# Valorization of Waste Produced in the Processes of Plating Technologies within a Vitreous Matrix

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*The paper presents the valorization of galvanic wastes with nickel content. This process consists in waste incorporation in a borosilicate glass, and the obtaining of some glasses which may be used in industry.There were prepared glasses using both wastes and natural material as raw materials.The dissolving of the samples was carried out in electric furnance at a temperature of 1400°C for three hours. The pre-roasting of the samples was accomplished at the temperature of 600°C for 25 minutes, and their cooling in the same time with the furnance. For the samples obtained the hydrolytic stability through the conductometric method and the viscosity through the penetrometric method were determined.The experimental results reveal a good chemical stability of the glasses obtained from the wastes and a viscosity that increases with the decrease of both the nickel oxide content and the temperature.*

*Keywords: galvanic wastes, nickel, borosilicate glasses*

The processing of the wastes by incorporating in the vitreous matrix consists mainly in their incorporation by dissolving in a glass with a specific composition (primary glass), synthesized from certain raw materials capable of forming a vitreous structure. By this procedure can be incorporated in vitreous matrix a great variety of chemical compounds existent in the waste, and also can be obtained some glasses, which may be used in industry [1]. There are existing compounds that cannot be incorporated in such glasses because one is aware of the difficulties of integrating the wastes in which there are elements such as: molybdenum, plutonium, ruthenium etc.; also, there is of course a limited amount of incorporated substances in vitreous matrix.

The vitrification of hazardous residues has been industrially applied for the treatment of electroplating sludge [2,3], leather industry wastes [4], wastes from mixed oxides fuel processing [5], radioactive wastes [6-10] and for the inertization of ashes from urban resulted garbage incinerators [11-19].

The vitrification of waste has three main advantages: first, the use of a zero cost raw materials, second, the conservation of natural resources, and thirdly, the elimination of the waste with the protection of the environment [20].

The waste vitrification process is more complex than the simple dissolution of waste components in the glass matrix. The melting high temperature can reduce chemically some melt components to their oxides forms. Consequently, it is inevitable that the oxides from harmful waste to interact with the oxides from the glass raw materials resulting a modified glass [22].

The composition of basic glass and the capacity of incorporation in the melting of the waste constitute the determinant factors that one has to take into consideration. The vitreous matrix should be able to tolerate minor variations of waste composition. Also, the glass matrix should have high chemical and thermal stability [5, 20].

The composition of a specific type of chosen glass is the result of a 'compromise' between the technological feasibility and the security requisitions of the final storing. But the resistance to the water chemical attack is essential. In fact, the water represents the main vector of degradation in spite of all the precautions taken to avoid it.

The use of the borosilicate glass constitutes an efficient solution from technical and economic viewpoints, bearing in mind the advantages offered, on the one hand, by the oxide composition, especially by the presence of boron oxide in 11 – 12% concentration, which confers special properties to the glass and, on the other hand, the energy incorporated, which may have a contribution to the reduction of fuel consumption [8]. The selected matrix has a low melting point as the incorporation of waste in base glass matrix usually leads to increase in processing temperature of vitrified waste product.

The paper presents the valorization of galvanic wastes with nickel content within a vitreous matrix and the obtaining of some glasses useful in industry.

## Experimental part

There have been prepared glasses using wastes as well as glasses from natural raw material. Table 1 presents the composition of borosilicate glass waste.

**Table 1**
COMPOSITION OF BOROSILICATE GLASS WASTE

| Oxides | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | $B_2O_3$ | $Na_2O$ | $K_2O$ | BaO |
|---|---|---|---|---|---|---|---|---|
| % | 74.1 | 4.9 | 0.03 | 1.55 | 10.9 | 6.8 | 1.35 | 0.37 |

**Table 2**
ELEMENTAL CHEMICAL ANALYSIS OF WASTE WITH NICKEL CONTENT

| Al % | Cd % | Total Cr % | $Cr^{6+}$ | Cu | Total Fe % | $Fe^{2+}$ | Mg | Mn |
|---|---|---|---|---|---|---|---|---|
| 17.1 | 0.05 | 9.8 | <0.05 | 12.3 | 16.1 | 0.22 | 9.8 | 0.06 |
| **Mo %** | **Ni %** | **P %** | **Pb %** | **Sb %** | **Si %** | **Sn %** | **Ti %** | **Zn %** |
| <0.05 | 17.2 | 1.4 | 0.4 | 0.02 | 1.2 | 0.28 | 0.04 | 14.5 |

