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Use of Sintering to Immobilize Toxic Metals Present in Galvanic Sludge into a Stabile Glass-Ceramic Structure

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Abstract:

Galvanization process requires the use a large amount of water and produces wastewaters that are usually purified by conventional cost-effective procedure. This kind of treatment generates waste sludge which becomes a hazardous if is not properly stabilized. Hence, the aim of this paper is to investigate the characteristics of galvanic sludge through the inspection of its physicochemical parameters and consider stabilization of waste materials, including waste glass and aluminum slag by their conversion into an eco-designed material referred to as glass ceramics. The obtained products have been studied by X-ray diffraction (XRD). XRD analyses confirmed occurrence of chemical and phase transformations in treated galvanic sludge and binding of toxic metals (Al^{3+}, Cr^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) into crystalline phases and very sTab. structure.

Keywords: *Sintering; Galvanic sludge; Toxic metals; Immobilization; Glass-ceramics.*

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1. Introduction

Galvanic sludge, generated by treatment of wastewater in conventional systems (such as chemical oxidation and reduction, neutralization, sedimentation, coagulation, and flocculation), is by its nature a mixture of toxic metal hydroxides ($Al(OH)_3$, $Cr(OH)_3$, $Cu(OH)_2$, $Zn(OH)_2$, $Pb(OH)_2$, $Cd(OH)_2$, $Ni(OH)_2$, etc). The amount and the composition of galvanic sludge depend on the technological process of galvanization, as well as production capacity and physicochemical properties of the components in the electrolytes and rinse water. Galvanic sludge has been acknowledged as hazardous waste, i.e. waste which by its origin, composition or concentration of hazardous substances poses substantial or potential threats to public health or the environment and exhibits at least one of the hazardous traits specifically defined by the regulations (environmental regulations and limits) [1-3]. If not properly disposed of, it easily spreads in the environment and becomes a serious environmental problem (Fig. 1).

Worldwide, a great deal of attention has been paid to testing, collection, storage, transportation and stabilization of galvanic sludge. First of all, this kind of care includes the characterization of galvanic sludge for the purpose of its classification as a hazardous waste,

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and secondly the stabilization in an appropriate manner in order to convert it into a valuable new product or dispose it safely on a landfill. Due to its complex composition, the classification of hazardous waste is conducted depending on the predominant metal or its physical properties [2]. A new valuable product provides solutions to environmental problems and confers potential economic benefit.

a)  b) 

Fig. 1. a) Storage of galvanic sludge; b) galvanic sludge.

Stabilization of heavy metals from galvanic sludge is carried out by various technological processes, such as the incorporation in bricks [4], borosilicate glass [5], glass-ceramics (along with aluminum slag) [6], clay ceramics [7], transparent glass-ceramics [8], red ceramics [9] or calcium sulphoaluminate cement [10], reuse in the metallurgical industry [11], vitrification [12], solidification by asphalt emulsion [13], etc. Besides, a lot of research has been conducted in order to develop various applications of waste galvanic sludge like obtaining malayaite ceramic pigments [14], Cu-concentrates [15] or binders (along with a petrochemical waste) [16], immobilizing heavy metals using of sodium silicate and tetraborate [17], recovering toxic metals by sulfate treatments [18], removing nickel, copper and chromium in an electrocoagulation system with Fe- and Al-electrodes [19], extracting chromium [20], performing chromium passivation [21] and others.

A great number of procedures for immobilization of toxic metals in galvanic sludge are based on adding binders, such as clay, after which a mixture is thermally processed to produce a kind of ceramics. The degree of inertization of galvanic sludge is usually monitored by following the amount of metal leaching out from the thermally treated mixtures. It was revealed that thermal treatment of the mixture of Kaolin Oka clay, galvanic sludge and sand could deactivate toxic metals. However, under the influence of atmospheric conditions these metals can be easily activated [22].

In this study, the stabilization of waste galvanic sludge has been carried out by sintering in the presence of waste glass and aluminum slag which is very heterogeneous and chemically and thermodynamically unsTab.. The main intention of the research was inertization of hazardous solid waste, generated during galvanization, to its insoluble form, in order to minimize or completely eliminate the risk of environmental pollution, in accordance with national, European and international laws and norms.

2. Experimental procedure

2.1. The materials used in experimental work

Galvanic sludge was obtained after purification of galvanic wastewaters in conventional treatment systems of a galvanization plant.

