

Parameters affecting the workability of container glass

Part 2. Influence of dissolved gases and of other parameters¹⁾

Franco Geotti-Bianchini

Stazione Sperimentale del Vetro, Murano-Venezia (Italy)

The hypotheses associated with variations of dissolved gases, structure, macroinhomogeneity (or cordiness), surface composition gradients and radiant heat transfer properties are presented in some detail in the second part of the review. While each of the physicochemical parameters considered was shown to be potentially influential by laboratory experiments, there is still no general agreement on the factors which are most relevant in practice. The most popular candidates are microstructure formation and variations of the content of dissolved gases; however, so far no conclusive evidence has been obtained. The influence of such parameters on stress-induced viscosity variations is also not well clarified. In order to decide what should be improved in the melting practice to achieve a better control of the forming behaviour, it is essential to solve the alternative with suitable experiments on carefully selected production samples.

Verarbeitbarkeit von Behälterglas und ihre Einflußgrößen

Teil 2. Einfluß von gelösten Gasen und anderen Parametern

Im zweiten Teil dieser Übersicht werden die Theorien ausführlich dargestellt, die mit Veränderungen der gelösten Gase, der Glasstruktur, der Schlierigkeit, dem Vorliegen von Gradienten der chemischen Oberflächenszusammensetzung und den Wärmeabstrahlungseigenschaften in Verbindung stehen. Während sich in Laborexperimenten gezeigt hat, daß jeder der hier betrachteten Faktoren möglicherweise einen gewissen Einfluß hat, besteht noch keine Klarheit darüber, welcher dieser Faktoren für die Praxis relevant ist. Die meisten Autoren halten die Mikrostrukturbildung und die Änderungen des Gehaltes an gelösten Gasen für die entscheidenden Größen, schlüssige Beweise liegen jedoch bisher nicht vor. Ungenügend geklärt ist auch der Einfluß solcher Parameter auf spannungsinduzierte Viskositätsänderungen. Um entscheiden zu können, was man in der Produktionspraxis verbessern sollte, um das Formgebungsverhalten besser in den Griff zu bekommen, ist es wichtig, diese Fragen durch geeignete Experimente mit sorgfältig ausgewählten Produktionsproben zu lösen.

3. Dissolved gases and redox state

The main dissolved gases in industrial soda–lime–silica glass are SO₃, O₂, H₂O and CO₂ (plus traces of N₂, noble gases, chlorine and fluorine). Most react either with the silicate network or with the modifying oxides producing ions such as SO₄²⁻, S²⁻, CO₃²⁻, OH⁻, F⁻ and Cl⁻ which either form bonds of the type Si–X or interact electrostatically with the modifying ions (Coenen et al. 1984; Goldman 1985; Krämer 1991; Scholze 1991). Dissolved oxygen oxidizes polyvalent elements, producing free oxygen ions, O²⁻. In this way they can affect the glass structure, both directly (through the just mentioned interactions) and indirectly (because they give rise to anions with different tendencies to complex or screen the cations or because redox reactions change the preferred coordination of polyvalent ions such as iron, chromium, etc. (Hirashima et al. 1988; Krämer 1991)). Finally, they interact mutually; in particular, the oxygen activity influences the redox state of sulphur compounds and directly or indirectly the concentrations of most other gases such as water

(Goldman 1985; Krämer 1991; Barbon et al. 1991). Water in turn is bound as “free” and “bonded” hydroxyls (or silanols, Si–OH), whose proportion varies with the ratio of bridging to non-bridging oxygens (Scholze 1959, 1991; Fernandez Navarro, Brückner 1976).

This brief discussion shows how dissolved gases can influence the structure of glass, even for a constant oxide composition. By influencing the structure, they can significantly modify viscosity, as shown by several papers which illustrate the influence of water, chlorine, fluorine and of the redox state on viscosity (Fenstermacher et al. 1965; Jewell et al. 1990; Hessenkemper, Brückner 1990 (c); Scholze 1991). In 1967 Poole reported an increase of forming problems in coincidence with variations of retained sulphate. In 1977 the same author stated that although in the last decade the melting process had become less sensitive to sulphate variations, the influence of the melting atmosphere was still a key parameter, as shown by the decrease of workability problems observed when the melting practice switched from oxidizing to partially reducing. Recently, several authors suggested that workability upsets might be caused by oscillations of the gas content, in particular of the redox state (Lenhart, Schaeffer 1986; Williams 1989). If this theory is

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confirmed, in principle the cyclic occurrence of problems might be attributed to oscillations of temperature, dwell time, batch humidity or cullet addition or to variations of the atmosphere above the melt.

