

Vanja Trifunović^{1*}

¹Mining and Metallurgy Institute Bor, Bor, Serbia

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Vitrification as a method of soil remediation

ABSTRACT

Various types of contaminated soil and hazardous waste that have a negative impact on the environment and human health can be treated with the vitrification process. This process is based on thermal treatment of contaminated soil or waste at high temperatures, with the addition of additives, whereby the soil/waste melts and a stable glass is formed. The resulting glass and glass-ceramic products have good mechanical resistance, chemically are resistant and immobilize contaminants, thus preventing their further negative impact on the environment. This paper presents a literature review of the vitrification process of different types of contaminated soil and hazardous waste.

Keywords: vitrification, contaminated soil, waste, environment protection.

1. INTRODUCTION

Pollution of the environment with various organic and inorganic substances is one of the biggest problems in the world. Environmental problems stem from human activities, such as exploitation and leaching of ores and industrial activities. These activities lead to contamination of air, water resources and soil, with organic and inorganic substances. Care for the environment has resulted in the development of many new technological processes for the treatment of solid, liquid and gaseous waste during industrial production, in order to reduce the emission of pollutants into the environment [1-12].

Contamination of the environment as a whole has not spared any of its components, as is the case with the soil itself, which is a very important component of it. The seriousness of this problem is reflected in the fact that soil damage and destruction can result in negative effects on other parts of the ecosystem, such as the hydrological regime of the environment, the diversity of plant and animal species and similarly [13, 14].

Heavy metals such as Pb, Cu, Zn, Cd, Ni, Co, Hg, Cr, etc., represent one of the largest groups of contaminants. They can be found in nature, most often in water and soil, as a consequence of ore exploitation and processing, industrial production, urban activities, use of artificial fertilizers in agriculture, etc. Heavy metals are very toxic, non-biodegradable and tend to accumulate in living organisms. With the change of physical and chemical parameters of the environment, heavy metals are leached from various industrial waste and industrial intermediates, which leads to contamination of groundwater and surface water, and thus they become available to living organisms. In this way, soil and sediments appear as potential sources of pollution, that is, reservoirs of heavy metals. Soil remediation is of great importance for the environment, and requires large investments [1, 3, 13, 15].

Sanation or remediation of soil is a procedure that reduces or removes contaminants from soil, in that measure that its contents allow the use of soil from the rehabilitated site. A large number of technologies for the remediation treatment of contaminated soil have been developed. Potentially possible and economically acceptable remediation technologies are: biological (bioremediation and phytoremediation), chemical (electrochemical, soil washing, soil flooding, solidification and natural cleaning), physical (encapsulation, excavation and soil mixing) and thermal remediation (incineration,

*Corresponding author: Vanja Trifunović

E-mail: vanja.trifunovic@irnbor.co.rs

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vitrification of soil and solar-photochemical soil decomposition). Which of the remediation technologies will be applied to the contaminated soil depends on the following parameters: type, sort and amount of pollutant, spatial contamination, soil type (soil reactions, organic matter content, proportion and type of clay), time of exposure to pollution, future use of soil, legally prescribed degrees of sanation (remediation). Based on all the previously mentioned parameters, the remediation site is also selected [1, 6, 16-19]. According to the location where remediation process is performed, the techniques are divided into *ex situ* and *in situ* [3, 20, 21].

2. SOIL REMEDIATION BY THE PROCESS OF VITRIFICATION

The method of vitrification, is one of the most promising techniques for treating contaminated soil and solid industrial waste. The technology is based on heat treatment of contaminated soil at temperatures of 1400-2000°C, and sometimes even higher, whereby the soil melts and a stable glass or glass-ceramic material (vitreous material) is formed, which drastically reduces their solubility and destroys organic compounds [1, 5, 15, 22-31]. Some of the materials on which this process can be applied are: municipal waste, dust from electric arc furnaces, hydrometallurgical waste of zinc, drainage sludge and granite sludge, tailings, fly ash from thermal power plants, nuclear waste, ash from the leather industry, etc. [30, 32 -46].

Waste is a mixture of different substances that have the possibility to form glass when melted. If the waste does not contain some of those substances, they can be added during melting process. Additives that can be added are: glass formers: SiO_2 , B_2O_3 , GeO_2 , P_2O_5 , V_2O_5 and As_2O_3 , intermediates which can't form glasses on their own, but aid with other oxides to form glasses: Al_2O_3 , Sb_2O_3 , ZrO_2 , TiO_2 , PbO , BeO , ZnO , and glass modifiers: MgO , Na_2O , K_2O , CaO etc. which modify glass and can improve the encapsulation of pollutants and reduce their possibility of leaching [23, 24, 31, 34, 47-50].

The vitreous material formed in the process provides satisfactory chemical stability (it is resistant to the leaching of "trapped" contaminants), immobilizes toxic elements (heavy metals) in the glass structure and decomposes dioxins. This is of great importance, because solid industrial waste usually has a very complex chemical composition [14, 24, 25, 47, 49, 51, 52]. Thus, metals and hazardous waste components can be immobilized through two main interactions with the glass matrix: chemical bonding and encapsulation. The vitrification process leads to a

significant reduction in the volume of waste, which has significant advantages in terms of storage or disposal. However, despite the advantages, this advanced immobilization technique has very high costs, so its application is justified mainly when it is difficult to use cheaper methods for inertization of waste and/or when value-added materials can be obtained [14, 24, 25, 47, 49, 51-53]. The agent costs of vitrification treatment range from 1000 €/m³ and up [54]. However, the cost of the process may be lower than the cost of disposing of the waste at the landfill, and there is a possibility of reusing the resulting vitrification product, so the costs can be reduced because the waste after the process has some value [15, 49, 53].

