THE INVESTIGATION OF THE LINE CORROSION OF HOUSEHOLD GLASS IN WATER SOLUTIONS

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Glass is generally considered to be a chemically durable material; nevertheless it is attacked by various corrosive solutions (corrosion process). A special case is so called line corrosion, which is caused by dissolution of surface layers of household glass during automatic washing. The goal of this work was to standardize visual method of homogeneity measurement by Shelyubskii method and to analyze the mechanism of creation of the line corrosion. Both goals consider the influence of temperature of glass melt in melting process on line corrosion. An attempt was made to identify relation between the homogeneity of glass and the extent of line corrosion as the means of estimation of the susceptibility of glass to line corrosion without necessity perform time consuming washing tests. Damaged samples coming from the dishwashing process were analyzed by optical microscopy, scanning electron microscopy and electron dispersive X-ray analysis after the visual control. Line corrosion origin was identified in the forehearth channel as a consequence of dissolution of AZS refractory. The most important parameter influencing the extent of the line corrosion is the temperature of glass melt in the melting tank.

INTRODUCTION

The usual deterioration of glass articles is a result of their corrosion. This occurs when the glass is washed with a detergent in hot water. The underlying physicochemical reactions depend on the composition and structure of glass and the properties of the washing liquid, e.g. composition, pH, temperature and flow rate. The regions consisting from larger lines that are smooth and transparent remain at the surface [1] - this is line corrosion.

The ridges (lines), which are enriched with sodium, magnesium, aluminum and oxygen, dissolve much more slowly than the rest of the glass. Therefore, after washing and dissolution of the surrounding, less durable, glass they become apparent. The ridges are parallel to the long dimension of the slide which presumably is also the direction of drawing operation. It appears that during melting, there are small refractory regions, which, although liquid, do not fully mix with the molten glass. They stretch out and maintain their identity during the formation of the slides by drawing [1].

Glass melting proceeds due to heterogeneous reactions, which inevitably produce inhomogeneous glass. The inhomogeneity means that the properties, such as refractive index, which are very sensitive to the change of composition cannot be measured accurately in such glasses, and inaccurate values may be obtained for others in which property and composition are not linearly related. To meet the high standards often required, inhomogeneities must be eliminated by diffusion, but diffusion alone can deal only with small scale inhomogeneities. Large scale segregation can often occur, and mechanical mixing of the entire melt is needed to produce homogeneous glass. Segregation is often present worst along the depth of the melt because of density differences. Good homogeneity thus requires efficient vertical mixing which can be difficult to achieve in small crucible melts [2].

The aim of this study was to standardize visual method of homogeneity measurement with Shelyubskii method, to investigate the influence homogeneity on the line corrosion and to analyze mechanism of creation of the line corrosion in a household glass of crystalline type.

EXPERIMENTAL

The tableware crystalline glass samples of glass were taken from five various melting aggregates: *a*, *b*, *c*, *d*, *e*. According to EU standards the glass belongs to crystalline glasses. The molten glass from the melting region is transported to the process of shaping through forehearth channels. There are generally two types of forehearth channels terminated either by an outflow bowl or by a platinum elbow. Stirrers are usually installed in the forehearth channels. The main difference between two forehearth channels lies in the use of refractory materials as shown in Table 1.

Table 1. Characteristics of refractory materials used in forehearth channel related to glass samples.

Forehearth channel		Used refractory based on AZS*
1	Ended by outflow bowl	stirrers, plunger, tube, outflow blow
2	Ended by platinum elbow	none

* alumina-zirconia-silica

The samples of glass for estimation of glass homogeneity were taken at the standard process time in the form of drops. The drops were cut into rectangular prisms with dimension 8 × 2 × 1 cm. The faces of bars were ground and polished. Grinding was carried out by Polpur disk with granularity 180. Polishing was carried out by polyurethane foam. According to standards, which are displayed in Figure 1, the values of homogeneity from 0° to 5° were assigned to individual samples. 0° - the best homogeneity, 5° - the worst homogeneity.