The problem was investigated in detail by Hessenkemper and Brückner (1990 (c)) on a laboratory-melted glass with a float-like composition, where the fraction of ferrous iron varied between 14 and 84 %. The following results were reported:

- the equilibrium viscosity of reduced melts is significantly lower at 550 °C, but differences become negligible at 750 °C;
- even drastic changes of the redox conditions have no effect on the load-dependent non-Newtonian flow behaviour;
- both temperature and pressure influence the ferrous/ferric equilibria;
- reduced melts show a smaller relaxation modulus (and therefore a lower stiffness and brittleness) and a higher high-temperature tensile strength (i.e., a larger crack-free degree of deformation); however, the relative differences between reduced and oxidized melts decrease with increasing temperatures.

Apparently opposite results had been reported by Coenen et al. (1985), who measured the mechanical glass transition temperature (an indicator of stiffness and brittleness) of melts of an alkali-earth alkali silicate glass bubbled with nitrogen and oxygen and found that it was lower for an oxidizing atmosphere. These authors suggested that their results could be generalized, being in agreement with the case of Sproull and Rindone (1974), where an oxidizing atmosphere had improved the strength of alkali silicate glass melts.

If extended to container glass such results would imply that the brittleness and the probability to suffer from workability upsets should vary with the ferrous/ferric ratio in the sequence: amber → green → flint glass. However, a great caution is required when comparing such laboratory experiments with the behaviour of industrial melts (or melts with quite different redox ratios or base glass compositions) for a number of reasons exemplified as follows:

- a) the glass composition exerts a great influence on microstructure, gas solubilities etc.;
- b) in order to limit the number of variables Hessenkemper and Brückner used no sulphates and varied the redox ratio and the water content independently, while in the case of industrial sulphate-fined melts redox state changes also influence the water content;
- c) in the case of green and amber glass large additions of foreign cullet might also in principle impair homogeneity;

d) each glass colour has a different radiation thermal conductivity;

e) the strength distribution is quite different for pristine, laboratory-drawn fibres as compared to articles whose surface is exposed to severe damage on the production line;

f) the concepts of high-temperature and room temperature brittleness are quite different, as explained in section 2. (see part 1 in no. 11, p. 311–314).

Indeed, according to plant experience, all colours seem to be sporadically affected by workability problems. In the industrial practice the critical point is rather to establish if a given type of container glass can significantly vary its gas content and therefore its viscosity within hours during the same job without affecting routine production controls. The answer is not straightforward because many parameters vary at the same time in industrial melts, particularly since large additions of foreign cullet force the plants to accept some oscillations in colour and oxide content (Mastaler 1990). Thus, while large redox variations are unlikely (as they would be revealed by changes of glass colour and of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio), moderate oscillations of the redox state, water and total sulphur content do normally take place. Although Fenstermacher et al. (1965) provided ample data about the variables which influence the water content and reported significant oscillations due to atmospheric and batch humidity, fuel changes and dwell time, water is seldom routinely measured.

In this situation only a quantitative assessment of all the variables relevant for industrial melts (including typical statistical oscillations of water and oxide content and of the redox state during time) can show if variations of the content of dissolved gases can produce significant viscosity oscillations (i.e. larger than those due to statistical variations of composition (Mastaler 1990)). Such a test might be performed conveniently in the course of a campaign using electrochemical sensors to monitor continuously the oxygen activity (Müller-Simon et al. 1990), by checking at regular intervals the water content and the chemical composition. Once available, the industrial data should be compared with laboratory evidence obtained in controlled conditions, of the type provided by Hessenkemper and Brückner (1990 (c)). In particular, there is still a lack of accurate, quantitative information about the influence of sulphates, sulphides and carbonates on viscosity and of water and redox state on rheology above the softening point. It is also essential to understand if the moderate differences of behaviour so far recorded at higher temperatures are real or produced by equilibration of the melt with the laboratory atmosphere.