Vitrification as a method of remediation of soil contaminated with heavy metals and solid industrial waste is usually performed in the following ways:

- electrical process - *in situ* process, where electricity is supplied to graphite electrodes imprinted in contaminated soil;
- thermal process in the furnace - *ex situ* process performed in special reactors, which are usually rotary furnaces lined on the inside with refractory material;
- plasma process - usually *in situ* process, which is performed by guiding plasma burners into contaminated soil, and the plasma temperature is extremely high (up to 7000°C), on which soil and pollutants are melting [16, 28, 55].

This method of remediation is the most efficient and most widely used method in cases of contamination with substances of inorganic origin. It is very often also used for the treatment of soil contaminated with metals and radionuclides, because by glazing they are trapped and their release into deeper parts of the soil is prevented [16, 34, 36, 53].

With the vitrification technique, it is possible to obtain monolithic glasses, which can be transformed into glass-ceramics by controlled thermal treatments, especially wollastonite ($\text{CaO}\cdot\text{SiO}_3$), anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), diopside ($\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$) and iron oxides (Fe_2O_3 , Fe_3O_4). These glasses may be suitable for potential reuse in new products and / or as coating materials with high chemical and mechanical resistance for use in the construction industry [11, 15, 49, 52, 56].

2.1. *In situ* vitrification

In situ vitrification turns buried waste and contaminated soil at their original location, without any excavation or transport, into an extremely durable form of glass and crystalline waste that is non-hazardous. These techniques are minimally destructive to the site and the costs of their use are lower compared to *ex situ* techniques. *In situ*

vitrification has a number of advantages over other technologies, especially due to its ability to treat mixed waste, including soil with buried waste or tanks, dried sludge, tailings, sediments, organic waste, chemical waste, radioactive waste, and mixtures of hazardous and radioactive waste [16, 19, 22, 25, 35, 36, 47, 51, 55, 57-64]. The application of in situ techniques depends on the type of pollution, the conditions prevailing in the contaminated medium as well as the conditions prevailing at that location [20, 21].

In this process, the soil is heated by applying an electric current to four electrodes inserted into the contaminated soil in a square shape. The electrodes consist of an inner core of molybdenum with a diameter of 5 cm inside a graphite tube with a diameter of 30 cm. The graphite tube provides a relatively inexpensive cross-section that accelerates the conduction of current into the melt, and also provides a protective layer for the molybdenum inner electrode. When the process is finished, the graphite tube is sacrificed because it is left in the melt, while the more expensive inner electrode can be reused, which provides cost savings [21, 22, 59, 65].

Melting of the soil takes place with a cold cap, i.e. by a batch layer floating on the surface of molten glass [66]. The electrode design has been developed to help the cold cap go down as low as possible and to achieve reliable electrode performance throughout the entire individual adjustment (up to 400 h). The lowering of the cold cap refers to the suppression of the porous glass layer that tends to form on the surface of melt [59].

The electrodes are placed in the soil to the desired depth of processing, and since most of the soil is initially non-conductive, a specially prepared mixture of graphite and glass frit (crushed glass) called starter, is placed between the electrodes on the surface of the soil to begin the melting process. The application of electric current heats the starter path and the surrounding soil to 2000°C, well above the initial soil melting temperature of 1100-1400°C. The high temperature leads to the melting of the soil layer, thus establishing a molten, conductive path that is transferred to the soil mass. This molten zone continues to grow and is transferred to the soil mass until it gains sufficient strength to overcome heat loss. In general, the melt grows externally at about 50% of the electrode spacing [22, 59]. The in situ vitrification system on the field scale melts the soil at a rate of 4-6 t/h. Accordingly, the rate of melting progress is in the range of 25–50 mm/h [22, 25]. The shape of the melt is roughly a cube with slightly rounded corners, a shape that reflects a higher power density around the electrodes [59].

As the thermal gradient progresses in the soil, solid and liquid organic pollutants first evaporate and then pyrolyze (i.e. decompose in the absence of oxygen) into their elemental components. The gaseous by-products of organic pyrolysis move slowly through the melt towards the upper surface of the melt. Some of these gases dissolve in the molten mass, but the remain that “escapes” is collected in the waste gas collection hood for further processing in the waste gas purification system [22, 25]. The entire area to be treated is covered with a hood to collect all the waste gases produced during the vitrification process. The hood over the process site is maintained at a slightly negative pressure of 125-250 kPa to retain any gas or particles that can be released. If a high concentration of solid or liquid organic constituents is present in the contaminated soil, the waste gases can reach a temperature of 750°C. The gases collected in the hood are cooled and directed to the waste gas purification system [21, 22, 57, 58, 65].

Although in situ vitrification is a widely applicable method of soil remediation, there are limitations to its application, such as geometry, soil variations, moisture, foreign material inclusions, and criticality. For example, as the soil, wet soil and groundwater are heated in the process, the water reaches the boiling point and the process cannot proceed until all the water has boiled and evaporated. That can cause significant electricity consumption just for water evaporation. This additional heat load reduces the amount of energy available for melting, which reduces the rate of soil melting and can reduce the maximum depth that can be achieved by in situ vitrification process [21, 22, 54]. Some soils with a concentration of organic chemicals greater than 5-10 wt.% will cause an overload in the gas purification system [22, 29, 59].

The in situ vitrification process can also receive a significant amount of scraps, debris or other inclusions within the treated area [22].

