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EFECTO DE LA REDUCCIÓN DE SODA ASH (NA_2CO_3) Y CALIZA ($CaCO_3$) SOBRE LAS PROPIEDADES MECÁNICAS Y FÍSICAS DE VIDRIOS DE SODA-CAL-SÍLICE USADOS EN LA MANUFACTURA DE ENVASES DE VIDRIO Y VIDRIO PLANO.

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RESUMEN

La *Soda ASH* (Na_2CO_3) es uno de los componentes más importantes para producir vidrio ya que este material es capaz de romper la red de SiO_2 y por lo tanto determina importantes propiedades, sin embargo, dicha materia prima también es muy costosa y existe un paradigma al interior de la industria del vidrio concerniente a posibles problemas que se pueden presentar cuando hay disminuciones de Na_2O. En este orden de ideas, una disminución progresiva y metodológica de *Soda ASH* fue desarrollada sobre vidrios fabricados acorde a un diseño de experimentos (DOE), pretendiendo medir y analizar diferentes propiedades mecánicas, físicas y químicas acorde con normas ASTM y procedimientos industriales, obteniendo como resultado cambios estadísticamente no significativos en las propiedades medidas cuando hay disminuciones de hasta el 2.64% en peso de Na_2O, lo cual permite pensar en estas disminuciones como una opción para los problemas de la industria del vidrio relacionados con este mineral.

Palabras clave: Soda ASH; Caliza; red de SiO_2; ANOVA y DOE.

EFFECT OF SODA ASH (Na_2CO_3) AND LIMESTONE ($CaCO_3$) REDUCTION ON MECHANICAL AND PHYSICAL PROPERTIES OF SODA-LIME-SILICA GLASSES USED IN THE MANUFACTURING OF CONTAINERS AND FLAT GLASS

ABSTRACT

Soda ASH (Na_2CO_3) is one of the most important components to produce glass since this material is able to break the SiO_2 network and therefore it determines important properties, however it is also so expensive and there is into the glass industry a paradigm regarding possible issues involved with the Na_2O decreases. In this order of ideas, a progressive and methodological decrease of *Soda ASH* was performed over glasses manufactured following a design of experiments (DOE), aiming to measure and to analyze different mechanical, physical and chemical properties according to the respective ASTM standards or industrial procedures, obtaining as a result non-significant statistical changes in all properties measured when there are decreases up to 2.64 wt. % of Na_2O, which allows to think about these decreases as an option for the glass industry issues related to this ore.

Keywords: Soda ASH; Limestone; SiO_2 network; ANOVA and DOE.

1. INTRODUCTION

Several attempts to modify chemically soda-lime-silica glasses and to measure their physic-chemical properties aiming to keep these materials as unaltered as possible have been developed [1]. Specifically, to decrease the quantity of *Soda ASH* (Na_2CO_3) in a batch of glass, several tests have been tried, mainly due to the high costs and unavailability of this raw material [2], however, if the quantity of *Soda ASH* is changed, the quantity of the other raw materials must be changed as well aiming to keep the chemical proportions, which in turn allows to keep the properties of glass as unaltered as possible, otherwise, the mentioned chemical changes cause variations in properties such as: glass transition temperature, softening temperature, density, hardness, elastic modulus, refractive index and the coefficient of thermal expansion, among others [3,4].

Soda ASH supplies R_2O to glasses and for this reason it is classified as a modifier, which is necessary for glasses given that it allows to achieve specific physic-chemical properties [1-5]. This modification of the vitreous network is based on the capability of R_2O to break the Si-O bondings, which can improve the properties, e.g. the addition of Na_2O improves the rare-earth solubility, which makes it suitable for the fabrication of optical waveguide devices by ion-exchanged process [6]. Alternatively, it also can affect the properties, e.g. high alkali concentration usually presents poor chemical durability and mechanical properties [6]. So that, it is important to know deeply and control carefully the raw materials that should be added into the batch in order to design glasses with suitable mechanical, physical and chemical properties [1-6]. However, despite all possible issues that reducing the R_2O quantities concerns, such as: increases in the melting point and as a result increases in the energy costs of melting, it is interesting to study and research about *Soda ASH* as raw material of soda-lime-silica glasses due to the potential savings in cost that these decreases can imply [5].