At first, the samples were evaluated visually, in full daylight at a bright background. Homogeneity of glass was then specified with the use of Shelyubskii's method. The glass bars were ground and sieved to obtain a fraction of grains 0.16-0.20 mm. The grains were washed in acetone, cleaned in an ultrasonic bath and dried in a drying oven at 50°C.

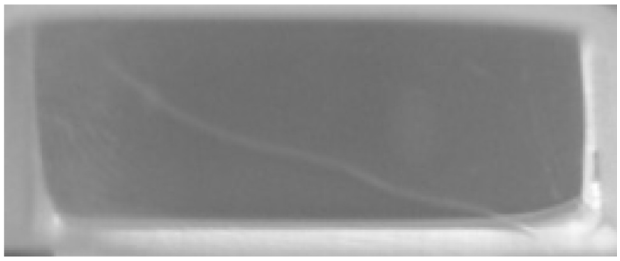
For Shelyubskii method, the spectrometer SPECORD UV VIS (VEB Carl Zeiss Jena, Germany), an automatic double-beam spectral photometer for measurement of the absorption in UV and VIS region was used. The measurements were carried out at the wave length 19.8 nm. The homogeneity of glass is estimated from the transmittance of a filter - temperature relationship (Figure 2) according to the Equation (1).

$$\sigma = \pm Ch\sqrt{\ln\frac{1}{\tau_m}} \qquad (1)$$

where σ - homogeneity of glass, C - constant of immersion liquid (from tables - chlorbenzene - $3{,}814.10^{-4}$), h - half-width of the curve [°C], τ_m - transmittance in the curve's maximum.

The glass samples used for estimation of the glass corrosion were real products having the shape of goblets. Samples were taken at the standard process time of production. Bowl rim of the products was cracked off, finely ground and fired by a set of gas burners. The dishwasher Winterhalter Gastronom GS 24 was used to test the samples. The solution F 30 from Winterhalter containing 5 % of amphotic tensides, 15-30 % phos-

a)



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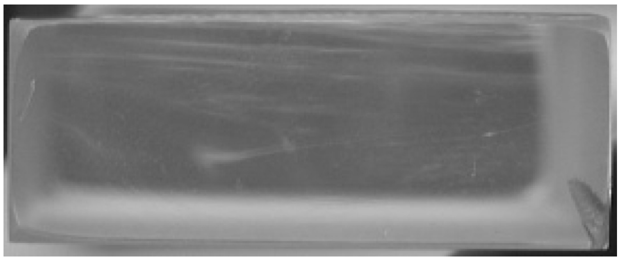


c)

d)

e)

Figure 1. The samples of glass with homogeneity a) 1°, b) 2°, c) 3°, d) 4°, e) 5°.

phates, and small amounts of an alkaline silicate (014-010-00-8) was used as a washing liquid. The dosing of 1.5-2 ml/l was carried out by a dosing machine. Rinsing agent N from Winterhalter with composition: 5 % phosphonate, polycarboxylate, 15-30 % nonionic tensides and conservation additive was also used.

The samples were located into a wash-basket and exposed to a wash cycle with maximum temperature of 65°C. Every 50 cycles the samples were evaluated visually.

To obtain higher resolution and better depth of field view of the surface, optical microscope (Nikon Eclipse ME600), scanning electron microscopy (SEM: JEOL 25S III.) and electron dispersive X-ray analysis (EDXA JEOL 25S III and EDS analyzer Noran,) were used. The glass surface was coated with carbon conducting layer for electron microscopy.

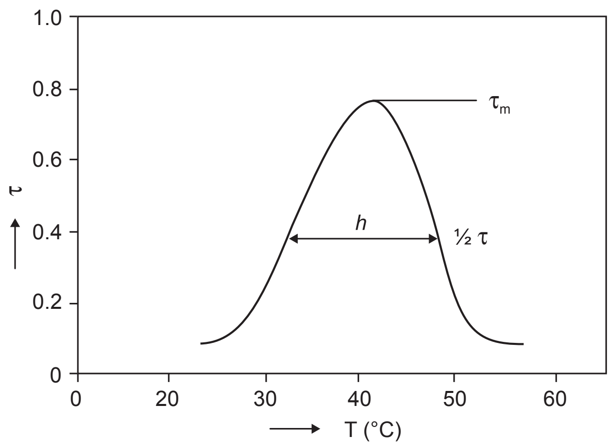


Figure 2. The relationship between transmittance of the filter and temperature.