2.1.1. Application of in situ vitrification process

In 1981, the Pacific Northwest Laboratory (PNL) [21] developed an in situ vitrification process to solidify radioactive transuranic waste. For demonstration and developing the process, two scales of non-radioactive experiments were used. The laboratory test unit of engineering scale, which uses two electrodes with a distance of 36 cm, vitrified 45 kg of soil per test, and the pilot test system, which uses four electrodes in a square sample of 1.2 m, successfully fixed up to 10000 kg of soil. Based on the obtained results, a full-scale in situ vitrification reference system was defined.

The thermal process that first involves the use of high-power currents that pass through the material that melts, then turns off and the material cools quickly is also called Joule heating vitrification. This vitrification procedure was successfully developed by the Pacific Northwest Laboratory (PNL) for the US Department of Energy (DOE) [27, 65].

Dellisanti et al. [27] reported in their work the details of vitrification with the Joule heating effect carried out using a specially designed pre-pilot scale plant for asbestos-containing materials and soil. The asbestos-containing material was encapsulated in uncontaminated soil, and its vitrification was performed in a steel container. The two electrodes were placed at a distance of 30 cm and between them a starter made of a mixture of unpolluted soil and graphite flakes. Average delivered power was 20 kW, which resulted in an average current of about 130 A. The maximum depth of penetration of the mobile electrodes into the ground was 30 cm. It took about 5 h to achieve complete melting of the material in temperature about 1600°C. The resulting vitreous product was cooled for about 24 h until it reached room temperature. The total vitrified mass was about 100 kg, and the vitrified volume was 55 cm × 50 cm × 40 cm, which means that all asbestos-containing material was placed in a steel container and distributed in uncontaminated soil embedded in monolithic glass. During process there was a reduction in soil volume of about 25%. X-ray Diffraction (XRD) analysis determined that the asbestos minerals were completely melted and incorporated into a glassy monolith or converted into high-temperature harmless silicates (enstatite and diopside).

In their next work, Dellisanti et al. [65] presented a method of remediation of several tons of ceramic waste rich in Pb and Zn based on vitrification of Joule heating. The waste was the sludge of the ceramic industry in the process of tile enameling and is characterized by the content of 2.85% Pb, 2.98% Zr and 0.75% Zn. XRD analysis showed that Pb was present in the waste as lead silicate (alamosite) and Zr as zirconium silicate (zircon), while Zn appeared as a dissolved element or in mineral phases. Waste also contained quartz, plagioclase, calcite and layered silicates (mica and kaolinite). X-ray fluorescence analysis (XRF) showed that the starting waste material contained 55.99% SiO₂, 11.41% Al₂O₃, 4.02% Fe₂O₃, 0.63% TiO₂ and 12.64% CaO. The in situ vitrification plant consisted of four main parts: (1) a high power generator made of a Scott transformer (three-phase/two-phase); (2) four identical graphite electrodes (150 cm long and 10 cm in diameter) for

supplying current to the ground; (3) waste gas collection system; and (4) a wastewater treatment system consisting of a filtration and treatment plant. The average delivered power was 450 kW which resulted in an average current of about 300 A. The electrodes were mobile and could be lowered by the motor during the process while the base melted and the maximum depth of penetration into the ground was 120 cm. By heating to about 1850°C, the waste material was completely melted, and the amount of 15 tons of monolithic glass was formed by rapid cooling of the melt. The monolith occupied an area of 200 × 200 cm and reached a depth of 130 cm. Mineralogical, morphological and chemical analyzes showed that the obtained glassy material was very homogeneous. Alkalinity tests confirmed that hazardous metals (Pb, Zn and Zr) were immobilized in a vitrified monolith indicating high durability and chemical resistance of the glass [65].

2.2. Ex situ vitrification

Ex situ vitrification technology is designed to inactivate and/or immobilize pollutants at locations away from contaminated soil/waste landfills, transforming them into a glass mass of molten soil in furnaces (chamber or rotary) at high temperatures. The resulting vitreous material has a high strength and is resistant to the release of pollutants contained in it, and thus prevents its dissolution, migration into groundwater or any impact on the environment, as is the case in the in situ process [16]. Immobilization degree of heavy metals in vitreous materials formed in the process is examined by leachability and toxicity tests [49, 53]. Depending on the type of vitrification process, the resulting molten mass can be abruptly cooled (quenching) or allow to cool slowly in air [16].

2.2.1. Application of ex situ vitrification process

The ex situ vitrification process is performed mainly when the waste to be vitrified does not contain sufficient amounts of oxides to form glass, and when it is necessary to add them, and this is not possible at the location where the waste is located.

Kavouras et al. [47] applied the ex situ vitrification method to stabilize solid waste rich in lead and iron oxides, ie. ash produced by the combustion of sludge obtained from storage tanks for tetraethyl lead (TEL) and leaded gasoline. The composition of the ash was as follows: 33.0% Fe, 29.6% Pb, 10.1% Br, 1.0% Si, 0.25% S, 0.8% Al, 0.3% Sb. Before melting, certain amounts of additives (SiO₂ and Na₂CO₃) were added to the ash. Melting was performed in a platinum pot, in an oven, at 1400°C. The resulting melt was quenched (cooled) on a stainless steel plate at room temperature. The vitrified product consisted of 60

wt.% of solid waste (ash), 25 wt.% of SiO₂ and 15 wt.% of Na₂O. The test results showed that this type of final product may be suitable for safe ash disposal, because the chemically resistant amorphous crust covers its inhomogeneous interior. However, it cannot be crushed by grinding so that, for example, it can be used for road stones, due to the fact that parts of the matrix would be exposed to the environment and toxic elements would be leached. If the melt was poured over the granulator, gravel material would be produced, which would solve the problem.

