

Utilization of Galvanic Sludge as Raw Material for Production of Glass

Ozgul Dere Ozdemir¹⁺, Aysel Kanturk Figen¹ and Sabriye Piskin¹

¹ Department of Chemical Engineering, Yıldız Technical University, 34210 Davutpasa, Istanbul, Turkey

Abstract. Galvanic sludge is a filter press cake that generated at the end of the waste water treatment process. It is very dangerous to human health and environment due to high heavy metal concentration. Treatment sludge of Bergama-Ovacık Gold Mine treatment plant is generated from waste water treatment process like galvanic sludge. High content of SiO₂ of this waste makes it desirable glass network former additive. In this study, vitrification of galvanic sludge was investigated by using gold mining treatment sludge, H₃BO₃ and Na₂CO₃. For this purpose, the effect of 10% and % 20 galvanic sludge additives on vitrification properties was determined by X-Ray Diffractometer (XRD) and Fourier Transform Infrared Spectrometer (FT-IR) instruments and Toxicity Characteristic Leaching Procedure (TCLP) Analysis method.

Keywords: Galvanic sludge, glass, vitrification, boron, characterization

1. Introduction

Metal plating is one of the important industrial branches which have used to gain high-level resistance against the environmental impact on the material, give a decorative image and provide special surface properties [1]. About million dollar economical lost was occurred all around the world due to corrosion [2].

Also, in this area production was carried out from gift shop to heavy industry in a wide range, so it has great importance. Galvanic sludge was taken place in class of hazardous waste due to containing heavy metals [3]. Therefore it is treated human and environment health.

The storage of uncontrolled industrial solid wastes is generated a big problem in Turkey, like as most of countries [4]. On the other hand transportation, manipulation and disposal cost of this sludge is very significant in terms of production cost [5]. Hence, it is a big problem for this industry because of its' uneconomic situation.

One of the potential uses of this hazardous waste is a raw material for production useful and environmentally sensitive materials [6]. Glass and glass-ceramic materials were obtained from industrial wastes such as galvanic sludge, fly ash, bottom ash, steel fly ash, red mud, zinc metallurgy waste and boron waste to recovery wastes by vitrification [7-14]. In addition to these wastes, vitrification is preferred method for radioactive wastes [15-17].

Vitrification term is coming from Latin word "vitrum", meaning glass. The simplest definition, it is a thermal disposal process that is carried out conversion to glass and glassy materials at high temperatures, 1000-1600 °C, in which destruction of hazardous compounds in the waste and to ensure a safe and immobilization. It is examined in to 2 groups as electricity heat process and fossil fuel heat process [18].

The advantage of production glass materials from wastes is homogeneously incorporation lots of element as in periodic table especially heavy metals.

Therefore the wastes that have very complex structure can be recovered [19]. In addition, this process does not generate wastes.

Corresponding author. Tel.: +90 383 4771; fax: +90 383 4725
E-mail address: odere@yildiz.edu.tr

In this research, recovery of galvanic sludge that is generated about tones in glass production by vitrification method was investigated. For this purpose, another waste, Bergama-Ovacık Gold Mine treatment sludge (BOGM-TS) was used as SiO₂ source. Mineralogical structure, functional groups and toxicity properties of obtained products were investigated.

2. Materials and Methods

2.1. Waste preparation

Contributions Galvanic waste used in this study was supplied by metal plating facilities located in Istanbul, Turkey. Galvanic sludge samples dried at 105 °C, ground and sieved with 63 µm ASTM standard sieve.

BOGM-TS used as SiO₂ source was dried at 105 °C, grounded, sieved to 63 µm grain size. Riedel-de Haene brand Na₂CO₃ and 99.9 % analytical grade H₃BO₃ supported Eti Mine Beypazarı as additive materials. All the raw materials and additives were homogenated by mixing (Fig. 1).

