Original Paper

Control of the glass melting process – Results of gas extraction investigations[1])

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Various parameters influencing the extractable gas content were investigated with the help of improved equipment for high-vacuum extraction experiments. Investigations of a tube melting tank, of the homogeneity of gas distribution in a TV screen and gob and of laboratory melts with different fining agents are described in detail. The different degassing behavior of different glass types are also described. It could be shown that the complex influence of technological and chemical factors determines the amount of physically and chemically dissolved gases. With experience in the analytical procedure, the use of statistical methods of data processing and the knowledge of technological parameters, it is possible to give hints for melting process control.

Steuerung des Glasschmelzprozesses – Ergebnisse von Gasextraktionsuntersuchungen

Mit Hilfe einer verbesserten Apparatur zur Hochvakuumheißextraktion wurden unterschiedliche Einflußgrößen auf den extrahierbaren Gasgehalt untersucht. Näher erläutert werden Untersuchungen an einer Rohrglaswanne, der Gasverteilung in einem TV-Schirm bzw. in einem entsprechenden Glasposten und von Laborschmelzen mit unterschiedlichen Läutermittelzusätzen. Das unterschiedliche Entgasungsverhalten von verschiedenen Gläsern wird gegenübergestellt. Dabei konnte gezeigt werden, daß in der Regel der komplexe Einfluß technologischer und chemischer Faktoren die Menge der chemisch und physikalisch gelösten Gase bestimmt. Mit einiger meßmethodischer Erfahrung und durch Anwendung statistischer Auswertemethoden können bei detaillierter Kenntnis technologischer Parameter Hinweise zur Prozeßführung gegeben werden.

1. Introduction

Various parameters influence the content of physically and chemically dissolved gases in glasses. Main factors for the extractable gas content are the technological parameters of the production process and the composition of the raw materials. Furthermore, the sampling conditions must be taken into consideration. Experience has shown that the high-vacuum extraction is a useful analytical method to characterize the volatiles of glasses. The equipment described by Stelzner and Heide [1] was further improved in the last years especially by a new mass spectrometer, high-vacuum design and a data handling system.

2. Experimental

In the analytical system the mass spectrometer QMG-420C (Balzers AG, Balzers (Liechtenstein)) [2 and 3] was used. The vacuum is generated by turbomolecular pumps (figure 1) producing a hydrocarbon-free vacuum. The sample device can be separated from the mass spectrometer to minimize the contamination with components of the atmosphere during sample loading. The gas extraction occurs in a total pressure range $<10^{-5}$ mbar. The partial pressures are measured by means of a Faraday or channeltron detector as ion currents. Usually glass specimens were ground, sieved and the powder (0.63 to 0.4 mm) was weighed into Al_2O_3 crucibles. The heating rate was 10 K/min [4].

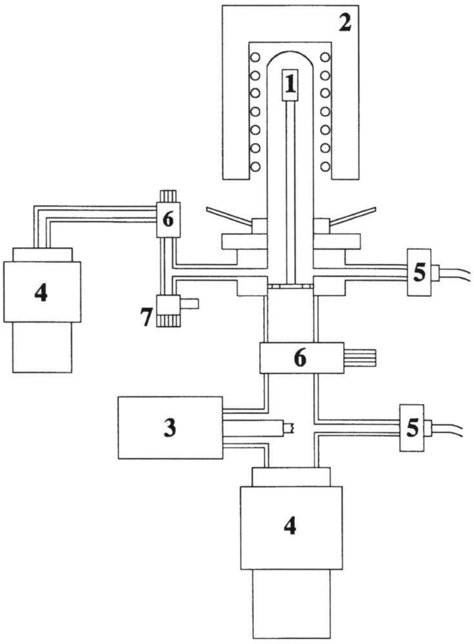

Figure 1. Equipment for high-vacuum extraction experiments. 1: sample chamber, 2: furnace, 3: mass spectrometer, 4: turbomolecular pumps, 5: measuring gauge for total pressure, 6 and 7: mechanical valves.