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Table 3

COMPOSITION OF THE RAW MATERIAL FOR THREE SAMPLES WITH NICKEL WASTE (DENOTED AS $N_1$, $N_2$ and $N_3$)

| Composition (g) | $N_1$ | $N_2$ | $N_3$ |
|---|---|---|---|
| Sand | 120.98 | 120.98 | 120.98 |
| $Na_2CO_3$ | 62.8 | 62.8 | 62.8 |
| $K_2CO_3$ | 9.68 | 9.68 | 9.68 |
| $H_3BO_3$ | 4.82 | 4.82 | 4.82 |
| $Na_3AlF_6$ | 6.23 | 6.23 | 6.23 |
| ZnO | 26.65 | 26.65 | 26.65 |
| Nickel waste | 0.6 | 0.9 | 2.8 |
| Borosilicate glass waste | 12.7 | 12.7 | 12.7 |
| Total | 244.46 | 244.76 | 246.66 |

Table 4

COMPOSITION OF THE RAW MATERIAL FOR THREE SAMPLES WITH NICKEL NITRATE (DENOTED AS $M_1$, $M_2$, $M_3$)

| Composition (g) | $M_1$ | $M_2$ | $M_3$ |
|---|---|---|---|
| Sand | 120.98 | 120.98 | 120.98 |
| $Na_2CO_3$ | 62.8 | 62.8 | 62.8 |
| $K_2CO_3$ | 9.68 | 9.68 | 9.68 |
| $H_3BO_3$ | 4.82 | 4.82 | 4.82 |
| $Na_3AlF_6$ | 6.28 | 6.23 | 6.23 |
| ZnO | 26.65 | 26.65 | 26.65 |
| Nickel nitrate $Ni(NO_3)_2$ | 0.6 | 0.87 | 2.16 |
| Borosilicate glass waste | 12.7 | 12.7 | 12.7 |
| Total | 244.51 | 244.73 | 246.02 |

The results of elemental chemical analysis for galvanic waste expressed in gravimetric percentages are presented in table 2.

Some compositions of nickel galvanic waste with different quantities of nickel were prepared and, in the other three compositions which were taken into consideration as evidence, the galvanic waste was replaced with nickel nitrate, respectively.

Tables 3 and 4 present the composition of the raw materials for the samples with nickel waste and the composition of the raw materials for the samples with nickel nitrate.

There have been prepared three samples with 0.6 g, 0.9 g and 2.8 g of nickel galvanic waste, and three corresponding samples with 0.6, 0.87 and 2.16 g $Ni(NO_3)_2$.

The oxide compositions of the studied glasses are presented in tables 5 and 6.

Table 5

OXIDIC COMPOSITION OF THE GLASS SAMPLES WITH NICKEL WASTE CONTENT

| Gravimetric composition (wt. %) | $N_1$ | $N_2$ | $N_3$ |
|---|---|---|---|
| $SiO_2$ | 55.82 | 56.25 | 56.45 |
| CaO | 0.12 | 0.12 | 0.12 |
| BaO | 0.04 | 0.03 | 0.03 |
| $Na_2O$ | 24.15 | 24.10 | 24.03 |
| $K_2O$ | 3.17 | 3.17 | 3.17 |
| $Al_2O_3$ | 0.73 | 0.72 | 0.72 |
| $B_2O_3$ | 1.9 | 1.89 | 1.89 |
| ZnO | 13.98 | 13.53 | 13 |
| NiO | 0.090 | 0.2 | 0.59 |
| Total | 100 | 100 | 100 |

Table 6

OXIDIC COMPOSITION OF THE GLASS SAMPLES WITH NICKEL NITRATE CONTENT

| Gravimetric composition (wt. %) | $M_1$ | $M_2$ | $M_3$ |
|---|---|---|---|
| $SiO_2$ | 55.89 | 56.25 | 56.45 |
| CaO | 0.11 | 0.11 | 0.11 |
| BaO | 0.03 | 0.03 | 0.03 |
| $Na_2O$ | 24.14 | 24.11 | 24.04 |
| $K_2O$ | 3.16 | 3.16 | 3.17 |
| $Al_2O_3$ | 0.72 | 0.72 | 0.72 |
| $B_2O_3$ | 1.89 | 1.89 | 1.89 |
| ZnO | 13.97 | 13.53 | 13 |
| NiO | 0.09 | 0.2 | 0.59 |
| Total | 100 | 100 | 100 |

In order to prepare the mixture charges, the component materials were dried, the galvanic waste and borosilicate glass waste were milled and sieved to a granulation under 0.5 mm, weighted and homogenized by grinding for 20 min.