A further often resumed suggestion, going back to English and Turner (1929), is that high cullet additions may modify the glass workability because of

different melting histories, possibly associated with a different gas content (in German: "totgeschmolzenes Glas") (Coenen et al. 1985; Klein 1973). Although this suggestion (based on pot melts and laboratory trials) may appear reasonable and although it is known that foreign cullet includes glasses with widely different water contents and redox states, no recent systematic study with quantitative measurements on tank-melted industrial glass is available to confirm it. However, the positive experience made by so many plants using between 70 and 100 % cullet (Mastaler 1990; Goerk et al. 1981) seems to contradict such negative predictions. Quite probably, the homogenizing performances of modern furnaces are better than those achieved in pot melts. On the other hand, recently Hessenkemper and Brückner (1991) measured the ultrasonic velocities of laboratory melts obtained from the batch and from 100 % cullet and detected no significant differences. Finally, it must be considered that on an industrial scale it is difficult to perform comparisons in identical conditions because large variations of the cullet addition often bring about adjustments of the temperature distribution in the furnace (and therefore of current pattern and dissolved gases including the redox state) because cullet melts long before the batch.

4. Structure

In view of the significant influence of glass structure on rheology, it is sometimes suggested that melting history changes (cullet, temperatures, dwell times) may modify it, altering the forming behaviour. The present section illustrates the possibility to attribute poor workability events to structural changes, rather than to other factors. An accurate definition of the structure of multicomponent soda–lime–silica glasses is quite difficult to achieve, since it includes an array of features such as: bond lengths and bond angles (both within and between neighbouring tetrahedra); the degree of polymerization of the silicate network and the type and distribution of polysilicate units (rings, chains etc.); the packing density, including the presence of voids; the ratio of non-bridging to bridging oxygens (or of modifiers to formers, also expressed as basicity, or oxygen ion activity) and the coordination of cations (which varies with their oxidation state (Scholze 1991)). Additionally, to define the structure one must establish how the chemically dissolved gases are incorporated, as mentioned in section 3. (Hirashima et al. 1988; Krämer 1991; Scholze 1991). The possibility that modifiers may be preferentially clustered rather than randomly distributed and other features of middle-range order are discussed in section 2.3. (see part 1 in no. 11, p. 311–312).

In view of the complexity of the situation and of the scarcity of experimental data (beyond the short-range order), over the years many alternative

structural models have been formulated, based on the degree of shielding of cations, or on the percentage of ionic or directional bonds (Scholze 1991) or on the presence of "atomic defects", such as oxygen deficiencies (Rindone et al. 1983; McKinnis 1986). As temperature increases, the observed volume increase and easier flow are attributed to the fact that the bonds become progressively looser (or depolymerization takes place). Rheological studies attribute the occurrence of shear thinning, described in section 1.2. (see part 1 in no. 11, p. 307–308), to load-induced structure changes. By analogy with polymer studies and with the support of various types of mathematical simulations it is generally believed that the silicate molecules orient themselves along parallel lines or planes (structural anisotropy), reducing the "degree of entanglement" and therefore facilitating flow (Simmons et al. 1982; Hessenkemper, Brückner 1988, 1989; Simmons, Simmons 1989; Guillemet, Gyonne 1990). Within the soda–lime–silica glass composition it is plausible to attribute the decreased tendency to undergo shear-thinning caused by alumina additions and lower alkali contents (Simmons, Simmons 1989) to the increasing difficulty to align a highly cross-linked network.

Similar considerations apply to the high-temperature fracture behaviour. Recently Hessenkemper and Brückner (1990 (a)) showed that in glasses with widely different structural configurations (ranging from phosphates to silicates) the load-dependent relaxation behaviour varies as a function of the degree of cross-linking. It remains to be confirmed if the presumably moderate structural changes actually occurring during the industrial production of a given type of container glass (conceivably due to oscillations of the redox state of polyvalent ions and to dissolved gases or to different cullet additions and thermal treatments), can significantly affect rheology and workability. Krämer (1991) proposed a practical way to quantify the fraction of modifiers (allowing to predict differences in gas solubilities when glasses with widely different compositions are compared): the basicity number, calculated in a standardized way from the analytical composition. But when this concept is applied to container glass with the aim to monitor possible structural variations produced by a different melting history, the computed oscillations are so small that it seems unlikely to explain rheological differences in this way.

