University of Belgrade, Technical faculty in Bor
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DISSOLUTION OF GLASS MADE FROM COAL FLY ASH, GLASS CULLET AND CALCIUM CARBONATE

Veljko Savić[1#], Vladimir Topalović[1], Jelena Nikolić[1], Srđan Matijašević[1], Snežana Zildžović[1], Snežana Grujić[2], Sonja Smiljanić[2,3]
[1] Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia
[2] Faculty of Technology and Metallurgy, Belgrade, Serbia
[3] Institute "Jožef Stefan", Ljubljana, Slovenia

ABSTRACT – Coal fly ash represents huge ecological problem and its reutilization should be considered. Vitrification of coal fly ash could be one of the solutions. The glass was obtained by melting a mixture of coal fly ash, glass cullet and $CaCO_3$ at T = 1500 °C and quenching the melt in air. The chemical durability of the glass was determined by dissolution test in distilled water, HCl and NaOH at T = 95 °C for t = 2 h. It was shown that dissolution rate of glass in distillated water and NaOH is negligible, while in HCl solution was shown significant mass loss.

Keywords: Coal Fly Ash, Glass, Dissolution.

INTRODUCTION

In Serbia, around 8 million tons of ash and slag, each year, has been generated (thermal power plants burn about 40 million tons of lignite annually and produce about 6 million tons of fly ash) [1], where about 2.5% is used in the cement industry. The development of glass and glass-ceramic based on various waste materials is an important area of research because the waste materials can be used to obtain glassy or glass-ceramic materials whose properties are comparable to the properties of commercially available materials.

Fly ash is generated in the process of burning coal in thermal power plants. The incombustible part of the coal matter after combustion stays at the bottom of the furnace as bottom ash and slag, and the part leaves the plant with flue gases and is collected on electrostatic filters, and is called fly ash. Fly ash is mostly disposed of in landfills, but due to its chemical composition where SiO_2, Al_2O_3, CaO, and Fe_2O_3 are dominant oxides, it can be used for road construction, in the cement industry and for obtaining glass and glass-ceramic. Therefore, it is important to find a solution for recycling the generated fly ash and remediation of landfills.

Worldwide, more than 65% of fly ash produced from coal power stations is disposed of in landfills and ash ponds. Large quantities of fly ash are deposited in landfills, which have to be wet to minimize the spread of dust into the environment. In all countries in the world, this is a huge economic and environmental problem. The negative

[#] corresponding author: v.savic@itnms.ac.rs

environmental impacts of fly ash landfilling are primarily connected with toxic metals that it contains.

The goal in the European Union is to phase-out coal consumption by 2030 and to increase the production of energy from renewable sources [2]. Some European and Western Balkans countries will still use coal thermal power plants after 2030 to produce energy. Even after the closing of currently operating coal-fired thermal power plants, there will be fly ash that isn't reutilized as secondary raw material and is disposed of in landfills or ponds. Landfills and ponds take great areas of land and represent a potential problem for human health, underground water, nearby crops and the whole ecosystem.

From the ecological point of view, during the high-temperature treatment of the fly ash in order to obtain glass, the destruction of the organic pollutants occurs. Vitrification is a known technology for the inertisation of various industrial residues that permits to obtain stable glasses [3,4]. By properly selecting the glass composition and thermal treatment this method gives possibility for re-utilization of the glass or glass-ceramic as raw material for different industrial applications. Additionally, heavy metals present in the glass batch can be successfully immobilized in the glassy matrix. These products can be classified as inert materials, which supports their potential use as eco-friendly building construction materials. Obtaining the glass by recycling of coal fly ash in the glass production includes three main advantages: using a zero cost material, the conservation of natural resources and the elimination of fly ash. The fly ash based glass materials can be used in building and construction, as well as a raw material for making glass-ceramic products [5].

Due to a good mechanical, chemical, and thermal properties, a wide application of glass and glass- ceramic materials made from industrial waste is possible, especially in the building industry.

EXPERIMENTAL

The glass was prepared by a standard melt quenching procedure. Coal fly ash, glass cullet from bottle glass and $CaCO_3$, were mixed and homogenized in an agate mortar in 37.5:37.5:25 ratio. The melting was performed in an electric furnace in zirconium silicate crucible at T = 1500 °C for t = 1 h and the glass was obtained by quenching of the melt on a steel plate. The obtained dark sample was black without visible gas bubbles. The chemical analysis was performed using spectrophotometer AAS PERKIN ELMER Analyst 703. The powder X-ray diffraction (XRD) analysis confirmed that the quenched melts were vitreous. The chemical durability of glass was estimated in distilled water, 0.01 M HCl and 0.01 M NaOH, respectively. In these experiments 2 g grained samples with sizes from 0.3 to 0.5 mm were placed in contact with 70 ml solution for 2 h at T = 95 °C [6]. Solutions were analyzed and loss of elements from glass was determined. The microstructure of the glass samples before and after leaching tests was examined using scanning electron microscope (MIRA3 XM TESCAN). The samples were gold coated using Leica SCD005 device.

RESULTS AND DISCUSSION

The chemical composition of the coal fly ash and glass cullet is shown in Table 1. Due to low concentration of glass network modifier cations viscosity of melted fly ash and glass cullet is very high, and it is imposible to pour it.

