REPLACEMENT OF POTASH WITH SODA ASH TO PRODUCE ECONOMICAL AND DURABLE GLASS

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ABSTRACT: Potash had been used as a flux for the production of table-ware glass for a long time. Gradually with the passage of time it has become an expensive flux. It has increased the cost of molten glass. Therefore, commercial glass production is not feasible with the potash. The present study has been based on the replacement of potash with some cheaper flux like soda ash. Required results are achieved by using soda ash with some minor additions of aluminum oxide and boric acid. The glass with these modifications was proved to be more durable and economical than potash glass.

Key words: Flux, melting, chemical durability, softening point, thermal expansion

INTRODUCTION

Potash (Potassium carbonate) has been used as a flux for the melting of quality glass for a long time. It helps the glass to melt in short time. It gives good shine, refining and durability to the glass. It also has the thermal expansion relatively less than the other fluxes like soda and fluorides. But with the passage of time, prices of potash gradually increased day by day. Now it is very expensive to use it as a flux in glass melting. So the glass manufacturers started to use an alternate flux i.e. Soda (Sodium Carbonate). Sodium Carbonate (Na_2CO_3) has the draw back that it has excessive thermal expansion ie. ($100x10^{-7}/^oC$) which is greater than the thermal expansion of potassium carbonate (K_2CO_3) i.e. ($85x10^{-7}/^oC$). Glass having high thermal expansion is poor in durability. It suddenly cracks by thermal shock, leaching of alkali is high.

When soda is used as a flux it increases the thermal expansion of glass (Werner, 1971 and Robert, 1973). Storage of chemicals and medicines in such container glasses for a long period causes the leaching of alkali from the glass. Similarly, when shelf life is long weathering effects also caused the alkali to leach out and the surface of glass become foggy. Glass of low chemical durability may be affected by moisture alone, due to weathering effect; alkali at the surface rises the pH value of the condensed moisture and thus promote the attack. Weathering tendencies increase as a function of soda contents in glass (Demirkesen and Goller, 2003, Portal and Sempere, 2003). While in potash glasses such defects are very least (Uhlmann and Kreidel, 1986, Han and Song, 1989). Therefore, soda as a flux should be used in such a way to overcome these defects. The present study shows the utilization of soda as an alternate flux against potash with some necessary modifications. The modifying agents used in this study are Aluminium Oxide (Al_2O_3) and Boron Oxide (B_2O_3). Al_2O_3 In the glass increases mechanical strength, resistance to acids, alkalies and corrosive chemicals, while B_2O_3 reduce thermal expansion, alkali extraction and devitrification of glass. B_2O_3 provides more thermal stability to glass (Avramov et. al., 2003, Liu, 2007).

MATERIALS AND METHODS

Good quality sand of mesh size between 30 and 100 was used for the study. Silicon dioxide (SiO_2) contents in the silica sand were 99.45% while Ferric Oxide (Fe_2O_3) contents were 0.035%. Other chemicals used in the study were like, sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), calcium carbonate ($CaCO_3$), sodium sulphate (Na_2SO_4), magnesium carbonate ($MgCO_3$), boric acid (H_3BO_3) and aluminium oxide (Al_2O_3). All the glass batches were melted in clay crucibles of one Kg. capacity. Standard potash glass containing oxide composition is as 69.5% SiO_2, 0.8% MgO, 19.0 % K_2O, 0.5% Al_2O_3, 10.0% CaO and 0.2% SO_3 was used for this study. While, batch composition is as silica sand (69.5 gms), magnesium carbonate (1.67 gms), potassium carbonate (33.32 gms), aluminium oxide (0.5 gms), lime stone (17.84 gms) and sodium sulphate (0.36 gms). For experimental study glass melting was done in four stages. In first stage of melting, amount of potassium oxide (K_2O) was gradually reduced while amount of sodium oxide (Na_2O) was gradually increased at the same rate. In second stage of melting amount of silica (SiO_2) was gradually increased while amount of sodium oxide (Na_2O) was gradually reduced at the same rate. In third stage of melting amount of calcium oxide (CaO) was gradually reduced while amount of aluminium oxide (Al_2O_3) was gradually reduced at the same rate. In fourth stage of melting amount of calcium oxide (CaO) was gradually reduced while boron oxide (B_2O_3) was gradually increased at the same rate. In all stages of melting, oxide percentage of raw material was kept 100%.

Temperature during all meltings was maintained at 1450 ± 10^{o}C by Thermo couple. After melting, each glass sample was chemically analyzed and compositions of all glass samples were written in weight percent.

Analysis of all glass samples was done by standard methods to see the exact percentage of oxides in each glass sample after melting (Portal, et. al 2001, Lee and Cheal, 2001). Important properties of glass like chemical durability, softening points, refractive index, density and thermal expansion were determined.