On the other hand, the literature on melting history often postulated that high-temperature treatments might cause major changes, whose effects remain at lower temperatures, such as chain length variations or even modifications of the bonding situation (Bobkova 1987). Unfortunately, the interpretation given is not supported by a rigorous experimental verification. Coenen et al. (1985) explained the cases of strength losses and the difficult

forming behaviour observed for high cullet additions reported by Russ (1931) on various silicate glass compositions and by Trier (1978) on container glass, as well as their own observations made at Schott Glaswerke, Mainz (FRG), on a low Al_2O_3 alkali silicate glass (Foturan) with the higher content of bridging oxygens which they attributed to all types of cullet. Their paper did not specify whether the different structure was attributed to alkali losses (changing the composition) or to longer dwell times in the furnace (modifying the gas content) and did not provide any direct experimental verification. Moreover, the lower OH content observed on cullet-rich Foturan melts was attributed to a decreased water solubility, caused by a (postulated) lower basicity of cullet. Alternative hypotheses (e.g., the possibility that a different water content might be produced by different melting conditions) were apparently not considered. Indeed, the IR spectra of the same glass – batch- and cullet-melted – reported in the paper show a negligible difference in the ratio between the bands of free and bonded hydroxyls (normally taken as an indicator of the ratio of network formers to modifiers).

In summary, so far most references to structural changes in industrial glass are confined to plausible hypotheses or based on indirect evidence (such as property changes, which in principle might also be explained by other factors), rather than on actual structural determinations, which are difficult to achieve. At present, the interpretation of the rheological behaviour of glass melts relies mainly on simplified models (generally based on spheres with a simplified bonding situation) and mathematical simulations. In the last decade the assessment of glass structure, including middle-range order, has made spectacular progress thanks to the use of diffraction and spectroscopical techniques (XPS, Raman, IR, visible, EPR, NMR, Mössbauer, XAS) and to improved modelling (Zarzycki 1990). Some of the advances concern multicomponent glasses. However, so far a complete assessment of the structure of commercial soda–lime–silica glass is considered beyond reach even at room temperature. In principle, using some spectroscopical techniques coupled with suitable structural models taking into account the analytical composition it is possible to assess possible variations of structure occurring in melts with different melting histories. However, no published examples applied to industrial glass are known. Thus, in practical situations the type and extent of the structural modifications produced on the “flow units” by high temperatures, shear stresses and dissolved gases are still unspecified.

In conclusion, the observed production problems cannot be attributed with certainty to modifications of a given structural feature, until sufficient experimental evidence is available.

5. Macroinhomogeneity

In the present content the term “macroinhomogeneity” (or cordiness) is used to distinguish it from the – submicroscopic – microinhomogeneity (or microstructure) presented in section 2. (see part 1 in no. 11, p. 311–314). The problem here is to establish if the elongated one- or two-dimensional inhomogeneities, extending between a few millimetres and several centimetres, which differ in composition and refractive index, can affect the forming behaviour.

Container glass consists of concentric layers, stretched and oriented parallel to the container axis during the forming process (Eitel 1932). Such “onion peel” structure is particularly evident when viewed in cross section in a microscope with a narrow diaphragm. While the presence of regular, low-contrast layers (reams) is considered harmless, strong, irregular layers (cords, threads, knots) are objectionable for aesthetic reasons or because they may affect strength.

The “ring section” technique uses a polarizing microscope to observe such layers and to classify them according to the tendency to lower the mechanical strength of the article. While it is indisputable that permanent stresses in the proximity of the surface are detrimental, it is not clear how far the presence of thin layers clearly visible but with low stresses can harm strength (Swicker 1939; NN 1961; Capps et al. 1980). A further technique normally used to detect the presence of inhomogeneous layers is the Christiansen filter or Shelyubskii method (Hense 1987). The method was shown to respond to the intensity of segregation in layers of a given glass (Hense 1987; Cable, Bower 1965). However, the interpretation of the results requires some caution because a sample considered inhomogeneous might be characterized by a high number of layers with moderate differences of composition or by a few pronounced cords (Hense), as well as by microstructure (Braetsch, Frischat 1988).

