the knowledge of the crystallization properties. Since sintering is a physical process of reducing the distance between particles under the influence of high temperature, glass is the basic ingredient due to its specific crystallization properties. As a result of the technological sintering process, solid glass-ceramics of reduced dimensions and increased density are obtained, and the degree of sintering depends on the temperature, annealing time and pressure intensity in the furnace, and above all on the choice of raw materials.

DIAGRAM OF INACTIVATION OF WASTE GALVANIC SLUDGE FLOW

Glass-ceramic materials are solid inorganic polycrystalline materials obtained by directed crystallization of glass. Unlike traditional ceramics, where polycrystalline materials are used as starting materials, in glass-ceramics, crystalline phases are formed from the glass phase. This treatment and adequate choice of glass composition affects the structure and phase composition, and thus the properties of the material. It results in the development of a group of materials having properties that are better than other inorganic materials (glass, ceramics and metals) or have a combination of properties of these three groups of materials. For these reasons, they are used to a significant extent in the mechanical, electrochemical, construction, optical industry, medicine, etc.

In previous research, stabilization of toxic metals from galvanic sludge was performed by various chemical-technological processes, such as: obtaining clinker for cement production [16, 17], inertization of toxic metals of galvanic sludge in clay-based ceramics [18, 19], production of red ceramics using galvanic sludge and diatomite as raw material [20], inertization of galvanic sludge by incorporation into clay bricks [21], use of ash and sulfoaluminate cement in stabilization of toxic metals from galvanic sludge [22], incorporation of toxic metals from galvanic sludge and galvanic sludge glass-ceramic solution [23, 24].

This paper presents a flow diagram of the inactivation of toxic metals from waste galvanic sludge by transferring it into a sintered product, using waste industrial materials, such as: slag from the technological process of iron production, fly ash, cathode glass and natural zeolite material, Figure 5.