Chemical durability test: Chemical durability of all glass samples was determined by powder test method. ASTM (C 225-54). For this test, each glass sample was crushed and sieved through 40 mesh screen and retained on 50 mesh screen. Ten grams of this powder was taken as sample. It was washed six times by acetone then sample was dried in a drier. After drying, sample was taken in a 250 ml Erlenmeyer flask with 50 ml of distilled water and autoclaved for 30 minutes at 121^{o}C. The amount of alkali extracted from the glass was determined by titration, using N/50 H_2SO_4 and one to two drops of methyl red as an indicator. Results are usually expressed as the volume of dilute acid required to neutralize the alkali extracted from the glass (Shand, 1984).

Softening point: It was determined by the cone method. Cone of each glass sample was gradually heated in an electric furnace. The temperature at which the upper pointer of the glass cone showed the initial bend was recorded as the softening point (Andrejev and Golberg, 2003, Machacek and Gedeon, 2003).

Thermal Expansion: Thermal expansion of all sample were determined by dilatometer (Clare et al., 2003).

RESULTS AND DISCUSSION

For experimental study, all glass meltings were done in four stages.

(a) First stage of melting: In the first stage of melting, potassium carbonate in the oxide form (K_2O) was gradually reduced while sodium carbonate in the form of (Na_2O) is gradually reduced at the same rate. In last melting, potassium oxide (K_2O) was totally replaced with sodium oxide (Na_2O) (Table 1).

(b) Second stage of melting: Glass No. 5 in the Table 1 was selected as a base composition for the experimental study. In the second stage of melting the amount of alkali i.e. sodium oxide (Na_2O) was gradually reduced to 1% in each composition while silica (SiO_2) was gradually increased to 1% in the same way so that an optimum amount of Na_2O was determined (Table 2). Glass No. 8 as shown in Table 2 was proved to be the optimum composition having appropriate amount of alkali (Na_2O) which was essential for proper melting of glass. If sodium oxide (Na_2O) was further reduced beyond No. 8 like glass No. 9 to 11, glass become harder and harder and it became difficult to melt the glass.

(c) Third stage of melting: Glass No. 8 in table 2 was selected as a base composition for experimental study. In third stage of melting, aluminium oxide (Al_2O_3) was gradually increased while lime (CaO) was gradually reduced in the same way. If CaO is reduced in the composition it does not affect the durability of glass (Table 3). In Table 3 Glass No. 14 is the most suitable and durable glass. Beyond Glass No. 14 it was very difficult to melt the glass due to excess amount of Al_2O_3. Excessive quantity of Al_2O_3 in glass increases its viscosity and melting point.

(d) Fourth stage of melting: Glass No. 14 in Table 3 was selected as a base glass for further experimental study. In the fourth stage of melting, boric oxide (B_2O_3) was gradually increased to 0.5% in each composition while CaO was gradually reduced to 0.5% in each composition in the same way. Results are compiled in Table 4. Glass No. 19 in Table 4 is proved to be the most suitable and durable glass. B_2O_3 in glass No. 19 is 2%. When B_2O_3 was increased beyond 2%, cords in finished glass were developed. So, glass No. 19 shown in Table 4 is the excellent glass composition. This glass was properly melted and was free from defects like bubbles, seeds and cords. The glass No. 19 also has good balance of properties like refractive index, softening point, thermal expansion and chemical durability. Glass No. 19 is a good composition for the production of container glass, tablewares glass and pharmaceutical glass. Beyond glass No. 19 it was not possible to melt good quality glass because excess B_2O_3 made the glass improper refined, full of cords, seeds and bubbles.

Experimental study showed that excess amount of alkalies like sodium carbonate and potassium carbonate (especially sodium carbonate) made glass easily meltable, soft, refined and free from seeds and bubbles but on the other hand excess amount of alkalies make the glass inferior in qualities. Excess soda in the glass increased the thermal expansion of glass, reduced thermal shock endurance, reduced the durability of glass and increased the weathering effect which is called as fogging of the glass (Boksay and Rohonezy 1993, Chakraborty, et. al 1986, Stadler and David, 2000). Such glass is not suitable for pharmaceuticals, chemicals and food packaging. The use of such glass is confined to decoration, cosmetics and cheap grade beverages packaging. Therefore, to improve the quality and durability of glass, experiments were done by making some changes in composition of glass in four stages.

Table-1. Effect of variation of K_2O and Na_2O on glass melting

S. No	Composition of Glasses							Remarks
	SiO_2	K_2O	Na_2O	CaO	MgO	Al_2O_3	SO_3	
1.	69.5	19.0	0.0	10.0	0.8	0.5	0.2	Glass was hard in melting and took more time to melt and refine
2.	69.5	15.0	4.0	10.0	″	″	″	Glass was slightly softer than No. 1 and took slightly less time to melt and refine
3.	″	10.0	9.0	10.0	″	″	″	Glass was softer in melting than No.1&2. Glass refining took less time then No.1&2 glass was free from seeds and bubbles
4.	″	5.0	14.0	10.0	″	″	″	Glass was uniformly melted in less time than No.1 to 3. Glass was softer than No.1 to 3. Glass was properly refined and was free from seeds and bubbles.
5.	″	0.0	19.0	10.0	″	″	″	Glass was easily melted and was much softer than No.1-4. Good refined glass free from sees and bubbles was produced