Some of the first authors who discussed the subject of melting history as a possible explanation for the bad workability or brittleness of glass obtained by remelting cullet several times (Ruß 1931; English, Turner 1929) considered the hypothesis that the presence of macroscopic inhomogeneities (cords, knots) might adversely affect its flow properties and therefore its forming behaviour. Indeed, in container production plant experience shows that a marked cord with a high or low viscosity as compared to the matrix can produce a thick or a thin spot in the sidewall (Swicker 1939). A quantitative treatment of the problem is suggested by Brückner (1962) for a single plane layer with a viscosity differing from the matrix.

If the presence of inhomogeneous layers can modify the forming behaviour, in principle it might also give rise to a damaged surface, with checks and

marks, and thus also impair strength. This possible connection between inhomogeneity, poor workability and low strength probably originated the suggestion to use the Shelyubskii technique in production control as a warning of poor workability or brittleness (Hense 1987). On the other hand, Poole (1967) found no correlation between general cordiness and bad workability. So far, the mentioned qualitative statements offer no clue to discriminate between a level of cordiness which is physiological (i.e., inherent to the process but harmless), and pathological (i.e., likely to influence the forming behaviour).

A quantitative evaluation of the problem would require detailed data on the size and frequency of layers and on the differences of composition (and viscosity) between them and careful experiments or rigorous modelling along the lines suggested by Brückner (1962). Unfortunately, the only available studies about the homogeneity and cord flow patterns in the forehearth, gob, parison and container are outdated (Eitel 1932).

Finally, it must be remembered that homogeneity is a complex property to be defined rigorously. Thus, the question of the size, intensity, frequency and orientation of the inhomogeneous layers most likely to affect workability is still open.

6. Skin effect of the gob

Poole (1967) observed that the complaints associated with poor workability resembled defects due to cold glass (checks, poor glass distribution). To explain this behaviour, he suggested that the contact with the atmosphere and the mould might have changed the surface composition (water losses, redox changes), increasing the viscosity of the near surface layers (which he postulated to exert a crucial influence on the forming behaviour). The fact that alkali release in hydrolytic tests correlated with poor workability and that workability problems often improved by adding minor ingredients to the batch or carbon and sulphur to mould lubricants seemed to offer an indirect evidence.

The hypothesis that the beneficial effect of sulphur in reducing checks may be due to its partial dissolution in the surface layers of the parison was made also by Coenen et al. (1984). However, rather than postulating viscosity variations, the latter authors suggested that an increased concentration of sulphates would lower the surface energy, produce a better spreading of glass on the mould surface, thus improving the thermal contact and therefore also the heat exchange rate. Accordingly, they attributed several forming problems observed lately to the progressive reduction of the sulphur content of fuels. In principle, also the beneficial effects of some minor ingredients might be attributed to their influence on the surface energy (improving the mould wetting behaviour) rather than to viscosity changes.

Recently, the dramatic influence of the atmosphere and surface composition on the rheology of fibres was demonstrated by Po Shen et al. (1990). It is obviously desirable to check how far the treatment can be extended to containers, where the surface-to-volume ratio is much smaller.

Further suggestions are provided by Winther and Schaeffer (1988), who investigated the glass-to-mould contact as a function of pretreatments with hot reactive gases and found that the strong dealcalization caused by HCl increased the sticking temperature and lowered the susceptibility to thermo-mechanical damage.

In spite of the recent advances in surface analytical techniques, so far the "skin effect" theory was never verified experimentally for industrially produced containers with data on composition profiles associated with a convincing model of the forming behaviour (rheology, metal wetting). An accurate study would require a careful sampling of gob and parison in order not to obliterate the surface condition existing in production. The "skin" theory is indirectly contradicted by the experience of the laboratories that reproduced the forming behaviour observed in production with high shear rate tests (normally performed on fibres, rods or plates, where the surface condition is expected to be different). In particular, Hessenkemper and Brückner (1989) explicitly concluded that the high-temperature strength (a key factor for workability) is a volume property.