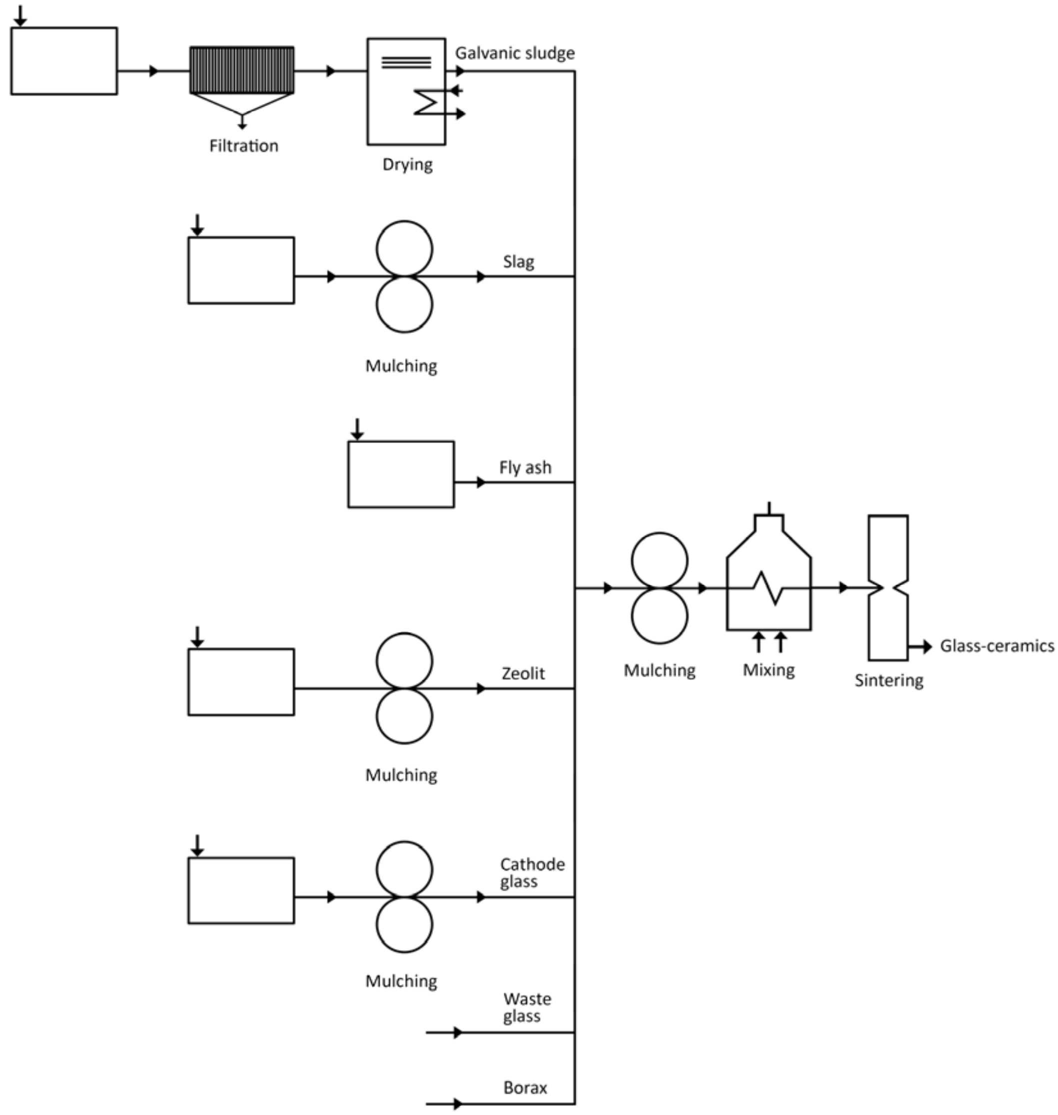


Figure 5. *Technological scheme of sintering glass-ceramics*

At the beginning of the sintering, the basic ingredients are prepared. First, the sludge is dried at 100°C, after which the slag, zeolite and cathode glass are crushed in a ball mill. When the raw materials are crushed, they are mixed until the mixture is homogenized. The homogenized mixture is placed in a melting crucible, which is subjected to high temperatures of 1200°C in an annealing furnace. The majority of the mixture is represented by hazardous waste materials: galvanic sludge, slag from the technological process of iron and steel production, flying ash and cathode glass. Auxiliary raw materials, waste glass due to their crystallization properties and borax (chemical formula: $Na_2B_4O_7$ x $10H_2O$) as a metal oxide solvent are also added. For phase changes to occur, the mixture must be completely liquid. Therefore, the crucible is kept in the oven for about 60 minutes, after which it is taken out of the oven with special tongs and the mixture is poured into preheated graphite molds or cooled spontaneously.

Testing the efficiency of this procedure is performed in different model systems, such as acidic or basic medium, high temperatures, the different granulometric composition of the solid solution, etc.

By incorporating toxic metals into the sintered product, chemically active substances, ie ions of toxic metals, are transformed by phase and chemical transformations into a stable structure of glass-ceramics in which these fractions cannot be started even in critical conditions.

The efficiency of the technological process of processing waste sludge into a stable structure of eco-sintered material was confirmed by an X-ray diffraction analysis (XRD). Based on the XRD spectrum, chemical-phase transformations with the binding of toxic metals (Al^{3+}, Cr^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) for the aluminosilicate phase in the form of solid solutions were confirmed, Figure 6.