Aluminum slag was obtained after secondary aluminum production where it appeared on the surface of the molten aluminum. The chemical composition of the slag consists mostly of Al_2O_3 but contains also Fe, Cu, Ni, Be, Ti, Bi compounds (oxides) and significant amounts of lanthanoids. In addition, the aluminum slag contains easily removable fluorides.

Waste glass is a bulky mechanical waste or glass powder obtained by grinding the edges of cut glass. This is soda-lime or "ordinary" glass with the following chemical composition: 12.9 % Na_2O, 11.6 % CaO and 75.5 % SiO_2 (wt%).

Borax (Disodium tetraborate - $Na_2B_4O_7x10H_2O$) is the only component used in experiment which is not classified as waste material. At a temperature of 350-400 °C, borax crystals are transformed into the anhydrous salt $Na_2B_4O_7$. At 880 °C it melts and becomes colorless glassy mass in which metal oxides are easily incorporated. Therefore, borax is used to facilitate melting of glass-ceramics mixture. The used disodium tetraborate comprises: $Na_2B_4O_7x10H_2O$, 99.5 %; insoluble substances in water, max 0.005 %; phosphate, max 0.002 %; heavy metals, max 0.001 %; iron, 0.0005 % max; calcium, 0.005 % max (wt% or mass %).

2.2. Laboratory procedure of obtaining glass-ceramics

At the beginning of the experiment, basic constituents are prepared. Firstly, the fluorides are eliminated from galvanic sludge and aluminum slag by dipping in water in separate vessels. This is done because fluorides are the main reason of dissolving of sintered material. Rinsing is carried out in a 500 cm^3 glass graduated cylinder. The insoluble part of the sludge is separated by filtration, while fluorides are regenerated by evaporation and crystallization. The obtained insoluble precipitates are dried in a low-temperature kiln at 100 °C in order to dehydrate. With the aim to facilitate the melting process, dried precipitates of galvanic sludge (5 g) and aluminum slag (4 g) together with glass waste (10 g) and borax (1 g) are comminuted and homogenized in a mortar. The homogenized mixture is placed in a crucible and then put into a fusion oven where it is heated to 1200-1400 °C.

After melting, the content from crucible was poured into a graphite mold, which was preheated at 250-300 °C. This is done in order to avoid cracking of a sintered material due to rapid cooling when placed into a cool mold. Fig. 2 illustrates some examples of the obtained product known as glass-ceramics.

Fig. 2. Glass-ceramics pieces.

2.3. Analytical methods

2.3.1. Physical, physicochemical and chemical analyses

The physical, physicochemical and chemical analyses were conducted according to the standards EN 12506 [2] and BS EN 12457-1-4 [3]. Heavy metals were extracted from the sludge particles smaller than 4 mm.

2.3.2. Radionuclides

Subsequent analysis was an analysis of the radionuclide content in the waste sludge. The examination involved the technique of low-phonic Gamma spectrometry including a

semiconductor HPGe detector according to ASTM C1402-98 and AOAC 955.50.

2.2.3. X-ray diffraction (XRD) analysis

The samples prepared from compact pieces or powders have been recorded on the SIEMENS D500 powder diffractometer. XRD patterns were obtained with Ni-filtered Cu*Ka* radiation (λ=1.54184 Å) produced in the X-ray tube at the current of 20 mA and a voltage of 35 kV. The samples were examined in the range of angles 5-90 º2θ, in the continuous scanning mode with the scanning speed of 0.02 º2θ/s. Diffracted radiation was detected with the scintillation counter, whereas measuring electronics have been used to obtain a number of pulses as a measure of diffraction intensity. XRD patterns and their analyses were realized using Diffrac^{plus} software. The program Eva, which is a part of this software, generated the values of intensity and angles 2θ of the diffraction peaks. The Search/Match program enables the phase identification by comparison XRD patterns of the recorded samples with a database containing diffraction data on numerous crystalline substances. For the phase identification were used PDF (Powder Diffraction File, PDF 2) cards, published by the Joint Committee on Powder Diffraction Standards (JCPDS) -International Centre for Diffraction Data (ICDD).

3. Results and discussion

3.1. Characterization of galvanic sludge

In order to characterize the galvanic sludge, we carried out physical, chemical and physicochemical analyses (see Tab. I), as well as the analysis of the content of radionuclide in the waste sludge (see Tab. II). In Tab.s are shown measured and reference values for comparison.