The aim of this paper is to investigate the effect of decreasing the quantity of *Soda ASH* in soda-lime-silicate glasses used in the glass containers and flat glass industries, aiming to keep the actual properties as unaltered as possible in order to mitigate the paradigm that exists into this industry concerning the manufacturing issues involved with the Na_2O decreases. For this propose, samples with different compositions were manufactured decreasing systematically the quantity of *Soda ASH* and subsequently they were subjected to different mechanical tests such as: compression strength, thermal shock resistance, fracture toughness, flexure resistance and hardness, as well as different physical tests such as: density, color and annealing and softening points in order to determine the degree of affectation due to the chemical changes performed. Finally, WD-XRF was used for the monitoring of composition.

2. MATERIALS AND METHODS

This research is based on the decrease of *Soda ASH* keeping the proportions with the *Limestone* (Soda/Lime Ratio=0.92), the other components involved into the batch were not modified. In this sense, the full factorial design of experiments (DOE) shown in Table 1 was developed, which statistically corresponds to a DOE with 1 factor: *Soda ASH*, with 10 levels of composition: from *Actual Composition* to *Composition 9,* and with repeatability: *5,* for a total of 550 samples. It is important to notice that all the samples were manufactured using an actual and operational furnace for glass production accomplishing with the requirements of the industrial procedures and ASTM standards to perform the tests listed in Table 2. Regarding the evaluation of the standardized tests, the description of samples and conditions of tests are described in the respective ASTM standard (Table 2). In addition, for thermal shock resistance, density, viscosity, annealing and softening tests were used equipments of own conception and design aligned with the respective ASTM standards. In the same way, for flexure resistance and hardness were used a universal machine of tests SHIMADZU autograph AG-250KNG as well as a MITUTOYO VLPAK2000 durometer respectively. On the other hand, concerning the evaluation of the non-standardized tests, the description of samples and conditions of tests are described in the respective industrial procedure (Table 2). Specifically, for fracture toughness and compression strength tests, a hammer Charpy CEAST and the same aforementioned universal machine of tests were used respectively. Finally, for the color and the WD-XRF tests, a GENESIS 10S UV-VI spectrophotometer and an ARL OPTIM’X spectrometer were used respectively.

Table 1. *Design of experiments (DOE) used in this research.*

Factor: Soda ASH	**Decreasing of Soda ASH [wt. %]**	**Type of decrease**
Levels		
Actual composition	0.00	Moderate
1	0.88	Moderate
2	1.17	Moderate
3	1.47	Moderate
4	1.76	Moderate
5	2.05	Moderate
6	2.35	Moderate
7	2.64	Moderate
8	4.00	Aggressive
9	4.10	Aggressive