The samples were vitrified using an electrical furnace with silicon carbide heating rods. The fusions were realized in a melting pot of refractory ceramics, the mixture of raw materials being gradually added beginning with a temperature of 500-600°C. After entire mixture was loaded in the melting pot, the temperature was maintained at 1400°C for three hours for the fusion to reach thermal and compositional equilibrium.

There resulted homogenous, clear and fluid melts with a very good workability that were easily casted in the mould.

The annealing was accomplished at 600°C for 25 min and then leaving the samples inside to cool slowly for 12-14 h.

The oxidic compositions of the studied glasses calculated on the basis of the designed prescriptions are presented in tables 5 and 6.

The following characterizations were done based on the obtained samples: the hydrolytic stability using the conductometric method, and the viscosity using the penetrometric method.

The glass samples for analysis have a grained shape (1 g). It is chosen the fraction of glass powder comprised between two sieves.

The electrical conductance of the glass powder suspension in water was measured using a Radelkis Conductometer.

To determine the glass viscosity and its variation with temperature in the range of large values of viscosity, a the viscosimeter – penetrometer type Telecomed was used with which can be currently measured the viscosity in the $10^8$ – $10^{13}$ dPa range.

The viscosity determination at a given temperature consists in the measurement of the ingression depth of a body with a cylindrical or spherical form and small dimensions into the glass sample at constant temperature and pushing force. Using bodies for penetration made from very hard materials (wolfram carbide) and resistant at high temperature and high pressuring forces, one may extended for the measurement viscosities upto $10^{15}$ dPa.

The equipment shown in figure 1 is composed by the following main elements:

- the thermostated furnance where the sample is introduced;- the penetration device with which the pressuring force is applied and that measures the penetration depth.

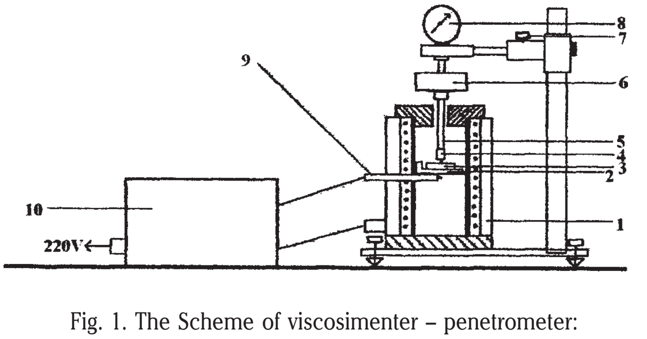


Fig. 1. The Scheme of viscosimenter – penetrometer:
1. Thermostat; 2. Refractory steel plate of furnance; 3. Glass sample; 4. Penetration head; 5. Porcelain stick or quartz glass; 6. Additional load; 7. Screw for vertical shifting; 8. Micrometric instrument for comparison ; 9. Pt-RhPt thermocouple; 10. Temperature programmer

**Results and discussion**

The standardized methods for the measurement of the glass hydrolytic stability do not provide information regarding the kinetics of reaction. Therefore these methods are used for glass compounds that have the same kind of kinetics being applied in the industrial practice for classification of the glasses according to classes of chemical stability.

The conductometric method is applied for glass suspension powder in water function of time, maintaining constantly – from one measurement to the other – the temperature, glass powder amount and its specific surface, as well the water amount from the suspension, therefore (the suspension concentration).

The results obtained for the studied samples are presented in figure 2.