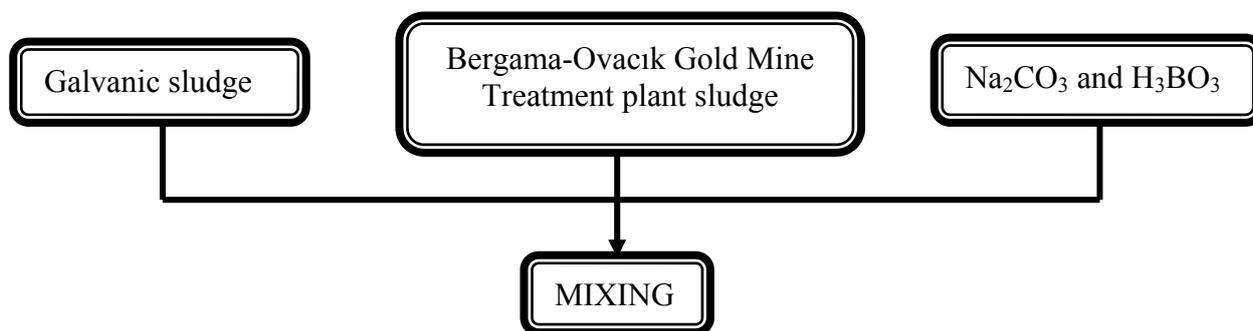


Fig.1: Raw Material Preparation

2.2. Vitrification

Vitrification of galvanic sludge was performed at 1350 °C by using refractor melting pot in Conrad Naber brand high temperature furnace. 2 different experiments were carried out (Table 1) and the melt obtained at 1350°C was cooled to room temperature.

Table 1. Composition (%) of raw materials prepared at different ratio.

	Galvanic sludge (%)	BOGM-TS (%)	Na ₂ CO ₃ (%)	H ₃ BO ₃ (%)
Experiment -A	10	67	7	16
Experiment-B	20	57	7	16

An amount of sample was taken from obtained product for characterization and it was rendered powder by using Retch brand ball milling grinder.

2.3. Product characterization

Characterization of obtained products as a result of vitrification was performed by XRD and FT-IR instruments. Leaching characterization was carried out by TCLP Analysis with Inductively Coupled Plasma-Optic Emission Spectrophotometer (ICP-OES).

2.3.1. XRD analysis

Crystal phase analysis of obtained glass products was performed by Philips Panalytical X'Pert Pro brand XRD instruments. It has Cu K α X-Ray source and 40 mA and 45 kV operation conditions. XRD patterns were recorded at 5-90 ° diffraction angles and were scanned in ICSD (Inorganic Crystal Structures Database) and ICDD (The International Centre for Diffraction Data) databases. XRD analysis results were given at Fig. 2.

2.3.2. FT-IR analysis

Perkin Elmer brand Spectrum One model FT-IR instrument was used to analyze functional groups of glass products. Powder sample was pressed by mixing 1/100 ratio Potassium Bromide (KBr). Measurements

were performed 4000-450 cm^{-1} wave number and 8 cm^{-1} resolution. Obtained FT-IR spectrums are given in Fig. 3.

2.3.3. TCLP analysis

TCLP Analysis was performed with regard to EPA 1311 [20] Standard method to investigate metal release from obtained glass material and leaching solutions were analyzed by ICP-OES.

In terms of EPA 1311 standard method, leaching solution was consisted of 5.7 ml acetic acid and 64.3 ml 1 N NaOH in 1 L of solution. Grounded glass samples as <9.5 mm placed in erlen mayer. Leaching solution was added in order to keep a liquid to solid ratio of 20 (L/S=20). Afterwards, erlen mayer is tightly closed and stored for 18 h. Leaching solution was filtered by 0.6-0.8 μm filter paper and heavy metal concentration was determined by ICP-OES (Table 2).

3. Results and Discussion

As a result of 2 different experiments and 2 different color glasses were obtained. Experiment-A has dark green, Experiment-B has Brown-purple color.

Result of XRD analysis, amorphous structures that glass materials characteristic properties was attracted to attention. As a different from Experiment-A, it is seen that there is a crystal phase in Experiment-B.