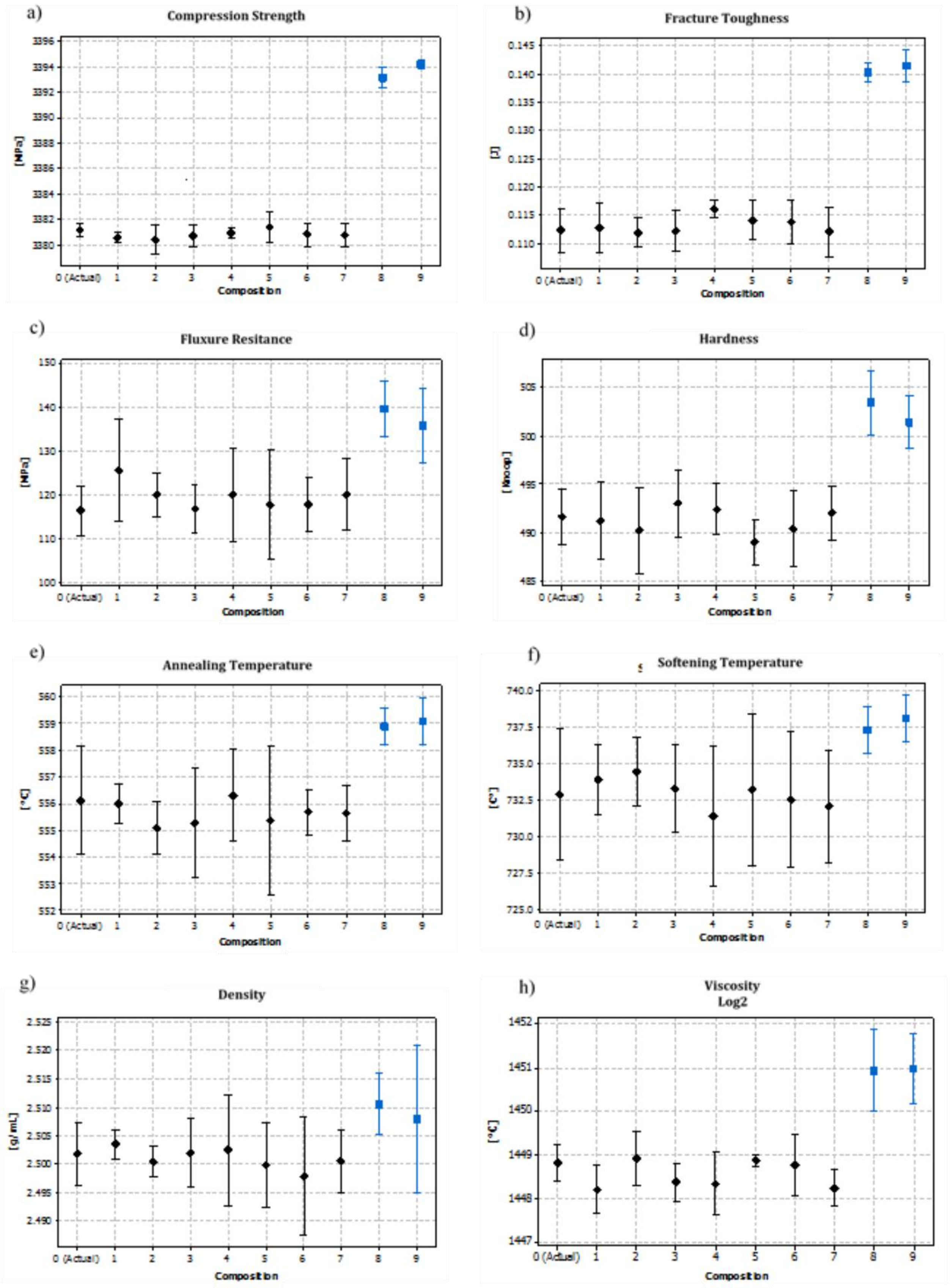
Table 2. *Tests and standards used in this research.*

Type of test	Test	Standard
Mechanical	Thermal shock resistance	ASTM C149-86 [7]
	Flexure resistance	ASTM C158-95 [8]
	Hardness	ASTM C730-85 [9]
	Fracture toughness	Industrial procedure
	Compression strength	Industrial procedure
Physical	Density	ASTM C729-75 [10]
	Annealing point	ASTM C336-71 [11]
	Softening point	ASTM C338-93 [12]
	Viscosity	ASTM C965-96 [13]
	Color	Industrial procedure
Chemical	WD-XRF	Industrial procedure

Subsequently, for both, moderate and aggressive compositions, as well as for the 11 tests performed, several analysis of variance (ANOVA) were used in order to determine statistically the degree of affectation over the properties of glass due to the decreases of Na_2O.

3. RESULTS AND DISCUSSION

All results obtained for the tests are summarized in the Fig. 1a-n and in the Tables 3-5. It is important to notice that for both, moderate compositions (samples: actual composition – 7) and aggressive compositions (samples: 8 and 9), in any case there are statistical differences when samples are compared among themselves, given that the p-values are always >0.05 and therefore H_0 (H_0: the differences among means = 0) is accepted, which means that the properties in general are equal when moderate and aggressive compositions are compare among themselves. However, when moderate compositions and aggressive compositions are compared, in general there are statistical differences since p-values are always <0.05 and therefore H_0 is rejected, which means that properties are not equal and for this reason the chemical changes are not viable. Finally, all assumptions required by the ANOVA analysis such as: normality of residuals, randomness and independency were accomplished.