Chromium salts (especially chromium sulfate) are the most commonly used tanning substances in the leather industry today. Vitrification of hazardous waste generated from the chromium-tanned leather industry, i.e. chromium rich ash, was applied by Basegio et al. [49]. Chemical analysis determined the chromium oxide content of 29.4 wt.%, of which only 2.5% of chromium was hexavalent. Vitrification was applied to original ash samples and ash samples mixed in different ratios with sodium-lime glass and TiO₂/MgO oxide. The samples were then annealed at 750, 800, 950 and 1000°C for 2 hours. Different ratios of additives and ash were used to test the immobilization of chromium in the obtained vitreous material. The degree of chromium immobilization in vitreous ceramic bodies was

estimated by leaching tests (toxicity tests). Also, an estimation of gas emissions during annealing was done in order to determine the possibility of any losses of chromium during gas emissions. For formulations containing ash and sodium-lime glass, when MgO was added as an additive, immobilization of chromium ions was achieved. Immobilization of chromium in ceramic bodies was more efficient at higher annealing temperatures, which leads to a decrease in the leaching rate of chromium. Data on gas emissions confirmed that it was not possible to observe the evolution of chromium by gas emissions during the annealing of ceramic bodies.

Treatment of chromium-rich waste was also examined by Varitis et al. [53]. Chromium-rich ash is obtained as a by-product of burning sludge obtained from tanning leather. Sludge was pre-treated first to remove as much organic matter as possible, and to avoid oxidation of chromium from the trivalent to the hexavalent form because hexavalent chromium and its compounds are toxic when inhaled or ingested. The pre-treatment consisted of annealing the sludge for 90 minutes at 500°C, after which six different batch compositions were made with a mixture: silicon dioxide (SiO₂), soda (Na₂CO₃) and lime (CaO) in different proportions as shown in Table 1.

Table 1. Conditions of experiments

Tabela 1. Uslovi eksperimenata

Sample	Batch mixtures (wt.%)				Vitrification temperature (°C)	Time (h)
	Ash	SiO ₂	Na ₂ O	CaO		
1	20	55	15	10	1400	2
2	15	55	15	15	1400	2
3	13	50	10	27	1400	2
4	13	56	7.5	23.5	1400	2
5	13	56	5	26	1500	2
6	10	55	15	20	1400	2

The mixtures were melted for 120 minutes in a platinum crucible at 1400°C and 1500°C, depending on the batch composition, to achieve a homogeneous melt. The melt was cooled rapidly after it was poured onto a stainless steel refractory plate. Vitrified products (monoliths) were either composed of silicate matrices with separate crystallites of molten eskolaite (Cr₂O₃) or were homogeneous glass (in one case). All vitrified products were subsequently heat treated to encourage crystallization and produce devitrified products. The vitreous nature of vitrified products

and the corresponding heat treatment temperatures were determined by Differential Thermal Analysis (DTA), while the characterization of vitreous products was performed by XRD analysis, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS). In devitrified products, crystallization led to the separation of the crystalline phases of devitrite (Na₂Ca₃Si₆O₁₆), combeite (Na₄Ca₄Si₆O₁₈) and wollastonite (CaSiO₃), while heat treatment did not affect the eskolaite crystallites. The alkalinity test of the obtained vitreous materials according to the

standard EN 12457-4 was also performed. The test results revealed that in the vitrified monolith successfully stabilized chromium and that devitrification reduces stabilization of chromium only in the case when the initial vitrified product was homogeneous glass [53].

Karamanov et al. [51] used metallurgical waste from a ferronickel smelter in Macedonia in their research. Three types of hazardous residues from the ferronickel smelter (filter dust, slag from the electric furnace and slag from the converter) were mixed with broken glass and vitrified for 2 hours at 1400°C. The crystallization process was very special due to the presence of 1.5 wt.% chromoxide in the parent glass, together with large amounts of iron oxide and magnesium oxide. It begins during the cooling of the melt with the deposition of preliminary crystals of Fe-Mg-Cr spinel, which then act as centers for further epitaxial growth of the pyroxene phase. The obtained glass is characterized by very good mechanical characteristics, high chemical durability, and a suitable coefficient of thermal expansion.

Ballesteros et al. [9, 11] used toxic sodium chromate sludge enriched with Cr⁶⁺ chromium from an industrial area in the city of Tultitlan, Mexico, in their studies of the vitrification process. A mixture of 75 wt.% dry sludge, 25 wt.% feldspar and 5 wt.% coke ash was melted for 8 h at 1450°C. The results of XRD and SEM/EDS analyzes showed the formation of the following crystal phases: chromium, iron and aluminum spinel (Mg, Fe)(FeAlCr)₂O₄, phases hematite (Fe₂O₃), magnetite (Fe₃O₄), pyroxene [Ca(Mg), Al][(Si,Al)₂O₆] and augite [Ca(Mg, Fe)Si₂O₆].

Kimura et al. [67] simulated zeolite waste vitrified into borsilicate glass with the addition of additives H₃BO₃, Na₂CO₃ or Na₂B₄O₇ at a melting point of 1100°C to 1300°C for a period of 3 hours. The results showed that the obtained glass products were in a completely amorphous state.

In the vitrification process of radioactive liquid waste, the waste is brought to the top of a pool of molten glass contained in equipment called Joule Heated Ceramic Melter (JHCM) [35, 36, 61, 65, 66, 68]. In the work of Goel et al. [61], the treatment of radioactive waste obtained from plutonium production and the melting rate of batch material were investigated. The melting rate of the charged material, depending on the properties of the raw material and the operating conditions of the melting furnace, can be calculated using the heat transfer properties of the cold cap [61]. The batch in the form of a suspension is charged from above, creating a cold cap on the surface of the molten glass that covers 90–95% of the furnace surface.

