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Contribution from the employment of volcanic tuffs to the chemistry of soda-lime glasses

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The present work shows a study to incorporate volcanic tuffs as raw material in the preparation of industrial glass that traditionally uses feldspar. The X-ray diffraction patterns obtained with hot camera depict an unstable mineralogical phase under special conditions of atmospheric pressure in which appears the quartz polymorphic transformation. Thermal analysis curves present a shoulder at 680°C and an endothermic peak around 840°C corresponding to reactions of formation of silicates. It suffers an overlapping effect toward smaller temperatures favouring glass formation.

Keywords: Glass, volcanic tuff, endothermic peaks.

INTRODUCTION

The objective of the work is to demonstrate the advantages of the substitution of the traditionally utilized feldspar in the production of glass containers by volcanic tuffs of the location of Guaramanao. Deposits of volcanic tuff are located at about 700 km of Havana City and it has reservoirs over 500 000 tons of the material. Due to its geologic formation, Cuba has numerous deposits of volcanic tuff, however feldspar deposits are scarce and in many cases they cannot offer the quality that requires the glass industry. In tropical countries with marine influence the effect of the atmospheric humidity, high temperature and presence of halogen ions in the environment cause an entire outline of high aggressiveness for vitreous materials (Hernández, 2004). It makes the necessity to investigate the substitution of the materials traditionally used in the fabrication of glass containers (Hernández, 2004; Navarro and El Vidrio, 1991). Feldspars have been widely used in container glass industry to introduce alumina to guarantee an appropriate chemical stability in glass (Hernández et al. 2005; Angell, 1996; Navarro and El Vidrio, 1991).

MATERIALS AND METHODS

Mixtures for glass get ready according to glass producers methodology and they melt in an experimental furnace that uses methane-oxygen mixture. They were heated for 5 h at 1560°C. When the mixes are properly melted, melted glass spills in to graphite mould to relax tensions. These samples are used for viscosity test. However, the samples for the thermal and difractometric study were taken before melting process that undergo to vitrifiable mixture.

A thermal study is carried out in a derivatograph NETZSCH STA 409. Alumina in normal atmosphere is used as test reference. The maximum temperature error is ± 2°C. The maximum sample-scale error (TG) is 50 mg.

A rotational viscosimeter, model HAAKE PT 1700 RV30 is used to determine viscosity test behaviour. The error reported in rotation mode is ±0.10% and fibres mode report ± 0.25%.

A diffractometer Phillip with HTK 16 Anton Paar hot chamber is used to obtained X-ray diffraction pattern. The test was carried out between 2-70 ° (2θ).

The work methodology is the following: mixture preparations, execution of thermal studies, X-rays diffraction pattern with a representative sample of prepared mixtures. In other way, the rest of mixture is fused in gas-air furnace up to over 1560°C, and then viscosity test is carried out.

RESULTS AND DISCUSSION

Glass formulation is selected among some Cuban bottle glass formulations (Table 1). Selected formulation uses potassium nitrate like refining agent in vitreous mass
Thermal analysis was carried out on glass samples. The obtained results were compared with specialized literature reports (Mckenzie, 1970; Navrotsky et al., 1997; Praga, 1963). Thermal analysis diagram (Figure 2) allow to study some particularities of chemical reactions of silicate formation (Navarro and El Vidrio, 1991; Praga, 1963; Paul, 1990).

Figure 1 shows thermal studies of traditional bottle glass with feldspar. There, they stand out two endoefects that mark two fundamental chemical reactions that happen according to:

**Effect 1.** (740-780°C) $\text{Na}_2\text{Ca(CO}_3\text{)}_2 + 2\text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CaSiO}_3 + \text{CO}_2(g)$

$\{\text{Na}_2\text{O}.2\text{SiO}_2\} \rightarrow \{\text{Na}_2\text{O}.2\text{CaO.3SiO}_2\} = \text{liquiud}$

**Effect 2.** (850-880°C) $\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_4 + \text{CO}_2(g)$

$2\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 + 2\text{CO}_2(g)$

$\text{Ca}_2\text{SiO}_4 + \text{SiO}_2 \rightarrow 2\text{CaSiO}_3$, Fusion of $\text{Na}_2\text{CO}_3$

These reactions play an important role in glass formation (Navarro and El Vidrio, 1991; Praga, 1963; Paul, 1990), because first and second order silicates are formed with liquidus. Liquidus formation set a start point to glass arising.