a)
Compression Strength
[MPa]
3396
3394
3392
3390
3388
3386
3384
3382
3380
0 (Actual)
1
2
3
4
5
6
7
8
9
Composition
b)
Fracture Toughness
[J]
0.145
0.140
0.135
0.130
0.125
0.120
0.115
0.110
c)
Fluxure Resitance
[MPa]
150
140
130
120
110
100
d)
Hardness
[Knoop]
505
500
495
490
485
e)
Annealing Temperature
[°C]
560
559
558
557
556
555
554
553
552
f)
Softening Temperature
[C°]
740.0
737.5
735.0
732.5
730.0
727.5
725.0
g)
Density
[g/mL]
2.525
2.520
2.515
2.510
2.505
2.500
2.495
2.490
h)
Viscosity
Log2
[°C]
1452
1451
1450
1449
1448
1447

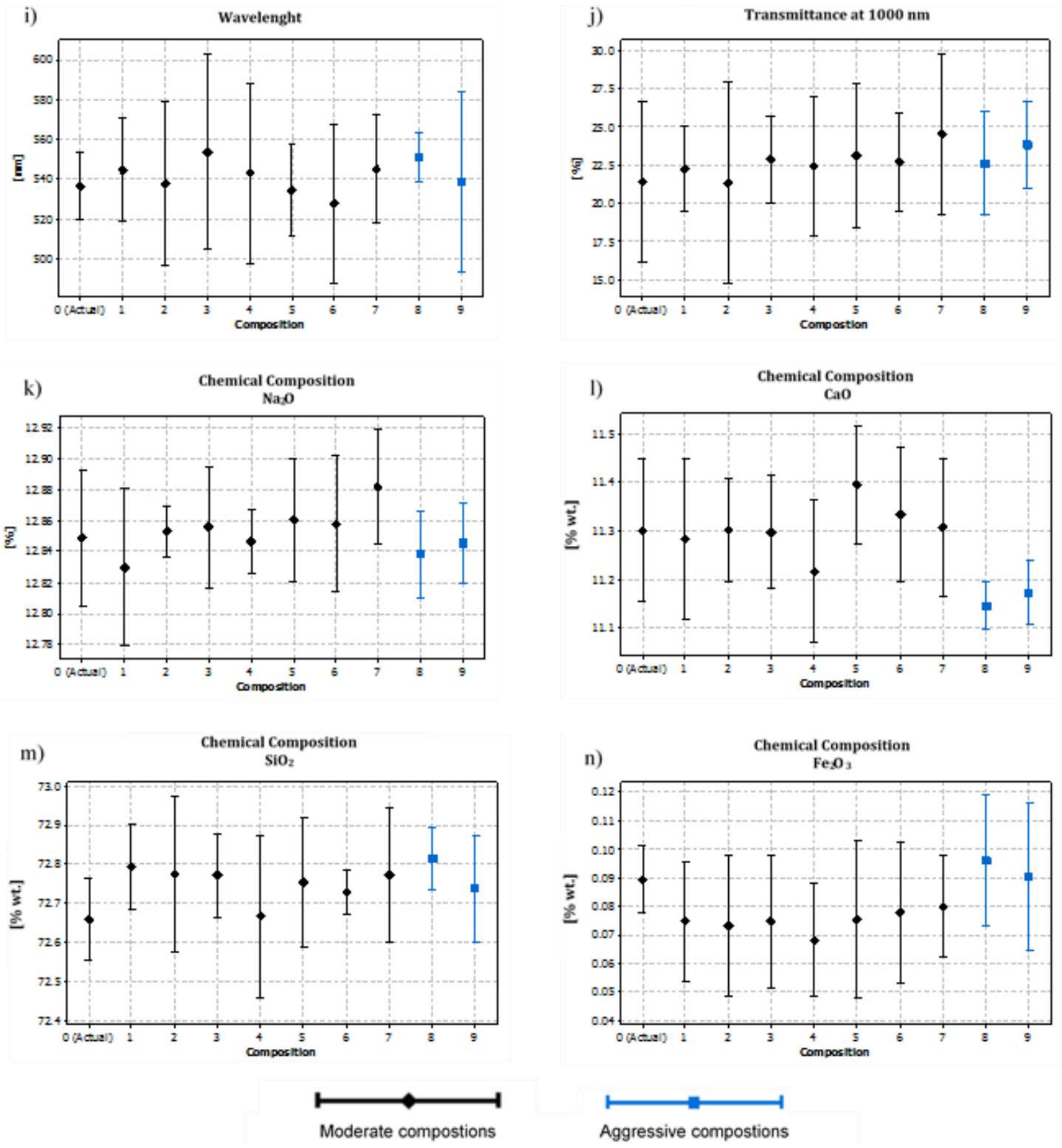


***Figure 1.** Results obtained after run the design of experiments (DOE) used in this research. a) Compression strength, b) Fracture toughness, c) Flexure resistance, d) Hardness Knoop, e) Annealing temperature, f) Softening temperature, g) Density, h) Viscosity, i) Wavelength, j) Transmittance at 1000nm, k) Na$_2$O, l) CaO and m) SiO$_2$, n) Fe$_2$O$_3$.*

Table 3. *Results obtained for moderate compositions (Samples from actual to 7).*

Moderate decreases of composition (Samples: actual - 7)				
Test		**Value measured (Samples: actual – 7)**	**p-value (Samples: actual – 7)**	**[H0: the differences between means = 0] (Samples: actual – 7)**
Compression strength		3380.8 ± 0.7 MPa	0.967	Accepted: values are equal
Thermal shock resistance		No failure	-------	-----------------------------