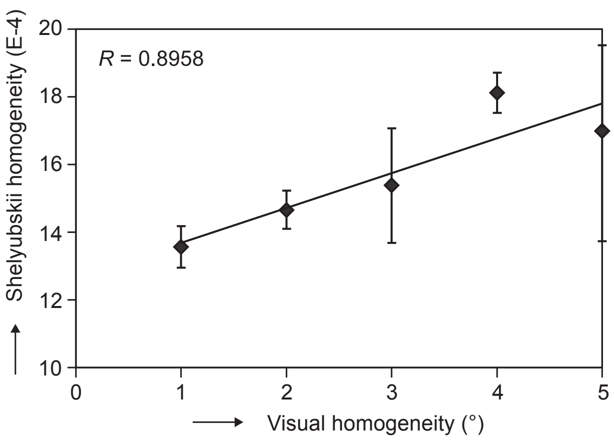


Figure 3. Dependency of results of Shelyubskii and visual homogeneity.

RESULTS AND DISCUSSION

The glass homogeneity determined by visual evaluation is too subjective: therefore the results were verified by the Shelyubskii method. Figure 3 shows the relation between the results from Shelyubskii method homogeneity and the visual homogeneity ranking.

Obviously, there is a clear correlation between the results obtained by two independent methods: higher degree of homogeneity determined by Shelyubskii method corresponds to higher degree of homogeneity estimated visually.

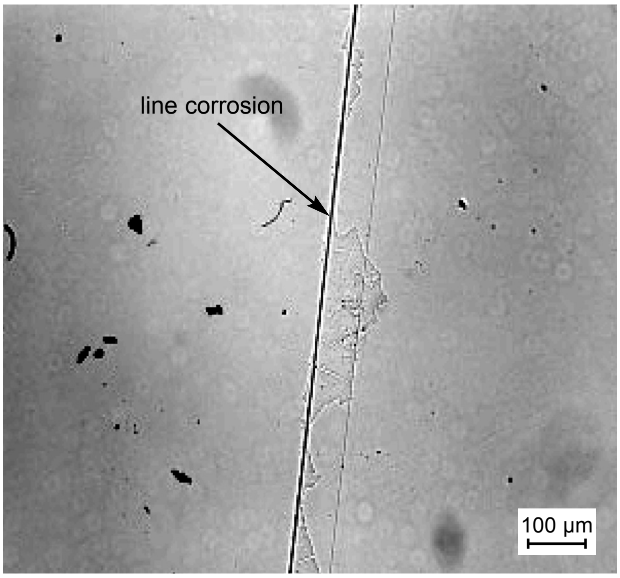
After finding the correlation between the two different methods we conclude that the visual estimation of homogeneity is sufficient for our purposes. This method is faster and cheaper, but includes higher degree of subjectivity.

The samples of tableware glass were washed in an automatic dishwasher. The washing process leads to dissolution of the surface layer and luminous transparent inhomogeneities, so called lines, that become visible at the surface. The intensity of lines was evaluated visually and subsequently by optical microscope (Figure 4). The character of lines is non-diffused (sharp) and suggests that the source of inhomogeneities could be in the forehearth channel [3].

The line corrosion was detected on both inner and outer side of the glass goblet. The SEM analysis has shown that the washed glass surface is formed by highly corroded depressed and the un-corroded elevated (lines) regions. The EDX analysis was used to find out the chemical composition of different parts of glass surfaces. The results of analysis are summarized in Table 2: the results come from the sites specified in the Figure 5a, b.

Table 2. The EDX analysis of damaged glass surfaces (wt.%), for chosen elements exhibiting significant differences in composition according to bulk glass.