The cold cap is a cover of the same thickness that receives even amounts of heat both from the molten glass from below and from the plenum space from above. As the batch moves through the cold cap, chemical reactions and phase transitions occur, through which the batch turns into molten glass that moves downward from the cold cap [36, 61, 62, 69, 70]. Upon melting, each batch particle travels vertically downward through the cold cap, and its properties (e.g., density, dissolution rate of solids, reaction kinetics) change in response to increasing temperature [61]. Different reactions of the cold cap develop gases that come out of the cold cap through open pores. A small amount of residual gases can remain in the glass-forming melt and cause foaming. The foam reduces heat transfer from the molten glass to the cold cap, reducing the melting rate [62].

To improve heat transfer to the cold cap, forced convection is caused by gas bubbles in the melt, which increases the melting rate because increased convection brings hot glass from the bottom of the furnace near the cold cap, with increased fluid velocity the thickness of the boundary layer near the bottom sides of the cold cap and also by increased convection and large bubbles of foam is achieved the removal of bubbles of insulating gas that form at the bottom of the cold cap. When the process is complete, the furnace temperature drops to 850–900°C, and then crystal types such as spinel are formed. Once formed, spinel deposits are difficult to dissolve because they are stable at temperatures much higher than operating temperatures (1150–1200°C) [61].

Rincón et al. [2] considered the vitrification of a combination of waste from abandoned vermiculite deposits, lithium-aluminum-phosphate amblygonite, mineral waste, and sodium borate. The melting process of a mixture of vermiculite-amblygonite (marked as Va1) and vermiculite-sodium borate (marked as Va2) was performed for 2 hours at 1400°C in a furnace. After pouring into brass molds, the glasses were cooled by thermal heating to 500°C for one hour to room temperature. The resulting glasses were green in color, transparent and smooth, which in the case of Va1 glass can give glass ceramics with an iridescent surface or a metal-like effect. Glass obtained by mixing vermiculite with commercial sodium borate showed a lower tendency to crystallize compared to that obtained by mixing vermiculite with amblygonite. Complete characterization of the obtained glass was performed by analysis of XRD, EDS, X-ray Photoelectron Spectroscopy (XPS) and the method of Hot Stage Microscopy (HSM) on the basis of which it was concluded that the main formed crystal phases are α-cordierite and β-spodumene.

The surface of this glass-ceramic made of vermiculite amblygonite is enriched with Fe_2O_3 . The relative variation in viscosity was determined by the HSM method on both Va1 and Vb1 glasses. This method determined that the tendency of crystallization on heating will be higher for glass Va1 than for glass Vb1.

Research on vitrification of organic waste (palm compost and palm leaf residues, volcanic lava used in local agriculture, natural organic peat, humus and sewage sludge) was performed by Jordan et al. [23]. The results of XRF analysis showed that all tested samples contain the main components for glass formation (SiO_2 , K_2O , CaO , MgO , Al_2O_3 , Fe_2O_3 and P_2O_5) but in insufficient quantities. Although the content of these components is lower, it is concluded that the tested samples in combination with some other waste could be used to obtain glass and glass-ceramic products.

A study by Stabile et al. [52] includes the chemical characterization of bottom ash derived from municipal solid waste produced at a

combustion plant in Rimini, Italy, and experimental investigations of vitrification process in which special attention is paid to the behavior of volatile metal components (e.g. Zn, As, Cd, etc.). Experimental tests were performed on a laboratory scale under atmospheric conditions. Melting of the ash was performed in a platinum pot in a chamber furnace at temperatures of 1000°C and 1100°C , for process times of 1h, 2h, 4h, 8h and 16 h. After melting, the pot removed from the oven was quickly cooled by immersion in a water bath. Electron Micro-Probe (EMP) analysis was used to examine the homogeneity of the samples and to obtain quantitative chemical data on the main amounts of metal oxides in the cooled glasses produced in the bottom ash vitrification experiments. Based on the obtained analysis, it can be concluded that the vitrified samples obtained by melting methods represent a homogeneous glass structure of dark vitreous appearance. Table 2 shows the conditions under which the process was performed, as well as the main oxide composition of the ash.

Table 2. Process conditions and main oxide compositions in tested samples

Tabela 2. Uslovi procesa i glavni sastav oksida u ispitivanim uzorcima

Initial sample	Temp. ($^\circ\text{C}$)	Time (h)	Chemical composition (wt.%)											Physical appearance
			SiO_2	TiO_2	Al_2O_3	FeO^*	CaO	MnO	MgO	K_2O	Na_2O	P_2O_5	Total	
			46.05	0.83	9.31	16.31	17.20	1.13	2.70	0.96	5.48	0.58	100.55	Gray, inhomog.
1	1000	1	42.52	0.17	5.60	4.66	30.76	0.17	3.41	0.56	5.60	0.38	98.83	Gray, inhomog.
2	1000	2	42.92	1.67	8.96	18.18	20.14	0.10	3.13	1.03	2.80	1.13	100.06	Gray, inhomog.
3	1000	4	50.88	0.51	7.05	6.38	24.51	0.09	3.17	1.11	4.95	0.32	98.97	Black, inhomog.
4	1000	8	71.68	0.22	1.91	1.71	11.09	0.12	2.62	1.62	7.08	0.01	98.06	Black, inhomog.
5	1000	16	60.43	0.50	9.32	4.56	17.42	0.07	0.79	1.68	4.40	0.05	99.22	Black, homog.
6	1100	1	48.84	0.74	11.88	8.43	21.12	0.13	1.80	0.91	5.23	0.46	99.54	Black, homog.
7	1100	2	48.55	0.97	12.75	7.50	18.79	0.17	3.72	1.07	5.95	0.41	99.88	Black, homog.
8	1100	4	51.64	1.47	7.26	7.37	22.66	0.12	3.59	0.90	4.11	0.56	99.62	Black, homog.
9	1100	8	48.41	1.36	13.09	8.34	18.53	0.14	2.09	1.19	5.56	0.72	98.43	Black, homog.
10	1100	16	48.59	0.92	11.90	10.40	17.52	0.15	1.79	1.27	6.15	0.63	99.32	Black, homog.