Flexure resistance		120.40 ± 7.00 MPa	0.635	Accepted: values are equal
Hardness		491 ± 4 HK	0.745	Accepted: values are equal
Fracture toughness		0.112 ± 0.007 J	0.681	Accepted: values are equal
Density		2.5011 ± 0.0008 g/cm^3	0.795	Accepted: values are equal
Annealing point		556.1 ± 0.6 °C	0.804	Accepted: values are equal
Softening point		733.1 ± 3.3 °C	0.855	Accepted: values are equal
Color	**Brilliance**	63.2 ± 2.7 %	0.608	Accepted: values are equal
	Purity	3.2 ± 1.0 %	0.119	Accepted: values are equal
	Wave length	540.2 ± 26.9 nm	0.900	Accepted: values are equal
	Transmittance at 1000nm	22.6 ± 3.5 %	0.907	Accepted: values are equal
Viscosity	**Log 2**	1448.7 ± 0.3 °C	0.543	Accepted: values are equal
	Log 3	1190.6 ± 0.3 °C	0.546	Accepted: values are equal
	Log 7	767.1 ± 0.3 °C	0.576	Accepted: values are equal
Chemical Composition	**SiO_2**	72.7397 ± 0.1193 wt. %	0.505	Accepted: values are equal
	Na_2O	12.8540 ± 0.0310 wt. %	0.356	Accepted: values are equal
	K_2O	0.4967 ± 0.0254 wt. %	0.145	Accepted: values are equal
	CaO	11.3040 ± 0.1101 wt. %	0.434	Accepted: values are equal
	MgO	0.5635 ± 0.0748 wt. %	0.116	Accepted: values are equal
	Al_2O_3	1.5121 ± 0.0465 wt. %	0.580	Accepted: values are equal
	Fe_2O_3	0.0766 ± 0.0169 wt. %	0.733	Accepted: values are equal
	Others	0.4534 ± 0.0621 wt. %	------	-----------------------------