Tab. I The results of physical, chemical and physicochemical analyses of the waste sludge.

Parameter	Determined value	Reference value
Water content (105^{o}C, %)	38.40	-
Metal content in the EP extract (neutral test, L/S = 10/1) mg/kg *		
Lead Pb	<0.4	100
Cadmium Cd	0.24	5
Zinc Zn	880.6	1000
Copper Cu	0.24	100
Nickel Ni	0.96	500
Total chromium Cr	24.6	300
Mercury Hg	<0.02	0.5
Arsenic As	0.04	50
Metal content in mg/kg*		
Lead Pb	<14	1000
Cadmium Cd	<2	60
Zinc Zn	4200	5000
Copper Cu	24.66	60000
Nickel Ni	<14	3000
Total chromium Cr	46200	2500
Mercury Hg	<0.20	7
Arsenic As	1.60	50
Content in EP extract (neutral test, L/S=10/1) mg/kg*		
pH value	4.7	6-13

Residual vapor at 105°C	22440.5	100000
Chlorides Cl^-	<70	100000
Sulfate SO_4^{2-}	8120	50000
Phenol index	<0.02	1000

Based on its chemical composition and in accordance with the Regulations on the Classification, Packaging and Storage of Waste Raw Materials [1], galvanic sludge is in the European *Waste Catalogue* classified under chapter 11 - Wastes from chemical surface treatment and coating of metals and other materials. Also, galvanic sludge is classified under chapter 19 - Wastes from waste water treatment plants and the preparation of water intended for human consumption and water for industrial use, more exactly 19 02 05 - sludge from physics/chemical treatment containing dangerous substances.

Only the chromium content was above the prescribed limit. Hazardous nature of hexavalent chromium has been well-recognized [23]. The International Agency for Research on Cancer declares it as a cause of lung cancer [24]. However, incorporation of chromium in glass-ceramics blocks completely its toxic action [4].

Tab. II The analysis of the radionuclide content in the waste sludge.

Description of the sample	^{40}K (Bq/kg)	^{232}Th (Bq/kg)	^{226}Ra (Bq/kg)	^{137}Cs (Bq/kg)
Waste sludge	9.2	<1.6	<3.7	0.8

The characterization of this type of hazardous waste was confirmed by the analysis of elutes according to the standard EN 12506:2007 [2] and the procedure defined by the standard BS EN 12457-1-4:2002 [3] which refers to the determination of content of heavy metals extracted from samples of sludge with high solid content and with particle size below 4 mm. [6].

3.2. Technological scheme of glass-ceramics production

Although the primary subject of the realized experiment was stabilization of hazardous waste materials, also the procedure should be applied on larger quantities of waste according to the defined technological process. Fig. 3 presents the proposal of a technological scheme of production glass-ceramics from waste galvanic sludge, aluminum slag and glass.

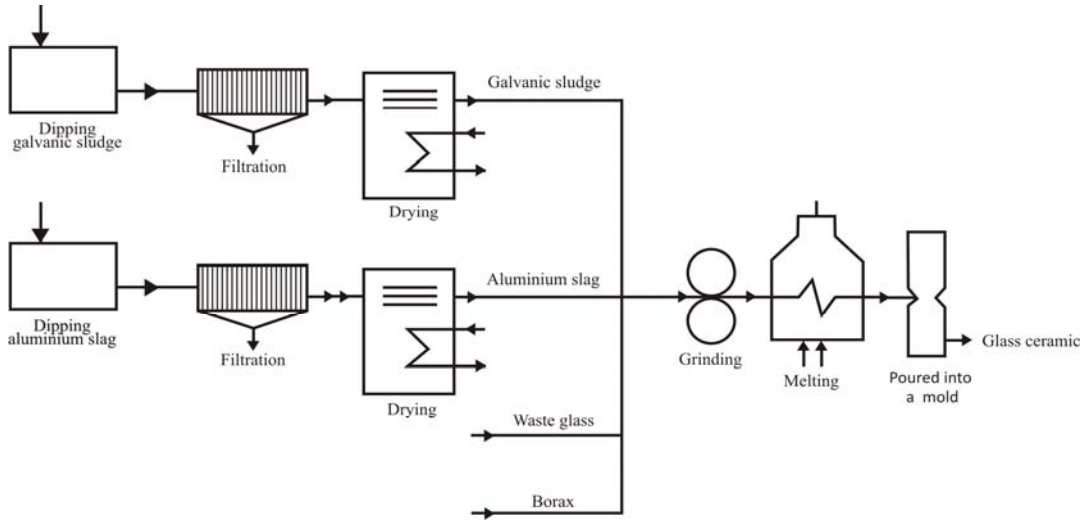

Fig. 3. Technological scheme of production of glass-ceramics.