From Table 2 it can be seen that the results for samples 1, 2, 3, 4 and 5 (all treated at 1000°C , for a period of 1-16 h) represent their poor vitrification and inhomogeneous glass composition. A lower temperature of 1000°C and a process duration of

less than 16 h were not sufficient to obtain homogeneous vitreous products. Taking into account the treatment with the higher temperature (1100°C) and the longest duration of the process (16h), the results of EMP analysis show that the

main components of the obtained glass are as following: 48.6% SiO₂, 11.9% Al₂O₃, 17.5% CaO, 10.4% FeO*, 0.9% TiO₂, 1.8% MgO, 1.3% K₂O, 6.1% Na₂O, 0.6% P₂O₅ i 0.15% MnO. The total oxide content is >99% by weight, while the rest are trace elements [52].

As a means of reducing the melting temperature of fly ash during municipal solid waste incineration (MSWI) and for promoting the formation of the glassy phase, in the work of Gao et al. [71], B₂O₃ was used. Ash Fusion Temperature (AFT), Atomic Absorption Spectroscopy (AAS), XRD and SEM analyses were performed. The results showed that the initial melting temperature decreased from 1211°C to 986°C with an increase in B₂O₃ content from 0 to 15 wt.%.

Sintering at 600°C, followed by vitrification of boiler (fly) ash generated in the municipal solid waste incinerator in the work of Yang et al. [30], was carried out at a temperature of 1400°C for one hour. After heat treatment and removal from the oven, the crucible with the melt was cooled with nitrogen gas. The resulting stable silicate slag was examined by chemical and mineralogical analyzes. The results of the leachability test according to the Dutch standard NEN 7341 show that the leaching rates of vitrified slag are significantly reduced compared to the values obtained by leaching the original ash.

In the work of Sheng [57], the application of vitrification for the treatment of borate waste from Chinese nuclear power plants was considered. Borate waste with a high content of B₂O₃ and Na₂O is combined with fly ash (generated from a coal combustion power plant) in which SiO₂ and Al₂O₃ occur as the main phases. Ash oxides can be used as suitable additives for vitrification of borate waste, so there is no need for additional costs of procurement of other additives. In this work, fly ash successfully vitrified borate waste. For experimental tests of the vitrification process, samples of a mixture of borate waste and fly ash were melted in a platinum crucible at 1200°C for 2 hours and then annealed for 1 hour at 520°C in a graphite mold. Analyzes of the obtained glass showed that the glass contained 70 wt.% of fly ash and 30 wt.% of borate waste oxides. The glasses showed good durability and adequate viscosity at 1200°C. The results indicate the possible potential application of fly ash in the treatment of radioactive waste.

Sheng et al. [72] also examined the application of vitrification for liquid waste with a high boron content, from Korean nuclear power plants. In this investigation, the influence of the addition of glass frit on the vitrification process of liquid waste was

examined, but this attempt proved unsuccessful. Using fly ash from coal-fired power plants, as in their previous work, obtained results showed that up to 30 wt.% of waste oxides are successfully vitrified in fly ash after the addition of 5-10% Na₂O at 1200°C.

Five different concentrations of natural UO₂(NO₃)₂·6H₂O were mixed with sufficiently dried regosol (at 100°C for 12 hours) by grinding in agate mortar to obtain a homogeneous soil powder contaminated with uranium in the work of Sua et al. [19]. Soil uranium concentrations were controlled at 5, 50, 500, 5000 and 50000 µg/g. Contaminated soil was sintered in the microwave at 1400°C for 30 minutes. Before being completely cooled to room temperature, melts were kept in the oven for 24 h. Characterization was performed by XRF, XRD, Nuclear Magnetic Resonance (NMR) analysis, Scanning Electron Microscopy with Energy Dispersion Analysis (FESEM-EDS) and High-Resolution Transmission Electron Microscopy (HRTEM). In vitrified products, it was determined that uranium is surrounded by a three-dimensional network containing polyhedra of silicon and alumina. Obtained results indicate that microwave sintering technology for vitrification of nuclear contaminated soil is feasible and may have further application.

Concentrated radioactive elements prevent the general use of red sludge (RM) in glass-ceramics and building materials. Gold tailings (GT) have unsuitable particle sizes (≤100 µm) for use in the ceramic industry, and waste limestone (WL) contains very little lime. Due to the fact that these materials cannot be vitrified individually, Park et al. [73] examined the process of vitrification and granulation of a mixture of these materials. The process of vitrification of red sludge was investigated, with the addition of gold tailings and waste limestone as additive. Different mass ratios of red sludge, gold tailings and waste limestone were investigated in order to find the optimal composition for the production of glass beads. The results of the XRD analysis showed that the main components of the tested materials are hematite, alumina, quartz and lime.