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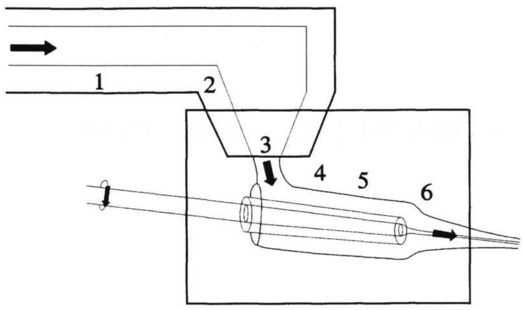


Figure 2. Feeder area of a tube glass tank with different locations of temperature detectors. 1 to 6: temperature measurement locations.

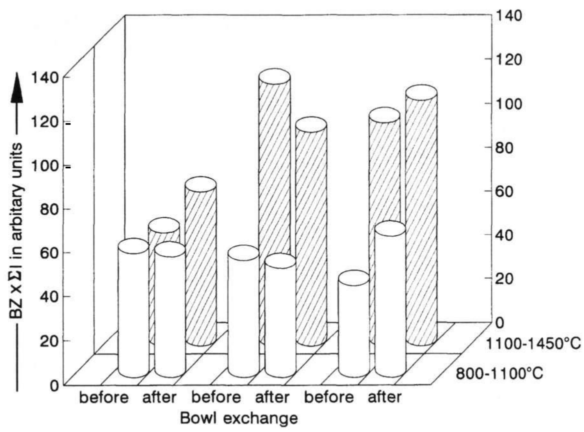
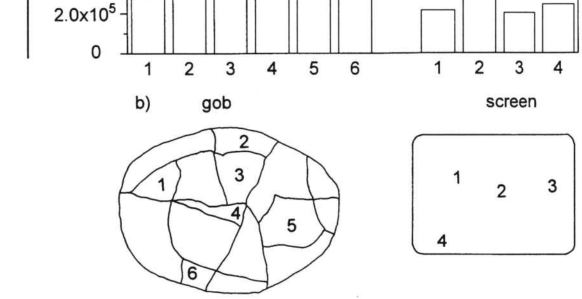


Figure 3. Comparison of the gas content before and after bowl exchange in different temperature ranges.



Figures 4a and b. Extractable gas content in dependence on the sample location; a) results, b) schematic representation of the sample location.

Dissolved gases escape from the sample as bubbles above the transformation range of the glasses. Changes of total pressure during the bubble bursting take a time of 300 to 500 ms. It was possible to measure 3 to 4 cycles per second (in every cycle 16 mass numbers). Spectra of masses, depending on the temperature, were obtained. The quantitative determination of the gas content of the glasses in absolute units was not the aim of this work and the problem is still an open question today. The qualitative characterization of gas content of the bubbles and the temperature of the degassing range of different fluids are very useful tools for the characterization of glassy specimens.

The total pressure was recorded on-line by an x-y recorder. The number of bursting bubbles (BZ) and the sum of their intensities (ΣI) represent a relative value permitting the comparison of extractable gas contents. In this way it is possible to compare the gas contents of samples of a series.

3. Results

3.1. Technological influences

The influence of technological parameters was investigated on a tube glass tank [3]. Because of corrosion of the ceramics the bowl has to be exchanged regularly. Samples before and after such a replacement were investigated. Additionally, the temperature parameters from the feeder area (figure 2) were determined. The results show (figure 3) that the extractable gas content of the final products undergoes no significant change due to the replacement of the bowl.

With the method of correlation analysis two essential relations were found. On distinct temperature measurement locations a correlation between the extractable gas content (1100 to 1450 °C) and the temperature at the respective location was found. The results also suggest a correlation between the extractable gas content and the defects caused by bubbles in the final product.