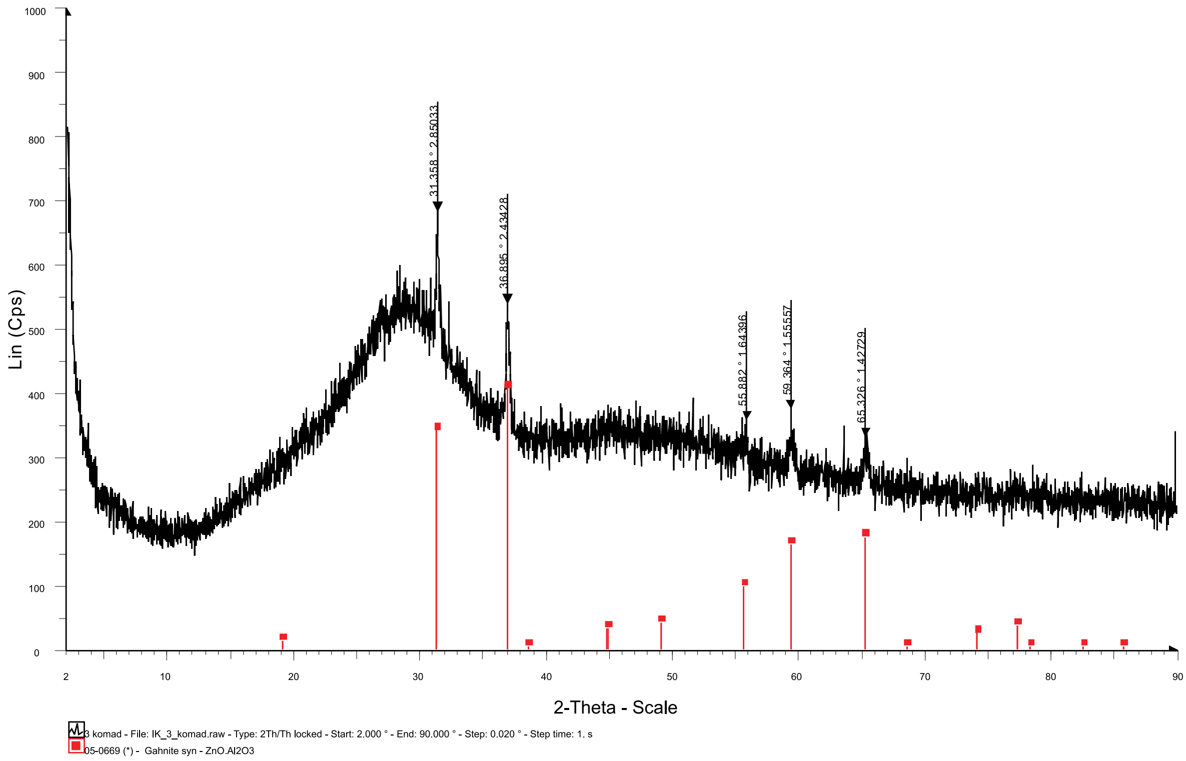


Figure 6. XRD spectrum of the glass-ceramics piece

CONCLUSION

Toxic metals found in industrial waste are one of the biggest problems of working and living environmental pollution. The state of the environment and the possible consequences of pollution indicate the imperative of developing procedures for minimizing toxic metals and their further processing and use. Accordingly, the paper presents the process of inactivation of toxic metals from the technological process of galvanization into a stable structure using slag, flying ash, cathode glass and zeolite as ingredients. In this way, the mobile fractions of toxic metals are permanently immobilized into a useful glass-ceramic product.

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REFERENCES

[1] D. Proctor, K. Fehling, E. Shay, et al., Physical and chemical characteristics of a blast furnace, basic oxygen furnace, and electric arc furnace steel industry slags, Environmental Science, Volume 34, (2000), pp. 1576-1582.

[2] B. Filho, M.P. Zimmermann, F.J. Pfeilsticker, et al., Influence of calcium silicate slag on soil acidity and upland rice grain yield, Ciência e Agrotecnologia, Volume 28(2), (2004), pp. 323-331.

[3] A. Džananović, Troska visoke peći kao agregat u asfaltnim konstrukcijama, Zbornik radova Građevinskog fakulteta, Međunarodna konferencija Savremena dostignuća u građevinarstvu 25, 24-25.april 2014, Subotica, Srbija, (2014), str. 979-986.

[4] B. Čađenović, V. Marjanović, V. Ljubojev, et al., Mogućnost iskorišćenja bakrenca iz topioničke šljake kod njenog direktnog izlivanja iz peći, Rudarski radovi, Broj 2, Bor, Srbija, (2012), str.137-148.

[5] M. Singh, M. Garg, Cementitious binder from fly ash and other industrial wastes, Elsevier, Cement and Concrete Research, Volume 29, Issue 3, (1999), pp. 309-314.

[6] ASTM C618-17, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete

[7] W. L. Daniels, B. Stewart, K. Haering, et al., The potential for beneficial reuse of coal fly ash in Southwest Virginia mining environments, Virginia Polytechnic Institute and State University, Virginia Cooperative Extension, Publication 460-134, 2002.

[8] S. Vassilev, R. Menendez, D. Alvarez, et al., Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 1. Characterization of feed coals and fly ashes, Elsevier, Fuel, Volume 82, Issue 14, (2003), pp. 1793-1811.

[9] D. Bechtel, R.F. Reischenbacher, R. Sachsenhofer, et al., Paleogeography and paleoecology of the upper Miocene Zillingdorf lignite deposit (Austria), International Journal of Coal Geology, Volume 69, Issue 3, (2005), pp. 119-143.