Three samples with different contents of red sludge (RM), gold tailings (GT) and waste limestone (WL) were melted at a temperature of 1500°C and granulated with air. Samples A, B and C were mixed in the following ratios RM:GT:WL - sample A (1:2:1), sample B (1:1:1), sample C (1:1:2). Viscous melt behavior is a key control factor which influence granulation behavior. For this reason, the viscosities of the liquid samples were measured to optimize the melt composition and granulation state. Viscosity tests of samples A,

B and C in relation to temperature were performed. The viscosity of sample A with a high content of SiO₂, increases with decreasing temperature below 1500°C due to the polymerization of the silicate structure. The high viscosity behavior of sample A explains the poor granulation. The viscosity of sample B increased slowly with decreasing temperature to 1200°C. Due to the fact that a wide range of granulation temperatures is available, this composition is considered optimal. Sample C containing the highest amount of CaO showed the lowest viscosity up to 1400°C, resulting in smooth granulation. The granules were evaluated according to the size distribution and average sphericity. Potential for commercial production is possible thanks to the high production yield and the improved sphericity of the glass beads. Alkalinity and toxicity tests were also performed on the obtained granules. Leaching of heavy metal ions was not detected, or was below the detection limit of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis. The chemical stability of the granules is obviously enhanced due to the structure of the glass network obtained by the vitrification process [73].

Vitrification of hazardous mining waste and tailings from old mercury and Ag – Pb mines in Spain has been investigated using solar technology by Navarro et al. [34]. Six samples were treated in a solar furnace, in the temperature range from 1050°C to 1350°C. Leaching tests of untreated materials and treated materials were also performed. Immobilization of Fe, Mn, Ni, Cu and Zn was achieved in samples treated at a temperature of 1350°C, while immobilization of Mn, Ni, Cu and Zn was achieved in samples treated at a lower temperature of 1050°C. Therefore, it was concluded that temperature is a very important factor for immobilization of heavy metals in soil samples when solar heating source is used, which is shown by high immobilization of metal samples treated at elevated temperatures. SEM-EDS analyzes of heat-treated samples were performed to characterize solids, especially glassy phases. It is easy to recognize the phases of the vitreous product by the vitreous texture and the presence of stains that formed as a result of the release of gaseous phases during heating. EDS analysis of the vitreous product showed the presence of Si, Ca, Al, Fe, Mg and Ti, which could be associated with unformed silicate phases. EDS analysis could not identify metals such as Pb, Cu and V, because their concentrations were below the detection limit of this technique. The main mineral phases identified by XRD analysis in the samples used in the experiments with heating were quartz, barite, dolomite, calcite, illite and Fe-Cu-As-Pb-Zn sulfides. Also, XRD spectra showed the presence

of mixtures of quartz and aluminosilicate compounds of low crystallinity (glass). In the samples treated at the highest temperature (1350°C) were identified minerals such as mullite.

Iron is also present in the glass structure in the forms Fe³⁺ and Fe²⁺. The Fe³⁺/Fe²⁺ ratio depends on the melting conditions and the composition of the glass. Since Fe₂O₃ is an intermediate oxide in the glass structure, and FeO modifies the increase in the Fe³⁺/Fe²⁺ ratio, the viscosity increases and the mechanical properties and chemical durability improve. Iron-rich silicate mixtures, at high temperatures, are characterized by liquid-liquid phases that do not mix, which leads to the formation of a liquid phase rich in iron, which can encourage the deposition of spinel magnetite during cooling. Iron-rich glass-ceramics can also be obtained by sinter-crystallization technology, which gives the possibility of obtaining materials of complex shapes and good mechanical properties, as well as the production of tiles for paving with a very beautiful appearance. When glass powder rich in iron is thermally treated above the range of glass transformation, Fe²⁺ oxidation occurs to form Fe³⁺, which leads to variation in the chemical composition of surface and subsurface layers, affecting crystallization and leading to the formation of hematite on the surface [37]. Vitrification of hazardous waste rich in iron, generated by flotation of slag in copper production, was studied by Karamanov et al. [37]. Two glasses, containing 30 wt.% of iron-rich waste (marked with W), were melted for 30 minutes at 1400°C. The first batch, marked as WSZ, was obtained by mixing iron-rich waste, blast furnace slag and zeolite tuff, while the second, marked as WG, was prepared by mixing iron-rich waste, broken glass, sand and limestone. By an additional heat treatment of 1 hour at 800°C, the glass obtained from the first batch crystallized very quickly and was converted into a glass-ceramic material with a crystalline phase content of 60%. The second glass crystallized slowly and had good sinterability. By mixing the fractions of fine and rough grains and additional crystallization by sintering at 1020°C, granite-like glass-ceramics was obtained. A TCLP test of the initial sample of flotation waste, and samples of glass products WSZ and WG was performed, and results are shown in Table 3. Limit values for TCLP test are as followed: 0.5 ppm Zn, 0.2 ppm Pb and 0.1 ppm Cu. The flotation waste itself must be characterized as hazardous waste, while the values of Zn, Cu and Pb concentration in both obtained glasses are below the limit values and the glasses show a very high chemical durability.

Table 3. Results of TCLP test - leached elements concentrations

Tabela 3. Rezultati TCLP testa - koncentracije izluženih elemenata

Sample	Batch content	Concentration (ppm)		
		Zn	Pb	Cu
Iron-rich waste (W)		114.4±1.2	7.2±0.4	94.9±1.0
Glass from the first batch (WSZ)	30% flotation waste + 30% blast furnace slag + 40% zeolite tuff	0.14±0.02	0.0012±0.0002	<0.005
Glass from the second batch (WG)	30% copper flotation waste + 45% glass cullet + 15% quartz sand + 10% CaCO ₃	0.17±0.02	<0.001	0.008±0.001

Other studies with other iron-rich glasses also have shown that vitrification significantly reduces waste leaching and that the transformation of glass into glass-ceramics with iron content further improves chemical durability [2, 15, 34, 37, 49-52].