3.2. Sampling conditions

To demonstrate the influence of the sampling conditions a gob of TV glass and a TV screen were investigated. The sampling location and the results of high-vacuum extraction are shown in figures 4a and b. Obviously, there exist great differences of the extractable gas content in the gob but only relatively small differences in the TV screen. An explanation could be that the thermal history of the gob due to processing (cutting process) is different in comparison to that of the screen (pressing process).

3.3. Different raw materials and refining agents

A model glass (composition in wt%: 74 SiO_2, 16 Na_2O and 10 CaO) was melted with different additions of Sb_2O_3, NaCl and Na_2SO_4 under the same melting conditions. The gas extraction yielded nearly exclusively oxygen. The extractable gas contents were extremely different (figure 5).

The comparison of partial pressures of different types (table 1) of glasses are shown in figures 6a to c. As it can be seen from table 1, the degassing behavior of

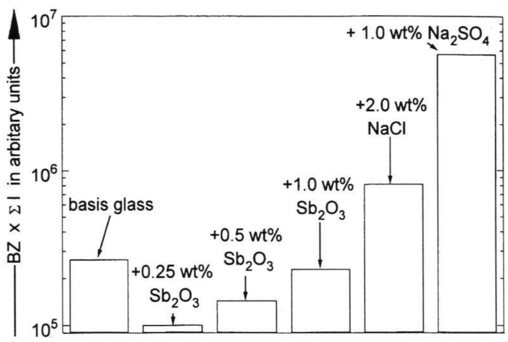


Figure 5. Extractable gas content of laboratory melts (model glass with composition (in wt%): 74 SiO_2, 16 Na_2O, 10 CaO).

Table 1. Composition of different glass systems

	borosilicate glass (I)	TV screen glass (II)	container glass (III)
SiO_2	75	60	73
alkalines	7	17	13.5
alkaline earths	<2.5	17	12.5
B_2O_3	10.5	–	–
Al_2O_3	5	2	1
ZrO_2	–	2	–
Sb_2O_3	–	0.6	–
remainder	–	1.4	–

glass melts is strongly determined by the glass type (borosilicate glass (I) and alkali silicate glasses (II and III)). The results of former investigations, carried out in the last years, are summarized in tables 2 to 4.

4. Conclusions

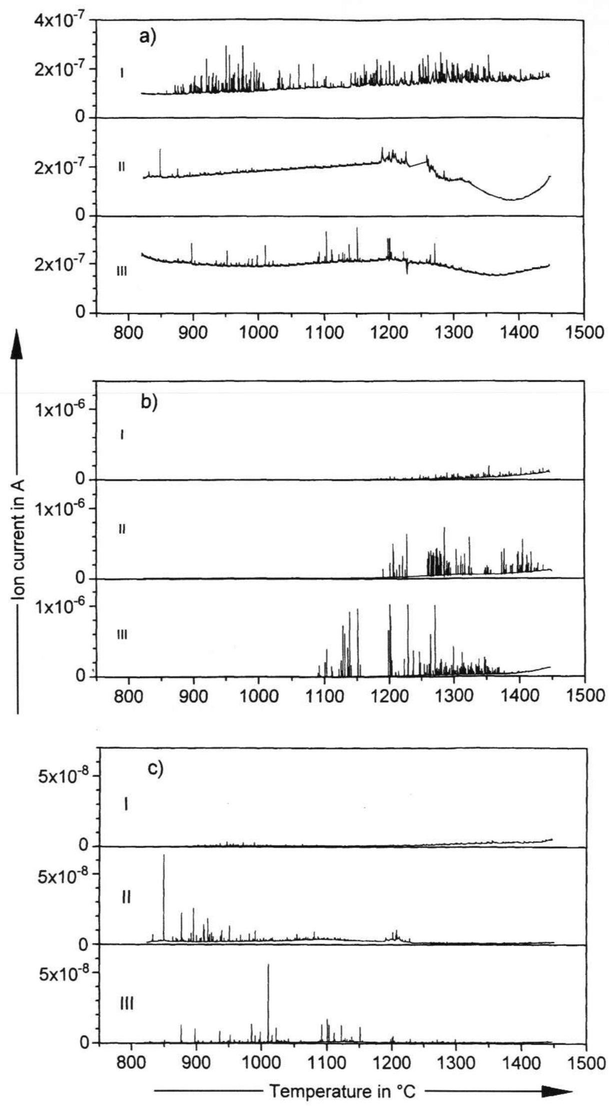
With the analytical system of gas extraction it is possible to detect simultaneously different evolved fluids. The composition of evolved gases depends on the glass system. The major fluids are water, carbon dioxide and oxygen. Furthermore, components like hydrocarbons, hydrogen as well as compounds of sulfur, chlorine and fluorine were observed. Nitrogen was observed quite rarely in the degassing experiments.

