Effect of Halides on the Early Stages of Glass Batch Melting

David Martlew

The late Ruth Hurst Vose made important excavations of early 17th century glassmaking furnaces at Bickerstaffe and at Houghton Green, in South Lancashire. The Bickerstaffe furnace was wood-fired and was close to Lathom House, an important centre for Royal progressions and the major administrative centre for the North West of England. The Houghton Green furnace at Denton near Manchester was notable for being an early coal-fired furnace.

Glass from both furnaces had a significant residual chloride content [9], which led researchers to speculate about the use of rock salt as an alkali source. Another potential source was soap-boilers' waste from Cheshire. The question was why the glassmakers chose to use these high chloride materials in conjunction with more conventional alkali sources.

Table 2: Glass sample BS 7/8/69 (3)

	Weight % as oxide*
SiO_2	58.5
CaO	19.7
Fe_2O_3	1.3
Al_2O_3	2.2
MgO	4.9
Na_2O	5.8
K_2O	1.7
P_2O5	3.5
Mn_3O_4	0.6
TiO_2	0.3
Cl	1.5
Total	100.0

*mean of three analyses

Analysis of glass from the Bickerstaffe furnace - Ruth Hurst Vose [9]

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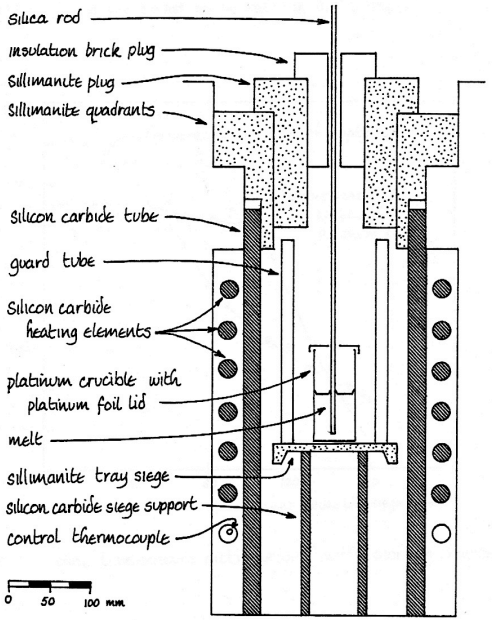
During the 1980s Cable and Martlew published a series of papers concerning the early stages of glass batch melting, with emphasis on the heterogeneous chemical reactions occurring between the silica grains and the liquid phases formed early in the glass melting process.

Studies were made using rods of vitreous silica suspended in a vertical tube furnace (right) with the lower part immersed in molten alkali, the compositions of which were designed to explore liquid phases likely to be present early in the glass making reactions [1-8]. The methods used for the corrosion experiments and subsequent measurements were detailed in the early papers [1,2].



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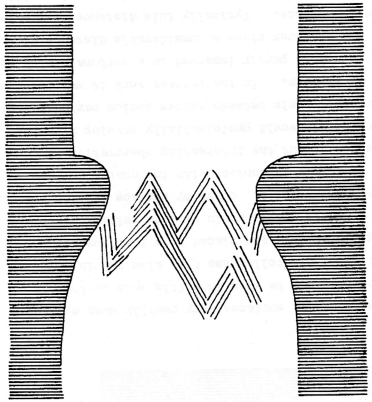
One series of experiments carried out at the time were not included in the published papers, because of concerns about materials and furnace control [10]. They concerned the effect on early melting reactions of adding sodium chloride and sodium bromide to the melts. The tentative conclusions from this work may be useful in explaining the presence of halides in historic glasses.

Corrosion rates at the level of maximum corrosion (right) were determined for sodium carbonate melts to which various amounts of sodium chloride and sodium bromide had been added. Also the heights to which the melts wetted the silica rods was measured, as a pragmatic (but very approximate) indication of effect on melt surface tension. Melting studies had shown that this would influence the rate at which wetting of silica grains would occur, and thus how quickly dissolution could begin.



Schematic diagram, showing a corroded silica rod seen against a dark background. The enhanced corrosion near the level of the free liquid surface is familiar in context of the corrosion of glassmaking refractories, and is often referred to as the "fluxline cut".

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Extents of corrosion at the "flux-line cut" were measured for rods corroded at 1120oC, a temperature selected as relevant to early glass-making reactions, and one which gave easily measurable corrosion profiles.

Corrosion depths increased substantially linearly with time over the experimental time scale, typically up to 400 seconds.

Corrosion rates were plotted against the molar concentration of alkali halide present (right). Over the range 0 to 15% halide the corrosion rate increased linearly by about 60% (right).

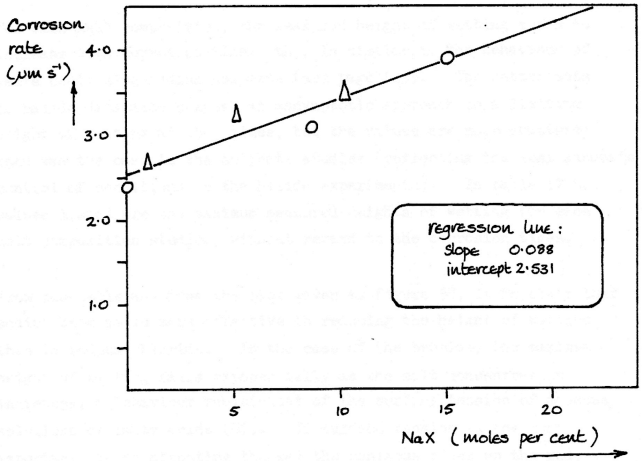

Figure 57 : corrosion rate and halide content in moles per cent.

"Δ" denotes NaBr

"o" denotes NaCl

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The maximum height of wetting recorded did not vary significantly with time of corrosion, but did show substantial variation with the amount of sodium halide in the melt (right). Sodium chloride at 15 moles % approximately halved the height of wetting; sodium bromide reduced it significantly more.

From these experiments, we can infer benefits to early glassmakers if sodium chloride were present in the batch. Their furnace temperatures were low by today's standards, so improved wetting of silica grains and more rapid early stage dissolution would be a great help to their melting operations.

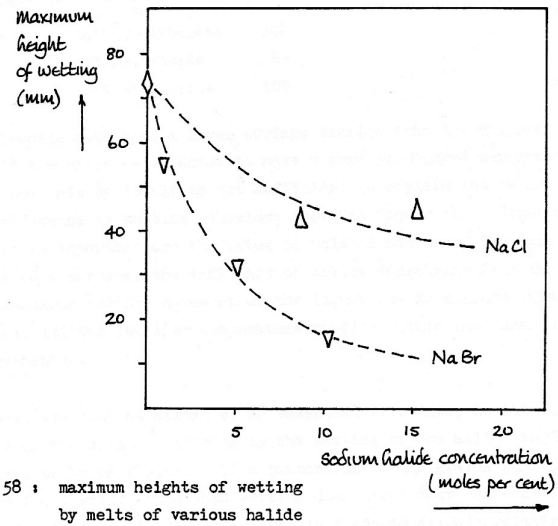

Figure 58 : maximum heights of wetting by melts of various halide contents

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Acknowledgement:

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