Table 1 Chemical composition of the coal fly ash and glass cullet

Sample	oxides	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	Cr_2O_3	L.o.i
Coal fly ash	mass%	55.33	25.11	6.26	1.42	0.32	1.23	7.08	0.50	/	2.52
Glass cullet	mass%	71.8	2.46	10.21	2.05	12.74	/	0.42	/	0.117	0.2

In order to make melt pourable chemical composition of batch should be altered introducing modifier cations in the batch using calcium carbonate.The homogenous dark glass was obtained by melt casting on steel plate is shown in figure 1.

Figure 1 Obtained glass sample

XRD patterns are shown in Figure 2.

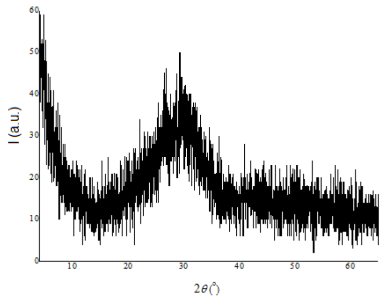


Figure 2 XRD patterns of the obtained glass sample

No crystalline phase was found which confirms that obtained material is amorphous. The chemical composition of the glass sample is shown in Table 2.

Table 2 Chemical composition of obtained glass

Oxide	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	Fe_2O_3	Cr_2O_3
Mass %	49.54	10.58	32.88	1.58	1.44	0.72	0.34	2.68	0.08

Obtained glass has high concentration of glass network modifier cations which enabled optimal viscosity for melt to be poured.

The results of dissolution test are shown in table 3.

Table 3 Dissolution test of fly ash glass

Solution	Weight loss (%)
Distillated water	negligible
0.01 M NaOH	negligible
0.01 M HCl	20.15

The dissolution of glass matrix is a complex process that consists of several characteristic steps. There are two possible mechanisms, explaining the release of cations from the glass structure in different aqueous solutions, ion-exchange leaching, and matrix dissolution [7].

In alkaline media, the dissolution of the Si-glass network by which the glass dissolves directly into the solution takes place.

In neutral and acid media, the initial dissolution is characterized by ion exchange processes between protons in solution and glass network modifier cations, resulting in the formation of a hydrated layer, through which the aqueous species diffuse. Therefore, in neutral and acid media, the initial stage of the reactions is the diffusion of alkali ions through the glass network and across the leached layer into the solution [8].

At the same time, the glass network composed of network forming tetrahedrons hydrolyzes, causing the release of cations into solution. As a consequence, the complete destruction of the polyanionic glass network occurs.

In figure 3 is shown the percentage of elements released during leaching in acid media and in figure 4 is shown SEM micrograph of glass surface before and after leaching in acid media.

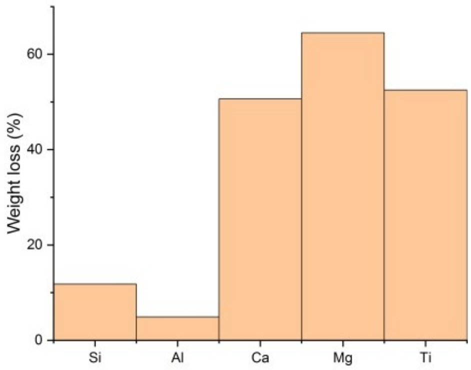
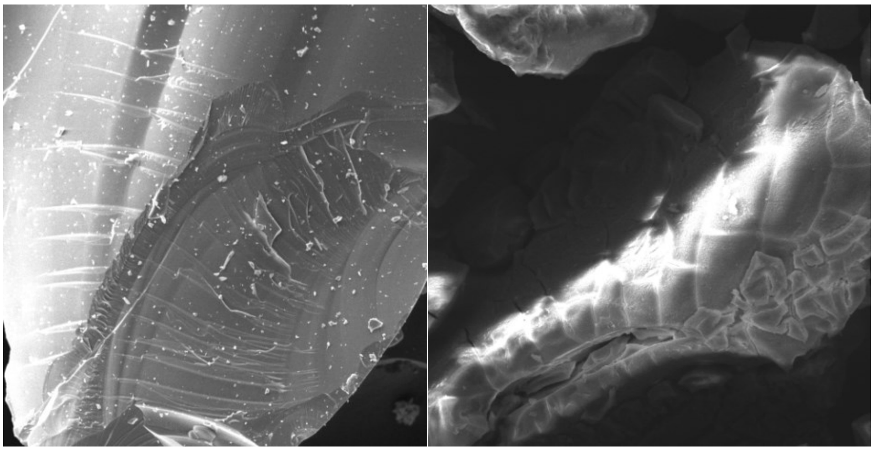


Figure 3 Weight loss of elements of glass sample leached in acid media

Results from figure 3 have shown that ion exchange process between protons in solution and glass network modifier cations is dominant mechanism of glass dissolution. More than 50% of glass network modifier cations leached in acid solution.

In figure 4 is shown change of glass surface after leaching test in acid media. Gel - like structure is formed on the surface of the glass, probably due the destruction of the polyanionic glass network.



a) b)

Figure 4 SEM micrographs a) before and b) after dissolution test in acid media

CONCLUSION

The glass was successfully obtained using coal fly ash, glass cullet and $CaCO_3$ as raw materials. The results of laboratory experiments have shown that the vitrification process can be considered as promising solution for utilization of industrial waste. The results of dissolution test of grained glass samples revealed a high durability in distilled water and in alkali solution. Weight loss determined after dissolution in HCl solution has shown a poor acid durability of the glass. Analysis of acid solution after leaching test has showed that ion exchange processes between glass network modifier cations and acid solution is dominant mechanism of glass dissolution. Obtained glass can find potential application as thermal and sound insulator, construction materials and wall tiles.

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