Table -2. Effect of variation of SiO_2 and Na_2O on glass melting

Glass No.	Compositions of glasses						Remarks
	SiO_2	Na_2O	CaO	MgO	Al_2O_3	SO_3	
5.	69.5	19.0	10.0	0.8	0.5	0.2	Composition of glass used for second stage melting.
6.	70.5	18.0	″	″	″	″	Glass was melted and refined properly. Glass was free from seeds and bubbles.
7.	71.5	17.0	″	″	″	″	Glass was properly melted and refined but took slightly more time than No. 6 to melt and refined glass was free from seeds and bubbles.
8.	72.5	16.0	10.0	0.8	0.5	0.2	Glass melting and refining was good but it was slightly harder than No.7 due to increase of silica content and decrease of flux (Na_2O). It took slightly more time to melt than No.7. Glass was free from seeds and bubbles.
9.	73.5	15.0	″	″	″	″	Glass melting and refining took more time than No. 8. Glass was harder than No.8. A few seeds and bubbles were observed in glass.
10.	74.5	14.0	″	″	″	″	Glass was very hard it took more time to melt and refine than No. 9. Lot of seeds and bubbles were observed in the molten glass.
11.	75.5	13.0	″	″	″	″	Glass was very hard and did not melt properly. A lot of seeds and bubbles and some unmelted batch particles were observed in the molten glass.

Table-3. Effect of variation of CaO and Al_2O_3 on glass melting

Glass No.	Compositions of glasses						Remarks
	SiO_2	Na_2O	CaO	MgO	Al_2O_3	SO_3	
8.	72.5	16.0	10.0	0.8	0.5	0.2	Composition No. 8 which was selected from table 2 as a base composition for third stage melting. Al_2O_3 was gradually increased while CaO was gradually reduced to improve the durability of glass.
12.	72.5	16.0	9.5	0.8	1.0	0.2	Glass was melted and refined. No seeds and bubbles were observed.
13.	72.5	16.0	9.0	0.8	1.5	0.2	Glass was properly melted and refined but it took slightly more time to melt. No seeds and bubbles were observed.
14.	72.5	16.0	8.5	0.8	2.00	0.2	Glass was properly melted and refined. But it is slightly harder and took slightly more time to melt. Glass was free from seeds and bubbles
15.	72.5	16.0	8.00	0.8	2.5	0.2	Glass was harder and tedious to melt than No. 14. Some seeds and bubbles are produced.

Table-4. Effect of variation of CaO and B_2O_3 on glass melting

Glass No.	Compositions of glasses							Remarks
	SiO_2	Na_2O	CaO	MgO	Al_2O_3	B_2O_3	SO_3	
14.	72.5	16.0	8.5	0.8	2.00	0.0	0.2	Composition No. 14 which was selected as a base composition for fourth stage melting by adding B_2O_3 reducing CaO gradually with same ration to improve durability of glass.
16.	72.5	16.0	8.0	0.8	2.00	0.5	0.2	Glass was properly melted and well refined. No signs of cords were observed.
17.	72.5	16.0	7.5	0.8	2.00	1.0	0.2	Glass was properly melted and refining was good. No any signs of cords were observed.
18.	72.5	16.0	7.0	0.8	2.00	1.5	0.2	Glass was properly melted. Glass refining was good. No any signs of cords were observed.
19.	72.5	16.0	6.5	0.8	2.00	2.0	0.2	Glass was properly melted. Glass refining was good. No any signs of cords were observed.
20.	72.5	16.0	6.0	0.8	2.00	2.5	0.2	Glass was properly melted. Glass refining was good. But some cords appeared in glass.
21.	72.5	16.0	5.5	0.8	2.00	3.0	0.2	Glass was properly melted. Some cords in glass were appeared which were more than composition No.20. It means as B_2O_3 was increased from 2% in glass batch, cords in the glass started to develop cords were increased as the quantity of B_2O_3 was increased

Table-5. Properties of glasses

No. of Glass	Thermal expansion X 10^{-7}	Softening pt ^{0}C	Chemical Durability (Vol. of 0.2 N H_2SO_4 used in titration)
1.	97	629	9.2
2.	97	625	9.3
3.	99	624	9.4
4.	101	621	9.6
5.	102	620	9.7
6.	99	635	9.5
7.	96	685	9.0
8.	93	685	8.5
9.	92	720	8.3
10.	Improper glass	Improper glass	Improper glass
11.	Improper glass	Improper glass	Improper glass
12.	93	690	8.1
13.	93	696	7.7
14.	93	705	7.2
15.	93	716	6.9
16.	93	704	7.2
17.	92	701	6.9
18.	91	698	6.5
19.	90	694	6.1
20.	Improper glass	Improper glass	Improper glass
21.	Improper glass	Improper glass	Improper glass

Conclusion: Present study has been made to use soda (Na_2CO_3) as an alternate cheap flux with some minor additions of Al_2O_3 and H_3BO_3. In doing so a more durable and quality glass has been developed which has excellent working properties. Results showed that when small amounts of Al_2O_3 and H_3BO_3 are used in a glass batch then soda proved to be the best and cheap flux for the production of quality glass.

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