Sample	Place of analysis	Al_2O_3	SiO_2	BaO	ZrO_2
	1	*2.0*	*74.8*	*3.1*	-
a	2	1.4	*73.2*	4.3	-
(Figure 5a)	3	*1.7*	70.7	*6.9*	*0.6*
	4 (glass)	1.6	72.5	5.2	-
	1	1.4	72.7	4.8	-
b	2	*1.8*	72.4	4.6	*0.3*
(Figure 5b)	3	1.5	71.2	*6.5*	-
	4 (glass)	*1.8*	72.3	5.2	-
Unwashed glass		1.1	72.4	5.5	-



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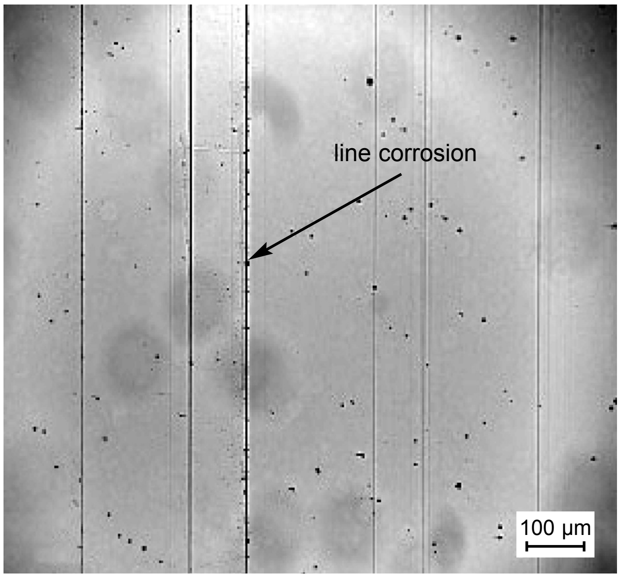
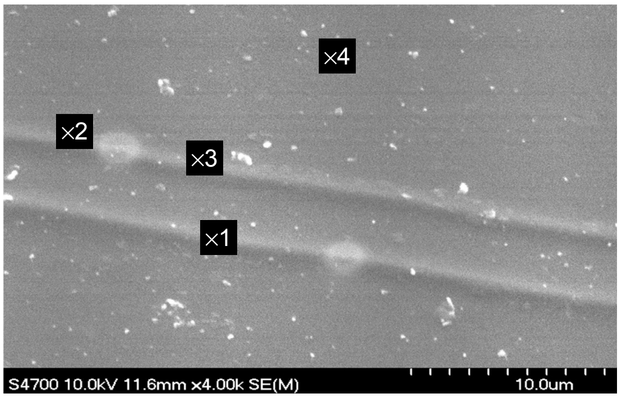


b)

Figure 4. The lines on glass surfaces after washing process. Observed by the optical microscope.



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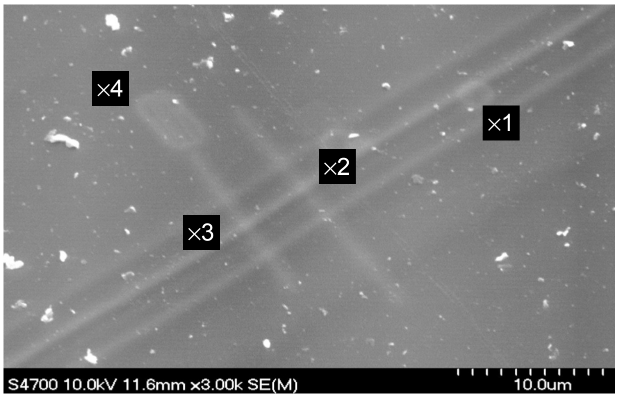

b)

Figure 5. Washed inner surfaces with line corrosion. Observed by SEM.