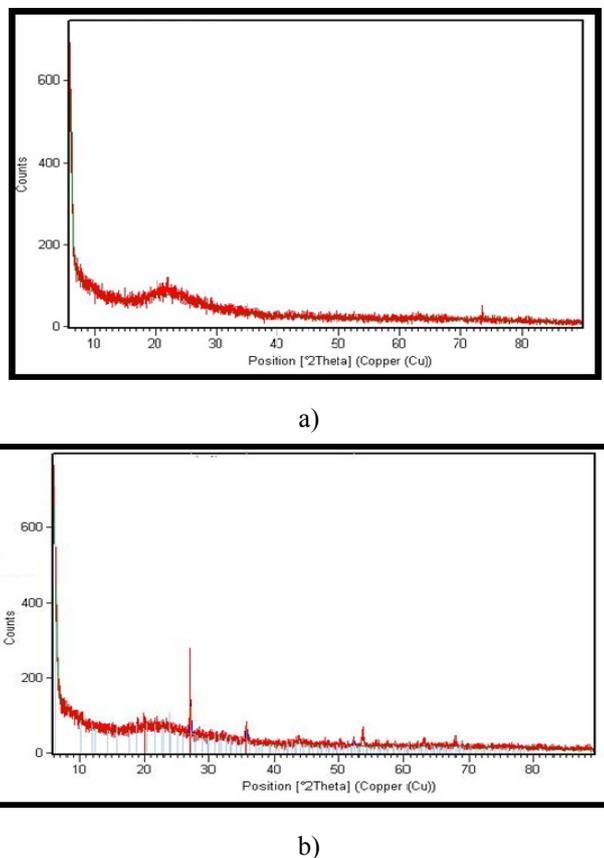


Fig. 2. XRD Analysis of obtained glass products; a) Experiment- A, b) Experiment-B

But it is indicated that this phase determined zirconium was formed because of the interference of melting pot which is included zirconium in the product during the glass production process.

According to FT-IR spectrums given in Fig. 4, a band was seen at 3435.45 and 3443.47 cm^{-1} respectively both Experiment-A and Experiment-B. This band was corresponding to H_2O molecules [21]. But it is an unexpected band. For this reason it is determined that this samples were absorbed humidity. Weak bands at 2853.44-2922.41 and 2853.44-2918.10 cm^{-1} can be attributed P-O-P stretching vibrations in both 2 experiments [21]. The bands at 798 and 1083.21 cm^{-1} in Experiment-A and 801.08 and 1071.78 cm^{-1} in Experiment-B have been assigned to Si-O bands [21]. Bands at 798 and 801.08 cm^{-1} should be correlated with Si-O-Si (SiO_2) bending vibration also 1083.21 and 1071.78 cm^{-1} should be correlated with SiO_4

asymmetric vibration [21]. Therefore, bands were seen at 1416.49 and 1411.87 cm^{-1} assigned to sodium oxide (Na_2O) [7].

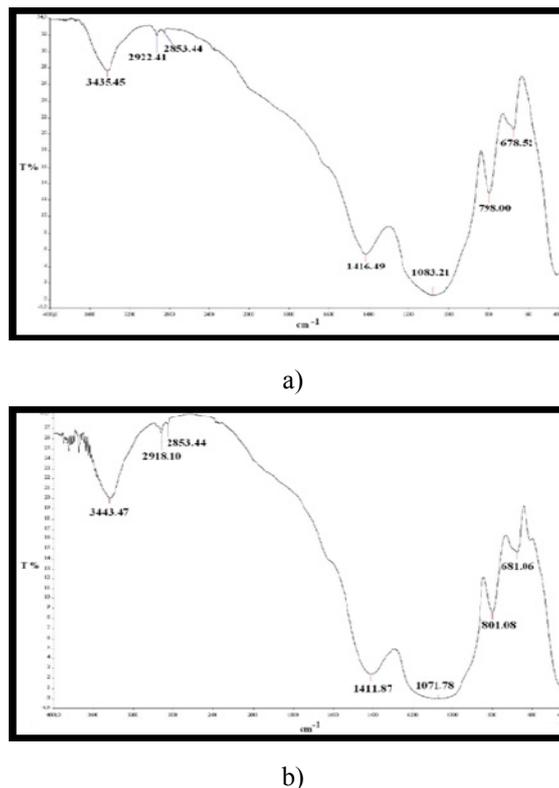


Fig. 3. FT-IR Spectrums of obtained glass products

TCLP Analysis, carried out to determine the toxic properties of obtained product, results are seen in Table 2. As it seen in table, metal release of heavy metal of glass product was under the United States Environmental Protection Agency (US EPA) limit values. Consequently, this product has not harmful in terms of environment.

Table 2. TCLP Analysis results of obtained product

	Cr (ppm)	Cd (ppm)	Pb (ppm)
Experiment-A	0.121	0.021	0.004
Experiment-B	0.107	0.009	0.078
EPA limit values (ppm)	5	1	5

4. Conclusion

In this study, the usage of galvanic sludge in glass production is investigated. It is seen that, amorphous properties of glass product were not destroyed after 10 % and 20 % galvanic sludge addition.

It was evaluated in terms of environment, when the galvanic sludge contains high concentration of heavy metals was used in glass production, metal release according to TCLP Analysis were under the EPA limit values. So hazardous waste for environment and another industry waste used for SiO_2 source instead of natural sources was converted to environmental friendly glass products.

5. Recommendations

In addition to studies, it is considered that in different color and properties glass products can be developed by changing the additives amount.