The experiments indicated that the technological factors can have the same relevance for the degassing behavior as the chemical composition of batches and raw materials. For a correct interpretation of the results, it is necessary to consider technological parameters in detail. By application of statistical methods on data handling it is possible to describe more complicated relations between parameters of technology and quality.

5. Discussion

The high-vacuum hot extraction can be applied to two principal areas to control the glass melting process.

In case of quality problems the extraction experiments can be used to optimize the melting process. Changes in the production process can be supported by



Figures 6a to c. Comparison of partial pressures of different glass systems (borosilicate glass (I), TV screen glass (II), container glass (III)); a) ion current of m/e = 18 (H_2O^+), b) ion current of m/e = 32 (O_2^+), c) ion current of m/e = 44 (CO_2^+).

gas extraction investigations. So it may be more easy to achieve regular production conditions. For such an optimization a vacuum pumping station with a mass spectrometer is necessary, because the evolved gases have to be characterized qualitatively.

A continuous control of the melting process is more difficult. It is essential to have samples from different parts of the glass tank over a long period of time. The melting process can be influenced by the sampling. After characterizing the glass system in respect to the extractable gas content, a total pressure characterization of the degassing behavior is sufficient.

For the interpretation of the results experience in the analytical procedure and the use of statistical methods of data processing are necessary.

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Table 2. Influence of technological parameters on the extractable gas content

glass system	parameter	results
container glass (brown) [5]	dependence on sample location (tank, gob)	– no significant differences between the extractable gas content, but lower standard deviation with longer melting time
TV glass [5]	influence of different temperature and convection current conditions in the tank (change in heating, bubbling)	– higher CO_2 and O_2 content during technological changes – correlation to the quality of glass – main influence: construction of the tank
optical glass (K 13) [1]	feeder arrangement	– significant differences in dependence on the convection current – main influence: tank construction and temperature variations in the feeder

Table 3. Investigations on representative sampling

glass system	purpose of the investigations	results
container glass (white) [5]	best time of sampling (every 5 min or 24 h)	large variation of results probably due to inhomogeneities in the tank
container glass (white) [6]	gas distribution in a gob	change in homogeneity in dependence on the sampling device
optical glass [7]	determining the most suitable sample location to correlate the results with quality parameters of the final products	some sampling locations in the tank correlate with the number of bubble defects in the final products

Table 4. Influence of raw materials

glass system	variation of raw materials	results
container glass (white) [5]	reduction of cullet content in the batch	more extractable gas (e.g. CO_2)
container glass [5]	change in the lime raw material (replacement of slag wollastonite with "Hüttenbims")	change of extractable gas content (CO_2, O_2)
container glass [5]	change in the lime raw material (replacement of quicklime with natural lime)	more extractable CO_2
optical glass (K 13) [1]	reduction of the amount of refining agent (As_2O_3)	change in extractable O_2 (lower amount of chemically dissolved oxygen)

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