[10] A. S. Mihajlov, Prirodni zeoliti. Nalazišta, sirovinska baza, fiziĉko-hemijske i tehnološke osobine, primena“, Priruĉnik Tom II Primena prirodnih zeolita, 1991.
[11] A. Kremenović, Fazne transformacije u kristalima, Rudarsko-geološki fakultet, 2007.
[12] S. Zhang, Y. Ding, B. Liu, et al. Supply and demand of some critical metals and present status of their recycling in WEEE, Waste Manage, Volume 65, (2017), pp. 113-127.
[13] M. Xing, J. Wang, Z. Fu, et al., Extraction of heavy metal (Ba, Sr) and high silica glass powder synthesis from waste CRT panel glasses by phase separation, Elsevier, Journal of Hazardous Materials Volume 347, (2018), pp. 8-14.
[14] N. Singh, J. Li, X. Zeng, Solutions and challenges in recycling waste cathode-ray tubes, Elsevier, Journal of Cleaner Production, Volume 133, (2016), pp. 188-200.
[15] J. Gregory, M.C. Nadeau, R. Kirchain, Evaluating the economic viability of a material recovery system: the case of cathode ray tube glass, Environmental science & technology, Volume 43, Issue 24, (2009), pp. 9245-9251.
[16] D. Espinosa, J. Tenório, Laboratory study of galvanic sludge’s influence on the clinkerization process, Elsevier, Resources, Conservation and Recycling Volume 31, Issue 1, (2000), pp. 71-82.
[17] S. Stepanov, N. Morozov, N. Morozova, et al., Efficiency of use of galvanic sludge in cement systems, Elsevier, Procedia Engineering, Volume 165, (2016), pp. 1112-1117.
[18] J.M. Magalhãesa, J.E. Silvaa, F.P. Castroa, et al., Effect of experimental variables on the inertization of galvanic sludges in clay-based ceramics, Elsevier, Journal of Hazardous Materials, Volume 106, Issues 2-3, (2004), pp. 139-147.
[19] J.M. Magalhãesa, J.E. Silvaa, F.P. Castroa, et al., Kinetic study of the immobilization of galvanic sludge in clay-based matrix, Elsevier, Journal of Hazardous Materials, Volume 121, Issues 1-3, (2005), pp. 69-78.
[20] V. Mymrine, N. M.S. Kaminari, M. J.J.S. Ponte, et al., Oily diatomite and galvanic wastes as raw materials for red ceramics fabrication, Elsevier, Construction and Building Materials, Volume 41, (2013), pp. 360-364.
[21] L. Pérez-Villarejo, S. Martínez-Martínez, B. Carrasco-Hurtado, et al., Valorization and inertization of galvanic sludge waste in clay bricks, Elsevier, Applied Clay Science, Volumes 105-106, (2015), pp. 89-99.
[22] C. A. Luz, J. C. Rocha, M. Cheriaf, et al., Use of sulfoaluminate cement and bottom ash in the solidification/stabilization of galvanic sludge, Elsevier, Journal of Hazardous Materials, Volume 136, Issue 3, (2006), pp. 837-845.
[23] M. Stanisavljevic, Tehnologija prerade otpadnih voda i industrijskog opasnog otpada, Visoka tehnička škola strukovnih studija, Požarevac, 2010, 754 str, ISBN 978-86-902261-8-4
[24] I. Krstić, S. Zec, V. Lazarević, et al., Use of Sintering to Immobilize Toxic Metals Present in Galvanic Sludge into a Stabile Glass-Ceramic Structure, Science of Sintering, Volume 50, No 2, (2018), pp. 139-147.

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Ana Stojković was born in Niš in 1989 and is still living there. She graduated from the Faculty of Occupational Safety in Niš in 2015, with excellent grades. She started her Ph.D. studies in 2015. Since 2018, she has been working at the Faculty of Occupational Safety as a trainee researcher within the development projects aimed at young talented researchers, funded by the Ministry of Education of Science and Technological Development.

INAKTIVACIJA TOKSIČNIH METALA IZ OTPADNOG GALVANSKOG MULJA DRUGIM OPASNIM OTPADOM

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Rezime: *U radu je prikazan postupak inaktivacije toksičnih metala otpadnog galvanskog mulja drugim otpadnim materijama, kao što su otpadna šljaka iz tehnološkog procesa proizvodnje gvožđa, otpadni pepeo iz termoelektrane, zeolit i otpadno katodno staklo. Inaktivacija se izvodi procesom sinterovanja na visokim temperaturama. Dobijeni sinterovani proizvod je takve strukture da se toksični metali prisutni u njemu ne mogu pokrenuti ni pod kritičnim uslovima. Takođe, takav proizvod može imati upotrebnu vrednost, a rizik zagađenja životne sredine se svodi na minimum.*

Ključne reči: galvanski mulj, šljaka, pepeo, zeolit, katodno staklo.