The EDX analysis of the line corrosion has shown enrichment with Al_2O_3 and ZrO_2, the last one was not even present in the original glass composition while Al_2O_3 was present in concentration around 1 wt. %. Only some of samples contained ZrO_2, but in all measured samples was identified higher content of Al_2O_3, compared to bulk glass. The results from EDX analysis confirm that inhomogeneities are caused by the presence of foreign substance containing high amount of Al_2O_3 and some ZrO_2 which was not added in glass batch. Both oxides should originate in the used refractories. The protruding lines are consequence of higher corrosive resistance of refractory materials. On the basis of chemical composition of lines, different from the surrounding glass it is possible to say, that the lines are inhomogeneities coming from the corrosion of refractory materials. These inhomo-geneities become visible only after washing process. We tested the correlation between the intensity of inhomogeneities (lines) and homogeneity of glass (Figure 6).

Figure 6 shows that there is no apparent correlation between the homogeneity of glass and the extent of line corrosion. The lack of expected correlation might be explained by the fact that only some inhomogeneities present in glass result in formation of lines after washing but the results of homogeneity measurements include all inhomogeneities present.

The presented work was furthermore interested in the analysis of the mechanisms of line corrosion formation. The source of the glass inhomogeneity and subsequent line corrosion is dissolution of AZS refractory materials, which were used for construction of the melting tank (high temperature region), as well as and also for the construction of stirrers, plunger, outflow bowl and tube (low temperature region).

At both the high- and low-melting temperatures, AZS refractory-containing regions can become the source of the inhomogeneities. Factors influencing dissolution of refractory from various regions are summarized in Table 3. These differences help us to identify the region, which could be the source of line corrosion.

The samples from both forehearth channels were taken at approximately identical conditions. The samples of glass from both forehearth channels were subjected to the washing process and then the surfaces were examined visually. Figure 7a shows the changes in intensity of the line corrosion in dependence on temperature of the glass melt in forehearth channel, which is terminated by the outflow bowl. Figure 7b shows the similar situation when the forehearth channel is terminated by the platinum elbow.

Clearly, there is an obvious trend, which indicates that higher temperature in the forehearth channel terminated by the outflow bowl increases the extent of line corrosion. The change of temperature in the forehearth channel terminated by the platinum elbow has no influence on the line corrosion as the extent of the line corrosion at all presented temperatures was 0°. This result indicates that the inhomogeneities, which result in the line corrosion, originate in the forehearth channel terminated by outflow bowl and not from the high temperature region of the surface. This is also confirmed by excellent glass homogeneity in the forehearth channel terminated by the platinum elbow.

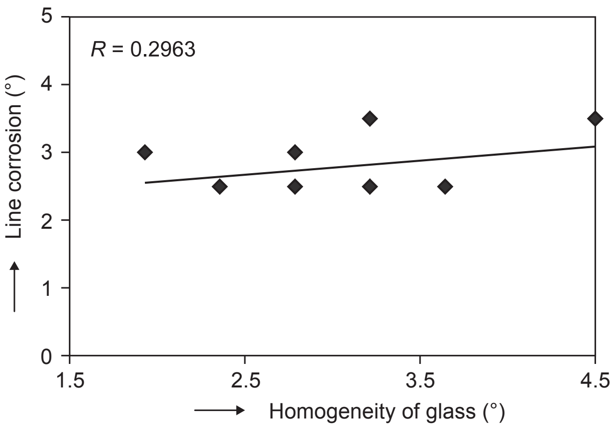

Figure 6. The correlation between the line corrosion and homogeneity of glass.

The experiment confirmed the hypothesis, that the source of the line corrosion is AZS refractory materials in low temperature region, the forehearth channel ended by the outflow bowl in given case.

Many reactions take place in the melting region, not only in the glass melt, but also between refractory materials and the glass melt. Higher temperature in the melting region or in the forehearth channel increases the rate of these reactions. The reactions can influence the properties of glass, particularly its homogeneity. Figure 8 shows the correlation between the extent of the line corrosion and temperatures of the glass melt in the melting tank [a) - glass from outflow bowl; b) glass from platinum elbow]. The samples were subjected to different forming process.