Table 4. *Results obtained for aggressive compositions (Samples 8 and 9).*

Aggressive decreases of composition (Samples: 8 and 9)				
Test		**Value measured** **(Samples: 8 and 9)**	**p-value** **(Samples: 8 and 9)**	**[H0: the differences between means = 0]** **(Samples: 8 and 9)**
Compression strength		3393.60 ± 0.70 MPa	0.076	Accepted: values are equal
Thermal shock resistance		No failure	-------	-----------------------------
Flexure resistance		137.05 ± 7.10 MPa	0.160	Accepted: values are equal
Hardness		502 ± 4 HK	0.106	Accepted: values are equal
Fracture toughness		0.142 ± 0.007 J	0.409	Accepted: values are equal
Density		2.5092 ± 0.0008 g/cm^3	0.621	Accepted: values are equal
Annealing point		559.0 ± 0.6 °C	0.665	Accepted: values are equal
Softening point		737.1 ± 3.3 °C	0.598	Accepted: values are equal
Color	**Brilliance**	62.1 ± 2.9 %	0.490	Accepted: values are equal
	Purity	3.0 ± 1.0 %	0.868	Accepted: values are equal
	Wave length	544.4 ± 26.1 nm	0.488	Accepted: values are equal
	Transmittance at 1000nm	223.2 ± 2.5 %	0.459	Accepted: values are equal
Viscosity	**Log 2**	1451.3 ± 0.3 °C	0.453	Accepted: values are equal
	Log 3	1192.6 ± 0.3 °C	0.435	Accepted: values are equal
	Log 7	770.1 ± 0.3 °C	0.378	Accepted: values are equal
Chemical Composition	SiO_2	72.7769 ± 0.0948 wt. %	0.219	Accepted: values are equal
	Na_2O	12.8418 ± 0.0208 wt. %	0.618	Accepted: values are equal
	K_2O	0.5041 ± 0.0235 wt. %	0.258	Accepted: values are equal
	CaO	11.1363 ± 0.0290 wt. %	0.361	Accepted: values are equal
	MgO	0.5415 ± 0.0680 wt. %	0.640	Accepted: values are equal
	Al_2O_3	1.5326 ± 0.0518 wt. %	0.938	Accepted: values are equal
	Fe_2O_3	0.0931 ± 0.0188 wt. %	0.647	Accepted: values are equal
	Others	0.4534 ± 0.0621 wt. %	------	-----------------------------

Table 5. *Statistical comparison between moderate compositions and aggressive compositions.*

Test		p-value Moderate (Samples: actual-7) vs Aggressive (Samples: 8 and 9)	[H0: the differences between means = 0] Moderate (Samples: actual-7) vs Aggressive (Samples: 8 and 9)
Compression strength		0.000	Rejected: values are not equal
Thermal shock resistance		-------	-----------------------------------
Flexure resistance		0.013	Rejected: values are not equal
Hardness		0.004	Rejected: values are not equal
Fracture toughness		0.002	Rejected: values are not equal
Density		0.000	Rejected: values are not equal
Annealing point		0.000	Rejected: values are not equal
Softening point		0.000	Rejected: values are not equal
Color	**Brilliance**	0.273	Accepted: values are equal
	Purity	0.474	Accepted: values are equal
	Wave length	0.657	Accepted: values are equal
	Transmittance at 1000nm	0.589	Accepted: values are equal
Viscosity	**Log 2**	0.001	Rejected: values are not equal
	Log 3	0.011	Rejected: values are not equal
	Log 7	0.008	Rejected: values are not equal
Chemical Composition	**SiO_2**	0.365	Accepted: values are equal
	Na_2O	0.047	Rejected: values are not equal
	K_2O	0.407	Accepted: values are equal
	CaO	0.000	Rejected: values are not equal
	MgO	0.402	Accepted: values are equal
	Al_2O_3	0.228	Accepted: values are equal
	Fe_2O_3	0.201	Accepted: values are equal
	Others	------	-----------------------------------

Theoretically, decreasing the quantity of Na_2O affects in a positive way mechanical properties such as: compressive strength, impact, flexural resistance, thermal shock resistance and hardness [14], and this due to the fact that for single component glasses all O^{2-} ions occur as bridging oxygens, while in the soda-silicate glasses non-bridging oxygens occur adjacent to the alkali ions as it is possible to see in the eq. (1):

$$\equiv Si - O - Si \equiv \; + Na_2O \; \rightarrow \equiv Si - O - Na + Na - O - Si \equiv \qquad (1)$$

So that, when Na_2O is increased, a splitting up of the network takes place, as a result there is a weakening effect of the glass [14], which affects the mechanical performance. In addition, it is important to remember that the quantity of CaO was modified as well in order to keep the Na_2O/CaO ratio, and this chemical change also has influence over the glass according to the eq. (2):

$$\equiv Si - O - Si \equiv \; + Ca = O \; \rightarrow \equiv Si - O - Ca - O - Si \equiv \qquad (2)$$