7. Radiation heat transfer

The spectral absorption of glass exerts a critical influence on the heat exchange of the container with the mould and the air and therefore on its temperature distribution. For temperatures between 800 and 1100 °C, about 90 % of the energy exchanged by radiation is included between 1 and 11 µm. In practice, the extent of cooling by radiation can be quantified by suitably integrating the optical absorption spectra measured on hot glass between 1 and 5 µm (Blazek 1983). Above 5 µm silicate glasses are opaque because the whole network absorbs. The main features observed in the relevant spectral range include the absorption bands of ferrous iron and of hydroxyl groups. Further contributions are due to Co²⁺ and to the NIR tails of the visible absorption bands of transition elements such as Cr³⁺ and of the amber chromophore. It can be concluded that for a given type of container glass heat exchange rates during forming can in principle change due to oscillations of the redox state, of the water content and of the ratio of free to bound hydroxyls. The relevance of such effects is demonstrated quantitatively by Coenen's results about the effects of melting conditions on the radiation thermal conductivity of soda-lime-silica glass coloured with iron, chromium

or other oxides (Coenen 1968; Coenen et al. 1984).

There is an evident overlap between the arguments of dissolved gases, radiation exchange and of the skin effect, since surface gradients of water, redox state and sulphur compounds might influence both viscosity, heat exchange rates, surface energy and other properties (Coenen et al. 1984).

In 1967, Poole found that small changes of the spectral transmittance of coloured glass could be observed in coincidence with workability problems. Similar suggestions had been made earlier by English and Turner (1929), Gehlhoff and Thomas (1930) and Dietzel (1939). In recent years, no further results confirming this observation were published.

While large variations of spectral absorption would be readily revealed by upset tank temperatures, it would be of great interest to verify how far moderate differences in radiant heat exchange produced by melting history variations can influence the forming behaviour by modifying the temperature distribution in the parison and container. Ideally, measurements aimed at verifying such theory should be performed in a controlled atmosphere in order not to modify the gas content of the melt.

8. Conclusions and outlook

Various types of problems affecting glass container production are grouped under the term "poor workability". Their common feature is the erratic occurrence and the fact that the behaviour varies without substantial composition changes. This literature review illustrated in some detail the theories formulated by various authors in an attempt to explain these problems. Special rheological measurements suggest a possible explanation, showing that above a critical deformation rate glass exhibits a non-Newtonian viscosity (which is substantially different from the equilibrium viscosity) and melt fracture can occur. At the present stage, there is not enough experience to exactly predict such behaviour and to specify the characteristics of the melt which can influence it. It is generally believed that while the oxide composition remains constant, the forming behaviour can vary under the influence of some physicochemical parameters of the melt (specifically microstructure, gas content, cordiness, redox state, structure, surface gradients etc.) whose shifts (caused by variations of "melting history" associated with raw materials and melting conditions) are not detected by routine controls.

Indeed, the multiplicity of factors proposed to be relevant is quite confusing and suggests a critical approach. *A priori*, each of the mentioned parameters seems to offer a qualitatively acceptable explanation for occasional events of poorly reproducible forming behaviour. However, quantitative predic-

tions and precise correlations in this field are difficult to formulate, mainly because a full characterization of glass requires sophisticated and time-consuming techniques. Most of the studies so far available are dedicated to model glasses (binary and ternary), while for industrial soda-lime-silica glass some analytical problems are still beyond the state of the art. Indeed, at present surprisingly little information is available about the required physicochemical characterization of container glass. In the industrial practice it is not known how far melting history changes associated with raw materials and melting conditions can produce variations of microstructure and gas content which can eventually explain periodical variations of forming behaviour. Of course, it is not a problem to admit significant variations of water content and viscosity when a melt is bubbled with water or dry nitrogen, or microstructure development after heat treating an alkali silicate glass. The real challenge is to explain drastic behaviour changes with the relatively small oscillations of the process, which are normally considered acceptable, or which can take place unnoticed (e.g., due to variations of cullet type or size, or to temperature shifts).

Therefore, in most cases only a subjective interpretation of forming problems can be given, due to the difficulty to weigh one of the factors against the others. Such lack of knowledge makes it difficult to decide how to modify the melting process in order to improve the consistency of behaviour. At present, the only practical suggestion a plant technologist can learn from the literature is to try to improve the reproducibility of the process – a goal already pursued for economy and quality reasons. Case histories reported in the previous literature are of little help in discriminating, because most of the authors considered just one hypothesis (in particular, either gas or microstructure), neglecting to check and to report how the other parameters had varied. The poor level of scientific understanding achieved so far can partly be explained by noticing that most of the studies published in the past concentrated on Newtonian viscosity effects, while most recent rheological studies show that the problems arise in high-shear situations. This is certainly a critical field, open for future developments. The analytical challenge still remains open to provide means of checking *in situ* the hypothesis of shear-induced phase separation (or changes of structure and gas solubility). A further possible explanation for the many discrepancies observed when reviewing the literature is the fact that as the melting and forming practice changes, also the boundary conditions of the problem change, so that not all the solutions can be generalized.