The main source of the line corrosion appears in the forehearth channel ended by the outflow bowl, but temperature in the melting tank has also influence on the intensity of the line corrosion. Temperatures in the platinum elbow forehearth were about 80-100°C higher than in the outflow forehearth channel. The possible explanation of line corrosion formation is that the higher diffusion rates at higher temperature facilitate better dissolution of inhomogeneities, therefore there is better homogenization of the glass melt. When homogenized glass melt is in touch with refractory materials in forehearth channel (in this case only in outflow bowl), higher concentration gradient exists between these two materials, which facilitates better dissolution of refractory material. As the dissolution of refractories take place close to the outflow end of the glass-melting aggregate, the inhomogeneities do not have any time to dissolve, and the inhomogeneities in glass, as observed in Figs. 5 and 6, have sharp character. The higher temperature therefore better dissolution of inhomogeneities and no contributions of AZS materials implied no line corrosion in glass products coming from the platinum elbow channel.

With increasing temperature in melting region including AZS materials, the extent of the line corrosion is also increasing. To avoid excessive dissolution of refractory materials it is required to hold the melting temperature at the value, which is as low as possible, but which is still sufficient for proper homogenization of the glass melt.

Table 3. The characteristic of factors of low and high temperature regions.

High temperature region	High rate of diffusion and corrosion of refractory materials, high residence time, good dissolution of inhomogeneities in glass.	Dissolution of tank walls.
Low temperature region	Low rate of diffusion and corrosion of refractory materials, low residence time, bad dissolution of inhomogeneities in glass.	Dissolution of stirrers, plunger, tube, outflow bowl.

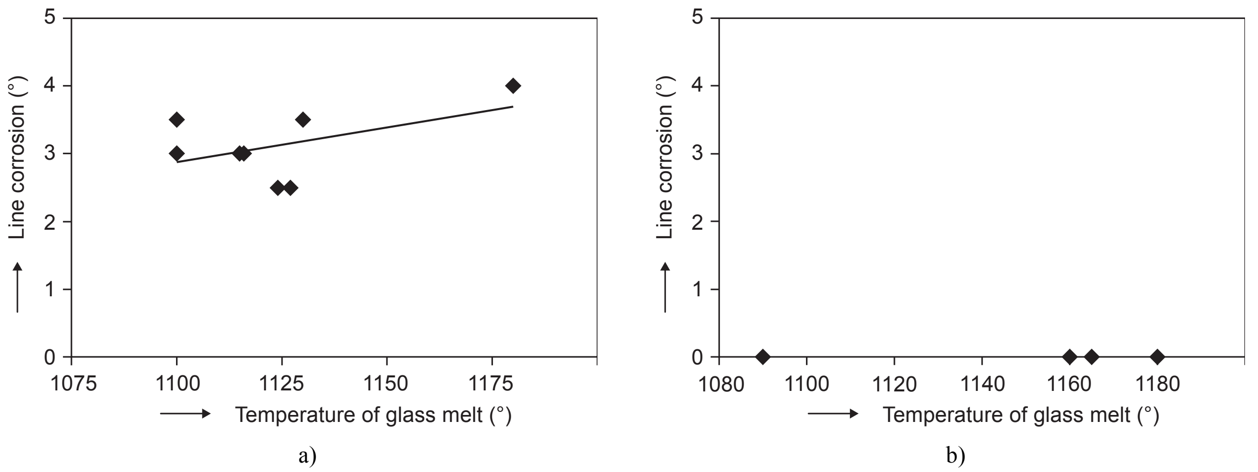

Figure 7. The correlation between the extent of line corrosion and the temperature of glass melt in forehearth channel terminated a) by outflow bowl, b) by the platinum elbow.