The Ca-O bond due to the valence 2 of the Ca^{2+} ion is clearly stronger than the Na-O bond, so that the two non-bridging oxygens that are formed maintain a certain bond over the Ca^{2+} ion, but in general, it also has a split function in the network [14]. However, in this particular case, mechanically non-significant changes were observed for moderate compositions (up to 2.64 wt. % of Na_2O) due to the small decreases involve, while relevant and positive changes were observed in aggressive compositions (up to 4.00 wt. % of Na_2O) (Fig. 1a-d), which correspond with the lowest quantities of Na_2O in the glass. On the other hand, mechanical properties of glass are also determined by the state of residual stresses in the near-surface region since the introduced compressive stresses generate a balancing tension, which can result in an increase of the material strength above its fracture threshold, which in turn can be altered by the chemical changes. So that, the Na_2O decreases in general produce increases in the relaxation temperature as it is possible to see in Fig. 1e-f, since there are more Si-O strong bondings [14, 15], however, in this case neither the moderate compositions nor aggressive compositions showed different behaviors in thermal shock resistance due to any sample failed.

Regarding physical properties such as: density, viscosity, annealing and softening points, the same pattern of behavior was detected due to non-significant changes were observed for moderate compositions, while relevant changes were observed in aggressive compositions (Fig. 1e-h). This due to decrease the Na_2O quantity allows to increase the viscosity value at a determined temperature (log 2, log 3, log 7) given that there are stronger Si-O bonds present in the network, avoiding the flux of ions, and therefore the annealing and the softening points are increased as well, which in this case is negative due to more energy, money and time are required to produce a good glass, however, these effects depend on the decreases magnitude.

In the same way, regarding the color tests, it is important to notice that in general, the indexes of brilliance, purity, wavelength (Fig. 1i) and transmittance at 1000nm (Fig. 1j) are affected by chemical changes due to the presence of non-bridging oxygen ions with higher polarizability when the Na_2O increases, which results in an increase of the index of refraction, as well as the redox index of glass because increases of Na_2O can increase the $Fe^{3+/}Fe^{2+}$ ratio (oxidized the glass), which in turn can changes not only the values of refraction, but also the quantity of absorption of the light [16]. However, once again, the magnitude of changes is small and therefore it is not enough to produce changes in color. On the other hand, neither *Soda ASH*, nor *Limestone* are suppliers of ions able to produce significant color changes as realized by: $Fe^{3+/}Fe^{2+}$ and/or Cr^{3+} [16].

Chemically, Fig. 1 k-n and Tables 3-5 show evidence of significant changes regarding the decreases of SiO_2, Na_2O and CaO in the aggressive compositions against the moderate compositions, which reflects the chemical changes performed, but comparing only the moderate compositions themselves, or only aggressive compositions themselves, there are not significant differences.

Finally, the constant behavior shown by the results obtained during all tests developed is due to the small magnitude of changes, which allow to keep the properties essentially unaltered for moderate compositions (decreases up to 2.64 wt. % of Na_2O), corresponding with the samples from the actual composition to 7, and showing statistical changes for aggressive compositions (decreases of 4.00 and 4.10 wt. % of Na_2O) corresponding with samples 8 and 9.

4. CONCLUSIONS

The values obtained from the 11 tests developed over the 10 different compositions allow to conclude that decreases up to 2.64% of Na_2O (moderate compositions) do not affect significantly the mechanical and the physical properties of glasses studied. This behavior is mainly because the magnitude of chemical changes is not significant neither at chemical level nor at statistical level. For these reasons, the moderate compositions proposed are technically viable. Additionally, the moderate compositions are also economically viable not only due to the raw material savings involved with the decreases, but also due to the variables related to the energy consumptions (annealing point, softening point, viscosity, etc) were not strongly affected compared with the actual compositions. On the other hand, the decreases corresponding with the aggressive compositions are not sustainable in an industrial production since reductions up to 4.00% of Na_2O affect mainly the viscosity, the annealing and the softening points, which means that more energy, and therefore more money must be used in the melting, the conditioning, the formation and the annealing of glass.

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