As it seems, the technologist is still faced with the fundamental questions: Is there a single factor behind workability upsets, or are they due to a combination

of factors as suggested by Simmons and Simmons (1989)? Can container glass really change behaviour from day to day, or should the problems be blamed on the "process inconsistency factors" listed in part 1 of this paper (section 1.1., see no. 11, p. 306–307), such as poor temperature distribution and machine operation or inadequate batching or foreign cullet quality? The author has the feeling that at least a part of the problems occurring in production can be explained in this way: a further reason urging to improve the process reproducibility.

A conclusion which can certainly be drawn by comparing practical experience with the literature is that workability is an elusive property (Fenstermacher, Rouda 1982), difficult to pinpoint exactly both in the plant and in the laboratory. The goal of a rapid test which production can use in real time is desirable, but still far from being achieved. Often high reject or poor strength cases whose origin could not be satisfactorily explained are labelled as bad workability cases and transferred to the laboratory. It is not easy for the latter to sort out "genuine melting history cases" from those simply due to plungers or wrong temperatures. High-shear rheological measurements can provide an objective evaluation, but are not yet suitable for routine controls. On the other hand, some of the possible explanations for the production upsets are not likely to modify permanently the properties of the samples delivered to the laboratory. Examples range from poor conditioning of the gob to transient phase separation under shear. The circumstance that in many plants the reproducibility of the melting, conditioning and forming process is far from being optimal leaves open several alternative explanations for poor workability claims. This situation creates communication problems between production and the laboratory, an unfavourable condition for problem-solving.

According to experts, in the last decade improvements in furnace construction and raw materials consistency led to a decreased frequency of workability upsets. On the other hand, higher quality and productivity requirements and higher cullet contents still demand a substantial effort to eliminate the residual problems. In fact, in the last years the frequency of papers dedicated to specific themes mentioned in the review has increased. Some classical laboratory experiments about the influence of melting history have been resumed and checked with more sophisticated equipment, having in mind the peculiarities of commercial glasses. There is ground to hope that in the near future many of the open questions concerning the physicochemical characteristics of container glass highlighted in the review will be clarified. The microstructural hypothesis is being critically evaluated (in an attempt to clarify the contradictory statements of the literature); various activities are also dedicated to a better understanding

of the influence of dissolved gases, of the skin effect and of radiant heat transfer. An effort is being made to re-evaluate the past literature and to distinguish ideas based on theoretical speculations (or applying only to laboratory melts or to special compositions and melting processes) from those relevant to the industrial practice. To solve the riddle it is necessary to keep a fresh, unbiased approach and to check all the statements dogmatically accepted in the past (including of course the fundamental postulate of the "hidden physicochemical parameter varying with melting history"). In order to shed new light on the problem, it is essential to perform careful experiments on critically selected samples allowing to reduce the number of plausible hypotheses, discarding some which do not apply to industrial container glass, and possibly solving with a suitable combination of analytical tests the alternative between the theories associated with microstructure and with dissolved gases.

The studies on industrial glass affected by various types of "workability" problems should be performed with a multidisciplinary approach, including both high-shear rheological measurements, a full physicochemical characterization and a process checkup. In particular, an effort should be made to clearly outline the associated case histories, checking if really the various industrial problems grouped under the term "bad workability" (see section 1.1. of part 1 in no. 11, p. 306–307) can be attributed to a single factor associated with melting history differences, or if they can be better explained by some process inconsistency factors. It is also worth trying to re-evaluate critically the empirical reports of plant engineers and machine operators, in an effort to correlate the erratic occurrence of various types of "workability" problems with small variations of the melting and forming process.

In a set of future papers the author will report the results of studies on container glass aimed at assessing how significantly its physicochemical parameters vary as a function of the industrially observed workability.

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