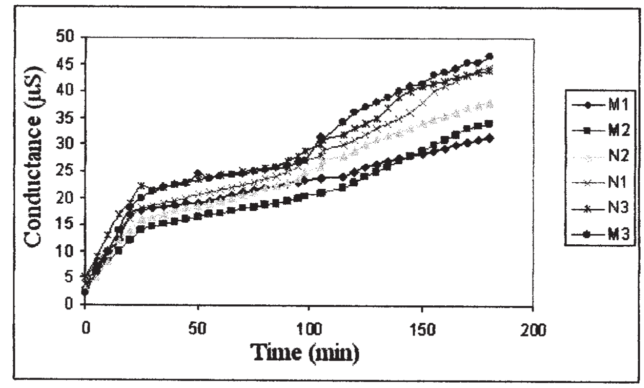


Fig. 2. The glass hydrolytic stability for the six samples listed in table 5 and 6. Temperature 20±2°C, suspension concentration 20g/L

From the analysis of the results it can be observed the significant increase of the conductance of the glass suspension in the first 10-20 min, after which the variation is slower, meaning a possible process of interdiffusion and a hydrolysis reaction developed at lower rate without stabilizing within the time interval of 0-180 min.

This variation of solution conductance in time was observed for all glass compositions.

From figure 2 it results that the glass samples N3 and M3 (which have the highest NiO content) have the highest conductance, i.e. the lowest stability in water, a fact that is illustrated by the increase of the waste content, which is NiO. However, on the whole the values of glass conductance are small enough, which suggests a good chemical stability of these glasses. We mention that the estimation of stability through the measurement of the conductance variation of the suspension of a glass powder in water is a quite qualitative feature and is used for comparison because it is clear that, following the interaction glass – water, only the alkaline ions are sensitive to the water activity within such a short interval of time. The long term stability of the vitreous matrix represents a decisive criterion for the valorization of the wastes produced by electrodeposition processes (technologies).

The figures 3 – 8 present the dependence of viscosity with temperature in the cases of studied glass samples.

The viscosity is a structural and technological parameter of great importance that offers information regarding the estimation of vitrification capacity of melt.

From the examination of the variation with the temperature of the viscosity of the studied glass samples the plotts presented in the figures 3 – 8 shown clearly a linear variation of viscosity with the temperature for all the glasses, with a mean quadratic deviation, $R^2$, comprised between 0.96 and 0.995. The viscosity values of the melts