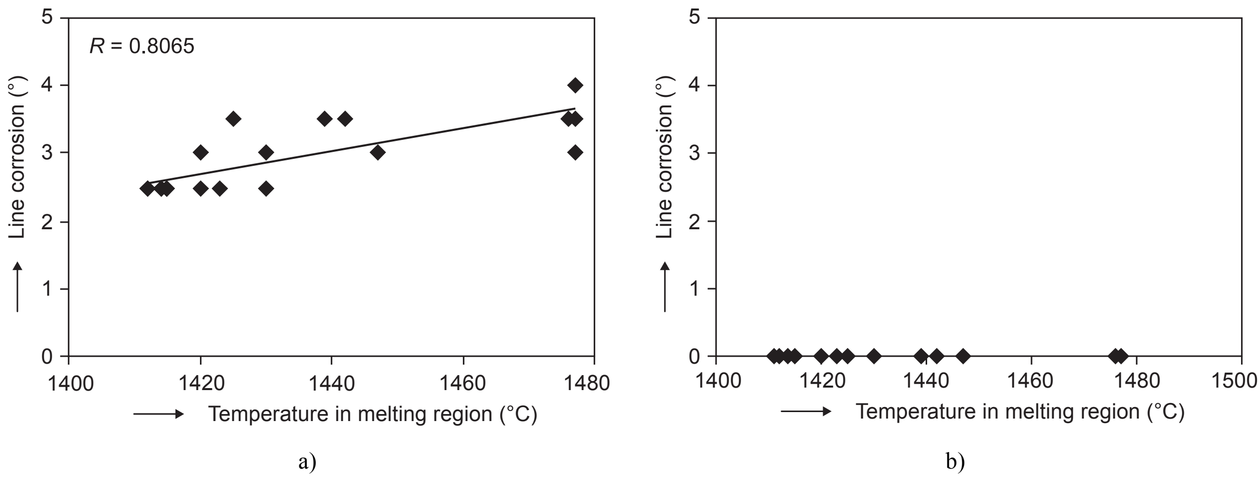

Figure 8. The correlation between the line corrosion and temperatures in the melting region a) glass from the outflow bowl, b) glass from the platinum elbow.

CONCLUSIONS

It was found that the visual method of glass homogeneity assessment correlates rather well with the Shelyubskii method and it is suitable for determination of the homogeneity of glass. No significant correlation between the extent of the line corrosion and the homogeneity of glass was found, as the homogeneity measurements include all types of inhomogeneities, while only one specific type of inhomogeneities results in the formation of corrosion lines after washing.

The line corrosion was identified only in samples of glass from the forehearth channel with extendables made of AZS refractories. The SEM and EDX analyses indicate that the source of the line corrosion is the dissolution of AZS refractory materials.

The influence of temperature on the line corrosion in the melting process was monitored in two parts of the melting aggregate - in the melting region and in the forehearth channel. Higher temperature of glass melt in the melting region leads to higher degree of the line corrosion. Influence of temperature in forehearth channel follows the same trend.

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SKÚMANIE LÍNIOVEJ KORÓZIE ÚŽITKOVÉHO SKLA VO VODNÝCH ROZTOKOCH

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Sklo je všeobecne považované za chemicky odolný materiál, napriek tomu podlieha korózii v rôznych korozívnych roztokoch (korózny proces). Špeciálnym prípadom je tzv. líniová korózia, ktorá vzniká rozpúšťaním povrchovej vrstvy úžitkového skla v automatických umývačkách. Cieľom tejto práce bolo štandardizovať vizuálnu metódu merania homogenity skla so Šeljubského metódou, analyzovať mechanizmus vzniku líniovej korózie, posúdiť vplyv teploty skloviny v taviacom procese na intenzitu líniovej korózie. Pokúsili sme sa nájsť vzťah medzi homogenitou skla a líniovou koróziou ako spôsob odhadu citlivosti skla na líniovú koróziu bez toho, aby boli vzorky skla testované v umývačke riadu. Po vizuálnej kontrole boli poškodené vzorky pochádzajúce z umývacieho procesu analyzované optickým mikroskopom, skenovacím elektrónovým mikroskopom a EDX analýzou. Pôvod líniovej korózie sa nachádza vo výtokovom žľabe a jej zdrojom je rozpúšťanie AZS žiaruvzdorného materiálu do skloviny. Najdôležitejším parametrom vplývajúcim na líniovú koróziu je teplota skloviny v taviacom agregáte.