Uruga et al. [68] examined a method that uses a liquid metal to remove a platinum group of metals (Ru, Rh, and Pd) during a high-level radioactive waste vitrification process generated by reprocessing spent nuclear fuels. Platinum group metals are extracted in liquid metal and can be separated from molten glass as an easily separable phase. Mixtures of glass containing Cu, radioactive waste and additives SiO₂, B₂O₃, Na₂O, were melted using an external and Joule heating system. Melting was performed in a tube furnace at 1200°C for 4 hours under an Ar atmosphere to prevent Cu from oxidizing. After glass melted, a spherical metal "button" was formed at the bottom of the furnace. These metal "buttons" can be easily separated from the vitrification of the obtained glass by crushing. Almost all Pd (93%) was extracted with liquid copper and removed as a separable Cu-Pd metal "button" of silver color.

In a study by Chua et al. [74], the plasma vitrification process was examined on a mixture of three waste materials: fiber reinforced plastic (FRP), gill net and waste glass. To generate the plasma argon was initially used, and as the main ambient gas during the vitrification process was used air. The plasma vitrification process was performed for 1 hour at 1250°C with heating and cooling rates <7°C/min. Temperature of the furnace was controlled by adjusting the plasma current, gas flow, and voltage. Following the plasma vitrification process, the vitrified product was further thermally treated with the addition of Ca(OH)₂ as an additive to form a reusable glass-ceramic sample. Two-stage post-thermal treatment was performed at high temperatures of 850 and 950°C, which were determined by DTA analysis. Final product has a

predominantly crystalline microstructure after an hour treatment. After vitrification treatment, two vitreous products were formed: one with transparent appearance due to the higher glass batch content, and other which shows the opaque and deep dark appearance.

After plasma vitrification process, the slag was characterized by SEM, XRD and ICP/AES analysis. A toxicity test (TCLP) of the obtained glass products was also performed, and obtained results indicate that the decrease in leaching rate and hardness of the obtained products increase with the amount of fiber reinforced plastic in the sample. This test proved that plasma vitrification is a sustainable technology for combustible and non-combustible waste in which the end products are in the form of inert and non-leaching slag with a reduction in volume and which can be safely disposed of [74].

Comparative studies of four treatments of fly ash generated by the combustion of municipal solid waste and their impact on the environment were performed in the work of Pei et al. [28]. Investigated treatments were: (1) plasma vitrification, including centralized treatment and plasma ex situ; (2) fuel-based vitrification in an induction furnace; (3) water washing treatment followed by rotary furnace combustion (co-treatment in the cement industry) and (4) conventional solidification and landfill disposal. The results showed that fly ash after plasma vitrification showed a large decrease in volume and mass, producing compact and strong vitreous slag, as well as that heavy metals showed a very small leaching rate. Also, organic compounds such as dioxins are destroyed due to the application of high temperatures. Regarding the toxicity to ecosystems and human health, the application of plasma vitrification technology has the smallest impact on the environment, while the application of a rotary furnace has the greatest impact.

Lee et al. [75] vitrified the flocculate obtained from the treatment of petroleum catalyst wastewater. The flocculate was directly vitrified at 1350°C without the addition of any additives, and results of the XRD analysis confirmed that that is possible. The chemical durability of the vitrified product can be compared to commercial sodium-lime silicate glass, but the melting viscosity of the glass was high, so shaping and refining of the melting glass was little difficult.

3. CONCLUSION

Environmental pollution with various organic and inorganic substances is a problem worldwide. A large number of technologies have been developed for the remediation treatment of contaminated soil or waste, and one of them is the vitrification process. The vitrification process is an efficient method based on heat treatment of contaminated soil or waste at high temperatures, without or with the addition of additives, where the soil melts and creates a stable glass mass that has good mechanical resistance, is chemically resistant and immobilizes contaminants, preventing their further negative impact on the environment. This technique can be applied in the treatment of different types of hazardous waste, such as: radioactive waste, tailings, slag, sludge, municipal (organic) waste, dust from electric arc furnaces, fly ash, etc. Also, if the composition of some of these wastes do not completely satisfy the necessary criteria for use in the vitrification process, it is possible to combine different types of waste resulting in a stable glass or glass-ceramic product. Although the obtained glass product can be reused in industry, the remediation of contaminated soil or solid industrial waste by the vitrification process is very expensive, so this method is less commonly used.

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IZVOD

Vitrifikacija kao metoda remedijacije zemljišta

Primenom tehnike vitrifikacije mogu se tretirati različite vrste kontaminiranog tla i opasnog otpada koji imaju negativan uticaj na životnu sredinu i zdravlje ljudi. Neki od otpada koji se mogu tretirati postupkom vitrifikacije su: radioaktivni otpad, jalovina, šljaka, mulj, komunalni (organski) otpad, prašina iz elektrolučnih peći, leteći pepeo itd. Postupak vitrifikacije zasnovan je na termičkoj obradi kontaminiranih zemljišta ili otpada na temperaturi od 1400-2000°C, uz dodatak agenasa za vitrifikaciju, pri čemu se zemljište/otpad topi i formira stabilna amorfn masa. Proces vitrifikacije prenosi toksične elemente u amforni proizvod koji ima dobru mehaničku otpornost, hemijski je otporan i imobilize zagađivače, sprečavajući na taj način njihov dalji negativni uticaj na životnu sredinu. U zavisnosti od lokacije procesa, vitrifikacija može biti in situ ili ex situ.

Ključne reči: vitrifikacija, kontaminirano zemljište, otpad, zaštita životne sredine.

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