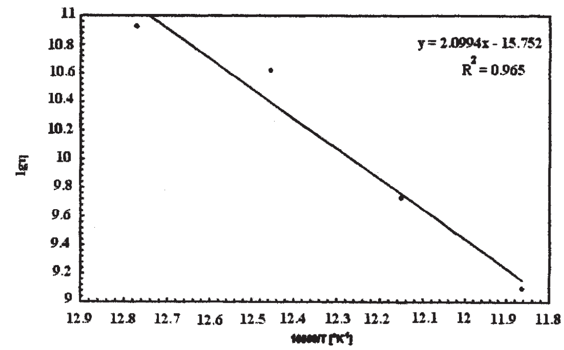


Fig. 3. Variation of viscosity with temperature for the glass sample N1

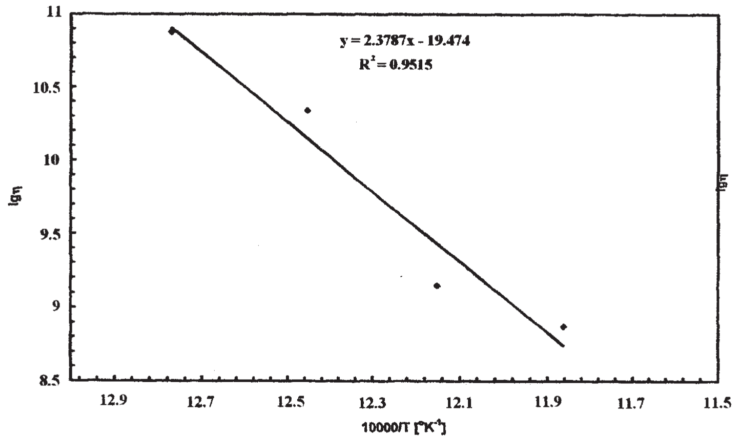


Fig. 4. Variation of viscosity with temperature for the glass sample N2

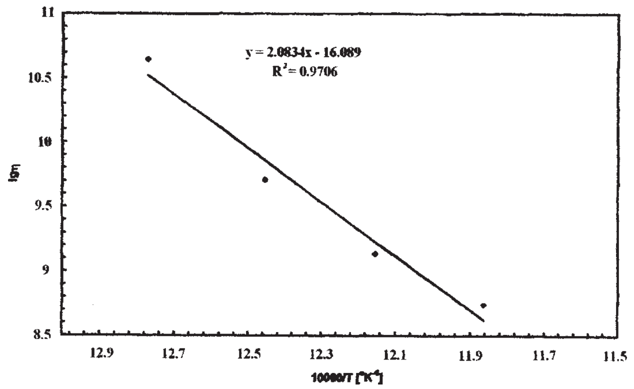


Fig. 5. Variation of viscosity with temperature for the glass sample N3

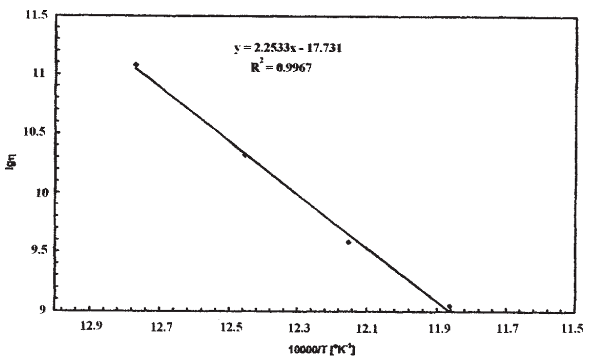


Fig. 6. Variation of viscosity with temperature for the glass sample M1

rapidly increase with the decrease of the temperature, and are specific to the vitrified melts which have a high tendency to form glasses. By keeping constant

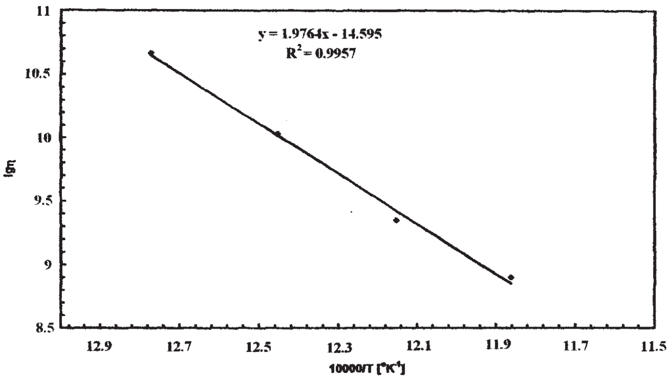


Fig. 7. Variation of viscosity with temperature for the glass sample M2

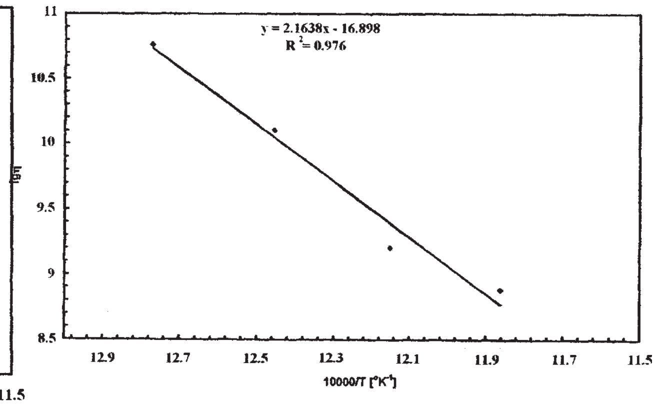


Fig. 8. Variation of viscosity with temperature for the glass sample M3

temperature, the viscosity decreases with the increase of the nickel oxide content, a fact that confirms its activity as a network modifier.

## Conclusions

Our experimental work demonstrated the possibility of processing the wastes resulted in the galvanic technologies by their integration within a vitreous matrix, stable from the chemical point of view and useful from the point of view of the employment.

The hydrolytic stability can be estimated by conductometric measurements; the values small enough of the conductance suggest a good chemical stability of the glasses.

From the examination of the variation behaviour of the viscosity on the temperature for the glass samples it has been concluded that: the variation of viscosity with the temperature for all the glasses is linear and belongs to the melt domain, in which viscosity rapidly increases with the decrease of the temperature that is peculiar to the vitrified melts which have a high tendency to form glasses. Also, for the same temperatures the viscosity decreases with the increase of the nickel oxide content, a fact that confirms its activity as a network modifier.

The obtained results indicate that the galvanic wastes can be exploited for different industrial glasses, being a viable alternative for the obtaining of some products such as glass boards or ornamental objects and, in the same time, for the protection of the environment through the valorization of a potential pollutant source.

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