Pakistan J. Sci. Ind. Res., Vol. 29, No. 2, April 1986

COMPARISON OF SODIUM SULPHATE WITH GYPSUM AS GLASS REFINING AGENT

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(Received October 22, 1984; revised October 2, 1985)

The refining action of sodium sulphate with respect to gypsum has been studied in a Sodalime-silica glass composition. The sulphate radical concentration was maintained at 21.2 g/1000 g of glass. It has been experimentally shown employing bubble count technique that gypsum is a better refining agent as compared to sodium sulphate. The advantage in using gypsum lies in its abundant occurrence and availability.

INTRODUCTION

As a glass batch is charged to a furnace, a variety of chemical and physical reactions take place. Some of the reactions are: evaporation of free water, loss of gaseous components (CO_2, SO_2, CO, NO, O_2 and water vapours) and water of crystallization, formation of crystalline and non-crystalline products and dissipation of gaseous products through buoyancy. Although a considerable amount of the decomposition products and gases entraped in the batch from the furnace atmosphere escape during early stages of melting, yet the residual gases like SO_2, CO_2, CO, O_2, No and water vapours in the melt create supersaturation and re-boil problems during the refning and homogenising of glass. Aids like sulphates and arsenic added in small amounts help in overcoming the above problems.

The behaviour of all refining agents is two-fold. At higher-temperatures they give out gaseous products which coalesce with the occluded gases and rise to the surface [1]. At lower temperatures, the occluded gases are absorbed by the refining agent and the glass melt making the finished product free of bubbles.

The use of sodium sulphate in glass batches is very old and a good deal has been written about it [2-4]. The effective component that brings about the refining of glass is the sulphate radical. Pakistan glass industry has to import sodium sulphate for soda-lime-silica glasses. Gypsum provides the sulphate radical and is abundantly available in Pakistan far less price than the imported sodium sulphate. Therefore, its use as a refining agent should be more economical. In the present study, the advantages and disadvantages of using gypsum instead of sodium sulphate have been examined.

EXPERIMENTAL

Raw materials: The sand used had SiO_2 content (99.92%) while the chemical analysis of gypsum showed CaO (32.26%) and SO_3 (45.96%) in it. The rest of the materials were pure chemicals. The batch compositions of the glasses as calculated from the raw materials are given in Table 1.

Table 1. Batch compositions of investigated glasses

Batch Constituents	1	2	3	4
Sand	500	500	500	500
Limestone	141	141	122	130.89
Magnesite	7.5	7.5	7.5	7.5
Feldspar	19.5	19.5	19.5	19.5
Soda Ash	198.12	178.0	189.12	188.1
Sodium Sulphate	–	27.0	–	13.49
Gypsum ($CaSo_4.2H_2O$)	–	–	32.68	16.34
Sulphate 1000 g Glass	–	21.2	21.2	21.2

Melting of the glasses: The glasses were melted in molochite-clay crucibles at a temperature of 1450°. All the melts were maintained at this temperature for 1½ hr.

Preparation of the samples for bubble count: The melt was poured on 1" thick iron plates and the circular discs of various sizes were prepared and annealed at a temperature of 550°. The above temperature was maintained for 1 hr. and then slowly lowered to room temperatre.

Counting of the bubbles: The bubbles of the discs were counted with the help of a magnifying lens by dividing the circular discs into small areas. The total number of the bubbles was divided by the volume of the glass discs to get bubbles per cu. cm. of the glass. The results are given in Table 2.

RESULTS AND DISCUSSION

The effects of imported anhydrous sodium sulphate (China) and indigenous gypsum ($CaSO_4.2H_2O$) on the refining of glass containing (wt.%) SiO_2 (71.5), CaO (11.0), MgO (0.49), Al_2O_3 (0.49) and Na_2O (16.5) have been investigated. The sulphate ions in the melts, except in glass batch No. 1 (Table 1), were kept constant and the amounts of Na_2CO_3 and $CaCO_3$ adjusted accordingly. The batch compositions of the four glasses studied are given in Table 1. Glass No. 1 is free from all sulphates. Glasses No. 2 and 3 contain sodium sulphate and gypsum respectively. Glass No. 4 contains a mixture of the two sulphates. At present for better productivity and increased pull rates, industrial units are operated at 1450°; and therefore, the temperature of the glass melts under investigation was also chosen the same.

It can be seen from Table 2 that the bubble count of glass batch No. 1 is 67 per cc in the absence of sulphate radical. The bubble count comes down to 20 per cc by the addition of sulphate. It is so because the sulphates, due to their high surface tension, separate from the melt and undergo thermal dissociation. The gases given off as a result of this dissociation sweep away the occluded seeds from the melt. In this way, the glass containing a sulphate is refined quickly as compared to the one devoid of it.

Table 2. Bubble count of the samples (samples maintained at 1450° for 1½ hr)

Glass specifications	wt. of the glass sample in grams	No. of bubbles	Bubble count per Cubic centimetre
1. Without refining aid	169	4563	67
2. Anhydrous sodium sulphate	125	994	20
3. Gypsum	95	285	7
4. A mixture of anhydrous sodium sulphate and gypsum containing equal amounts of sulphates.	64	435	17

Glass No. 3 containing gypsum showed a bubble count of 7 per cc as compared with glass No. 2 (7 against 20). This means that gypsum acts even better than sodium sulphate. This is because sodium sulphate melts and dissociates at a lower temperature leaving behind unreacted silica on the surface which creates seeds. Gypsum melts and dissociates at 1450°, a temperature higher than that at which sodium sulphate dissociates, according to the equation:

$$CaSO_4 \xrightarrow{1450^\circ} CaO + SO_3$$

CaO so formed reacts with the unreacted SiO_2 floating on the glass surface:

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

These studies have also shown that a mixture of sodium sulphate and gypsum is more effective than sodium sulphate by itself, but it is less effective than gypsum alone in the refining of the glass melts. This is because the amount of CaO and SO_3 available from gypsum in glass No. 4 (Table 1) is nearly half that of glass No. 3. At 1450°, gypsum and not sodium sulphate controls the refining process, and therefore, reduction in its content lowers the refining action. This fact is supported by the results reported in Table 2.

Acknowledgements: The authors express their thanks to Dr. M.K. Bhatty, Director, PCSIR Laboratories, Lahore for his valuable suggestions in the improvement of this manuscript. The help of Mr. Rafique Mohammad and Mr. Bashirullah, J.T.Os in experimental work is also acknowledged.

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