6. Acknowledgements

Vitrification studies were supported by Remsan Refractory Material Industries Inc. especially Fehmi Kula R&D Laboratory chef.

7. References

- [1] K.L. Wang, Y.T. Hung, H.H. Lo, C. Yapijakis. Handbook of Industrial and Hazardous Wastes Treatment, CRC Press, 2004.
- [2] http://www.dedekimya.com/web_7046_1/index.aspx
- [3] A. Miškufova, T. Havlik, M. Laubertova, M. Ukašik. Hydrometallurgical route for copper, zinc and chromium recovery from galvanic sludge. *Acta Metallurgica Slovaca*, 2006,12: 293-302.
- [4] V. Ritesh, T.A. Sihorwala. Identification and leaching characteristics of sludge generated from metal pickling and electroplating industries by toxicity characteristics leaching procedure (TCLP). *Environ Monit Assess.* 2003, 84: 193-202.
- [5] F. Vegliò, R. Quaresima, P. Fornari, S. Ubaldini. Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning. *Waste Manage.* 2003, 23(3): 245-252.
- [6] E. Mejia-Ramirez, A. Gorokhovskiy, J.I. Escalante-Garcia. Crystallization behavior of glasses in the system of Na₂O–CaO–MgO–Fe₂O₃–Al₂O₃–SiO₂ with high contents of nickel oxide. *Journal of Non-Cryst Solids.* 2007, 353: 366-373.
- [7] A.C. Silva, S.R.H. Mello-Castanho. Vitrified galvanic waste chemical stability. *J Eur Ceram Soc.* 2007, 27:565-570.
- [8] A.C. Silva, S. Mello-Castanho. Incorporation of galvanic waste (Cr, Ni, Cu, Zn, Pb) in a soda-lime-borosilicate glass. *J Am Ceram Soc.* 2008, 91(4): 1300-1305.
- [9] M. Erol, S. Küçükbayrak, A. Ersoy-Meriçboyu. The influence of the binder on the properties of sintered glass-ceramics produced from industrial wastes, *Ceram Int.* 2009, 35: 2609-2617.
- [10] E. Bernardo, L. Esposito, E. Rambaldi, A. Tucci, Y. Pontikes, G.N. Angelopoulos, Sintered esseneite-wollastonite-plagioclase glass-ceramics from vitrified waste. *J Eur Ceram Soc.* 2009, 29: 2921-2927.
- [11] M. Pelino. Recycling of zinc-hydrometallurgy wastes in glass and glass ceramic materials. *Waste Manage.* 2000, 20: 561-568.
- [12] J. Sheng. Vitrification of borate waste from nuclear power plant using coal fly ash: (I) Glass Formulation Development. *Fuel* 2001, 80: 1365-1369.
- [13] L. Barbieri, A.C. Bonamartini, I. Lancellotti. Alkaline and alkaline-earth silicate glasses and glass-ceramics from municipal and industrial wastes. *J Eur Ceram Soc* 2000, 20: 2477-2483.
- [14] M. Romero, J. Ma Rincón. Preparation and properties of high iron oxide content glasses obtained from industrial wastes. *J Eur Ceram Soc* 1998,18: 153-160.
- [15] J. Park, M. Song. Feasibility study on vitrification of low and intermediate level radioactive waste from pressurized water reactors. *Waste Manage* 1998, 18: 157-167.
- [16] W.L. Gong, W. Lutze, A. Abdelouas, R.C. Ewing, Vitrification of radioactive waste by reaction sintering under pressure, *J Nucl Mater*, 1999, 265: 12-21.
- [17] K. Uruga, K. Sawada, Y. Enokida, I. Yamamoto. Vitrification of high-level radioactive waste considering the behavior of platinum group metals. *Prog Nucl Energ* 2008, 50: 514-517.
- [18] G. Demir, Çinko endüstrisi atıklarının termal yöntemle arıtımı, Master Thesis, On Dokuz Mayıs University, Institute of Science and Technology. Samsun, 2007.
- [19] G. Scarinci, G. Brusatin, L. Barbieri, A. Corradi, I. Lancellotti, P. Colombo, Hreglich S, R. Dall'Igna. Vitrification of industrial and natural wastes with production of glass fibres. *J Eur Ceram Soc* 2000, 20: 2485-2490.
- [20] EPA 1311, US EPA, US Environmental Protection Agency Method 1311, Toxicity Characteristic Leaching Procedure. Washington DC, 1992.
- [21] E. Erdik. Spectroscopic Methods In Organic Chemistry. Gazi Kitapevi, 1993.