3.3. XRD analysis of the products

The samples were recorded in the form of compact piece or as pressed powder. Inclusions, which were isolated during preparation of samples, were recorded separately (Fig. 4) and was recognized as elemental lead (Pb, PDF 04-0686). According to the broad diffraction profile at about 28 º2θ, diffraction patterns of glass-ceramics piece (Fig. 5) and glass-ceramics powder (Fig. 6) indicate the presence of a substantial part of the glassy amorphous phase. The crystalline phase identified in these samples was $ZnO{\cdot}Al_2O_3$ (gahnite, PDF 05-0669), while the sample of powder (Fig. 6) contained still a small amount of elemental lead (Pb).

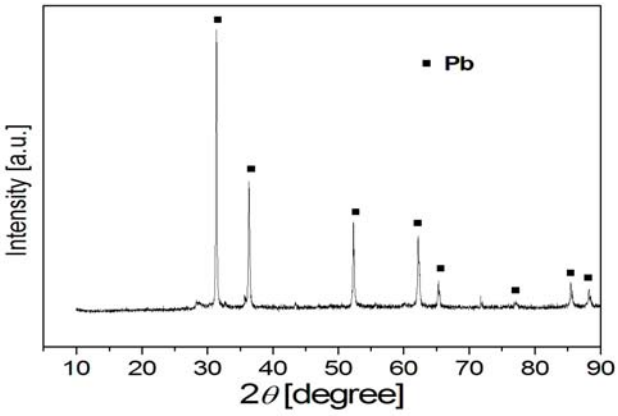

Fig. 4. XRD pattern of inclusion isolated from glass-ceramics.

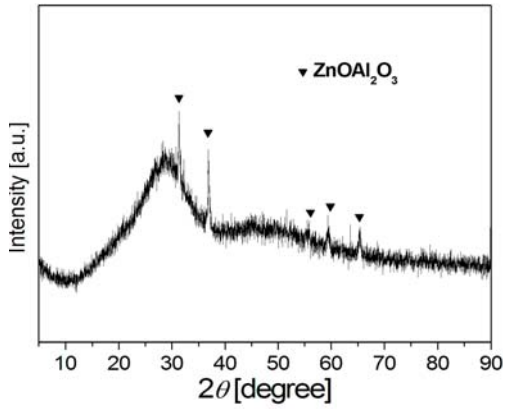

Fig. 5. XRD pattern of glass-ceramics piece.

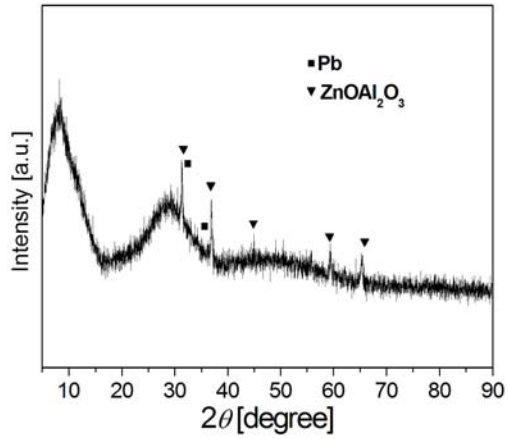

Fig. 6. XRD pattern of glass-ceramics powder.

The sample of homogenized mixture was separated from crucible, pulverized and then recorded. The diffraction pattern (Fig. 7) was similar to the previous ones and in addition to the broad diffraction profile, arising from the amorphous phase, it contained reflections of crystalline phases, $ZnO{\cdot}Al_2O_3$ and elemental Pb.

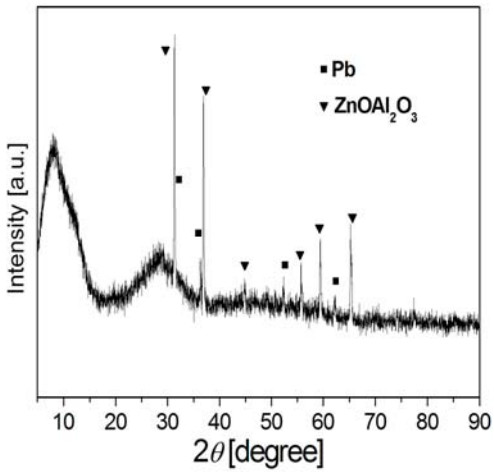

Fig. 7. XRD pattern of glass-ceramics from crucible.