Vitricable mixture with feldspar sets these effects according to literature values (Mckenzie, 1970; Navrotsky et al., 1997; Liu et al., 1996). Figure 2 shows thermal analysis results of glass formation with volcanic tuff from Guaramano deposit. There, studied effects are varying. They appear at 700 and 800°C respectively. The first effect is considerably less than the other in a traditional glass with feldspar, but the second effect is bigger than the similar in a traditional glass.

Specialized literature shows another important effect as follow:

Figure 1. Thermal study of bottle glass with feldspar.

Figure 2. Thermal study of bottle glass with volcanic tuff.
Table 1. Chemical composition of glasses.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical values (mass %)</td>
<td>72.80</td>
<td>1.50</td>
<td>11.82</td>
<td>12.60</td>
<td>1.28</td>
</tr>
<tr>
<td>Real values (mass %)</td>
<td>72.75</td>
<td>1.50</td>
<td>11.80</td>
<td>12.55</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 2. Results of viscosity test.

<table>
<thead>
<tr>
<th>Glass type</th>
<th>Immersion point(10⁴dPa.s)</th>
<th>Point of Fluency(10⁴dPa.s)</th>
<th>Drop point(10⁴dPa.s)</th>
<th>Liquidus point(10²⁵dPa.s)</th>
<th>Fusion point(10²⁵dPa.s)</th>
<th>Littleton point(10⁷⁶dPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass with Feldspar</td>
<td>1043</td>
<td>927</td>
<td>1207</td>
<td>1333</td>
<td>1490</td>
<td>723</td>
</tr>
<tr>
<td>Glass with Volcanic tuff</td>
<td>1011</td>
<td>900</td>
<td>1167</td>
<td>1280</td>
<td>1480</td>
<td>717</td>
</tr>
</tbody>
</table>

Effect 3. (650-700°C) \[3[Na₂Ca(CO₃)₂] \rightarrow 10 SiO₂ \rightarrow 2[Na₂O·2SiO₂]⁺ [Na₂O·3CaO·6SiO₂]⁻ 6CO₂↑

Effect 3 marks the beginning of silicates formation. They are a product of reaction between Na₂Ca(CO₃)₂ with SiO₂.

The presence of an overlapping effect at 830°C has an important significance, because effect is developed at less temperature than literature reporting and traditional obtained glass with feldspar.

Unypical behaviour is caused by amount of amorphous material (almost 60% in mass) present in volcanic tuff of Guaramanao deposit. Results of viscosity test support this affirmation. Table 2 shows results of viscosity test.

X-ray diffraction patterns with hot camera support some of these affirmations too (Chung et al., 1992). Figure 3 shows different diagrams at different experimental temperatures up to 870°C. From the beginning, diagrams vint. Both, Coesite (monoclinic system, C 2/c) and Stishovite (tetragonal system, P 42/mnm) have crystalline systems of low and medium symmetry, unstable at normal temperature and pressure. For that reason it is impossible to visualize these effects by means of traditional tests like thermal studies or X ray diffraction pattern (see Figure 4).

Conclusions

The substitution of the feldspar for volcanic tuff favours the processes of formation of silicates and of glass due to the high concentration of amorphous material that it possesses. The appearance of unstable mineralogical phases favours the formation of silicates. X ray-diffraction pattern with hot camera constitutes a powerful tool that allows studying the physical and chemical transformations that occur during the formation of the silicates.
exhibit two silica polymorphic phases: Coesite and Stishovite.

REFERENCES