A sintered glass-ceramics sample was recorded only in the form of powder. In addition to a small part of the amorphous phase, there have been identified several crystalline phases, mainly silicates of Zn, Pb and Al (PDF: 32-0543, $Pb_8Zn(Si_2O_7)_3$; 19-1479, Zn_2SiO_4; 32-1456, $Zn_2Al_4Si_5O_{18}$) togheder with the guite amount of cristobalite (PDF: 11-0695, SiO_2), hematite (PDF: 33-0664, Fe_2O_3) and zincochromite (PDF: 22-1107, $ZnOCr_2O_3$), as shown in Fig. 8. These compounds were formed during cooling of termaly treated mixture of waste materials in crucible.

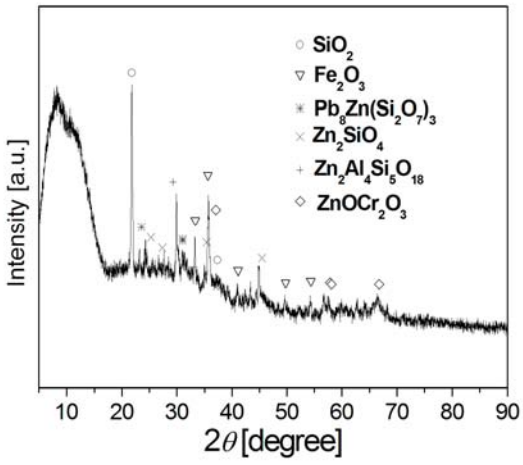

Fig. 8. XRD spectrum of glass-ceramics a sintered sample.

Based on the above presented and discussed research results, we can draw the following diagnostic criteria and parameters for technological method of processing galvanic sludge and aluminium slag:

- Toxic metals (Al^{3+}, Cr^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, etc.) from the soluble phase have been transformed to the state of low chemical activity. These metals have been incorporated from the structure of aluminosilicate phase into the form of a sTab. glass-ceramics structure;

- Glass-ceramics is a practically applicable product without the possibility of decarburization of metals in normal conditions. Moreover, the metals contribute to a better aesthetic design of the glass-ceramics structure, behaving as pigments.

4. Conclusion

Galvanic sludge has been defined as hazardous waste by law. If it is not processed or disposed properly, easily movable fraction of metals can be eluted in atmospheric precipitation thus polluting the environment. To avoid this, waste galvanic sludge, aluminum slag and glass have been inactivated and incorporated into a useful eco-designed material, referred to as glass-ceramics. An XRD spectrum showed the existence of chemical and phase transformations as well as binding of toxic metals to aluminosilicate phase in the form of solid solutions, where active toxic substances (such as Cu^{2+}, Cr^{3+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) were transformed, by phase and chemical transformations, into a very sTab. structure. In such a structure, none of the pollutants can be triggered under critical conditions such as high temperature, the effect of acids and bases, and the like. The applied laboratory analysis is the basis of the technological process focused on the stabilization of large quantities of the above mentioned waste materials into a useful product known as glass-ceramics, with the aim to meet the demands of clean technologies.

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Садржај: *Процес галванизације захтева велику количину технолошке воде што има за последицу стварање отпадних вода, које се из економских разлога пречишћавају конвенционалним системима. Овим третманом настаје отпадни муљ који, уколико се адекватно не стабилизује, представља опасан отпад. У том смислу, у раду је извршена карактеризација галванског муља анализом физичкохемијских параметара компонената, а затим стабилизација ових отпадних материја, укључујући отпадно стакло и алуминијумску шљаку, превођењем у еко-синтеровани материјал стакло-керамика. Добијени производ анализиран је рендгенском дифракционом анализом (XRD). На основу XRD спектра потврђене су хемијско-фазне трансформације третираног галванског муља и везивање токсичних метала (Al^{3+}, Cr^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) у веома стабилну кристалну структуру.*

Кључне речи: *синтеровање, галвански муљ, токсични метали, имобилизација, стакло-керамика.*