The advantages of the fast colour monitoring technique to control the glass stability

Ph. Floriot, Th. Mêlé

Research and Development Glass Department, European Technical Center - BP16 - Saint Romain en Gier - 69702 GIVORS Cedex 02

Fast Glass Colour Monitoring or FGCM is not only an automatic device allowing to obtain directly from a bottle the transmission spectrum of glass but also a complete system able to give relevant and high frequency indication indispensable to manage the tint. Colorimetrics characteristics are the first data generally required by the customers specifications but this information is not enough to make the correct adjustements of redox or batch composition. System offers the possibilities to estimate the concentration of polyvalent ions under their valence states and also to evaluate redox state of glass. Furthermore by its measurement principle the system supply quickly a representative mean value of colouring ions in glass. This is particularly helpful when coloration evolves (color transition) or is somewhat heterogeneous (e.g. in reduced glass or in forehearth coloring). On the other hand, others extra informations can be obtained from acquisition results such as the article thickness profil or statistic data. The paper explains what we consider as important to control on glass for the plant and the reasons which we have led to develop a such application

Introduction

In the container glass industry, with the increasing furnaces pull rate and also the use of more recycled glass, the risk of deviating from the specifications or even losing production becomes much more important with heavier financial consequences. To quickly face up to this changing and challenging environment needs to be more reactive because the time to take decision becomes shorter. Unfortunately, plants neither have the possibility to measure in real time the key parameters nor to interpret correctly the data available however the corrective action should be appropriate to overcome any instability.

The flexibility or scheduling constraints sometimes leads to a change in the glass coloration either in the whole furnace or in the forehearth. To insure the color transition, a lot of reliable information concerning color has to be taken regularly in order to control the color evolution homogeneity. Due to higher pull rate and the increasing and ever changing origin of cullet, the glass characteristics must be controlled with more accuracy and more often. This means having quick access to useful and pertinant information such as the evolution of glass chemical analysis and physical properties.

When a drift occurs the question is often to know which element is at the origin of the problem and in what proportion. The interpretation of the transmission curve or colorimetric characteristics is generally the affair of specialists. It is often very difficult to have a correct opinion and to determine which element is responsable. The understanding of the problem asks then requires a chemical analysis which can not be carried out on the spot and thus leads to prohibitive delays to obtain the relevant information.

Daily density measurement is a very useful, reliable, low cost and simple technique to follow up the glass composition stability. Today, there is an automatic tools allowing us to execute the measurement in situ. The control can be carried out daily without the help of expensive X-ray fluorescence analysis (XFA). If a significant shift of density occurs, an alert is immediately given leading to the release of a checking procedure.

However some important information such as the content of polyvalent ions and the redox state of the glass can't be obtained in this way. Nowadays no tools equivalent to the densimeter, reliable and simple to use, allows us to obtain this information directly and simply. Sensors in situ were developed but experience has often shown their short life expectancy under industrial conditions. This data represents essential information because it determine not only the color of glass but also the thermal conductivity. This parameter is as important as viscosity. The variations of transmission in the infrared range lead to fluctuations in the heat transfer by radiation and so are susceptible to create strong disturbances during the process : Either by modification of convection stream in the furnace or by altering the thermal glass homogenization in the forehearth or heat exchanges during the glass forming process in the machine.

Procedure of follow-up of the stability of the glass parameter

Strictly concerning the question of the quality of the molten glass, the mission of the glassmaker becomes more and more delicate taking into account the hight stacks.
He has to be careful to respect the customers specifications not only external (in terms of color and absence of heterogeneity) but as well as internal by guaranteeing the preservation of the stability and the homogeneity in the mass of two fundamental parameters for the glass process, namely viscosity and thermal conductivity.
He must be capable of identifying a drift early enough and of being able to act as a consequence.
He must also master the progress of specific operations such as the color change.

Traditionally in the glass industry, the means of checking glass chemical stability are either of sensors on-line (by electrochemical cell and viscosimeter) or more commonly by off-line analyses of glass sample by tools such as the densimeter and spectrophotometer. The first offers the advantage of supplying continuously and in real time information but only from a local point of the process. These sensors are not really reliable over time. The second does not allow us directly to identify the exact nature of the problem. In both cases, no system to our knowledge allows us to manage effectively the redox issue in plant.

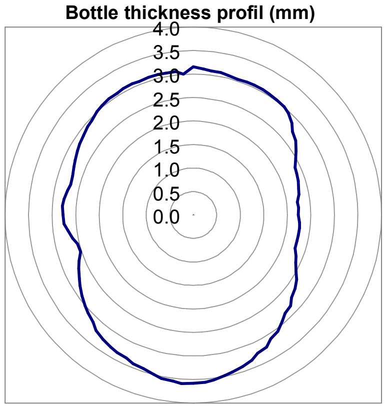
Due to very high temperature the relevant properties of molten glass cannot be measured (thus controlled) on-line during the melting process so suitable sensors are not reliable and not available. If it is relatively easy to follow the density as we have seen previously, on the others hand it is quite difficult to handle the variation of thermal conductivity which can be due to the contribution of different parameters such as fluctuation of coloring agents, redox or furnace.

Possibilities of the device FCGM

A system has been developed allowing us to measure at the same time and strictly in the same place on the article, the thickness and the optical transmission of the glass wall, in the concerning spectral UV - visible – NIR. The non destructive measurements are carried out without glass contact at different locations on the article. The vertical and angular location as well as the number of points of measure are customizable to optimize operating conditions according to the purpose: either to obtain a mean value or to determine the nature of a color heterogeneity (e.g. colored streak).

Thickness profil

The thickness profile is an essential data in the location of the healthy zones of articles, which only will be taken into account for colorimetric calculations.



Colorimetric characteristic specifications control

The spectrum allows us to determine UV filtration and colorimetric characteristics calculated for different color spaces (e.g. X, Y, Z or Lab system) or sources of light (A, B, C, D65) and expressed under different thicknesses. The purpose is to give a quantitative and objective appreciation of color but also to be positioned with regard to very precise customer specifications generally defined in term of DWL and brightness or purity.

Concentration of colouring species

The color of the final glass depends on the valence states of the different polyvalent species. With information given by the transmission curve and the precise measurement of the glass thickness, the system is capable of appreciating the concentration and redox state of polyvalent elements.
The principle is the following: The rate of coloring agents is obtained by mathematical resolution from the computerized transmission values handled and by using the extinction coefficients of polyvalent species.

Knowing that in case the factor of reflection is eliminated, transmission obeys Lambert Berr's law.

$$T(\lambda) = 10^{-D(\lambda)} = 10^{-\varepsilon(\lambda)\,.\,c\,.\,e} \text{ either } D(\lambda) = \varepsilon(\lambda)\,.\,c\,.\,e$$

With D : optical density
e : Thickness of the sample
$\varepsilon(\lambda)$: extinction coefficient of the coloring agent in the wavelength
C: Concentration by coloring in % weight

And that this law can in certain conditions (means no interaction between ions and low concentration in colorings agent) be simplified in the following way:

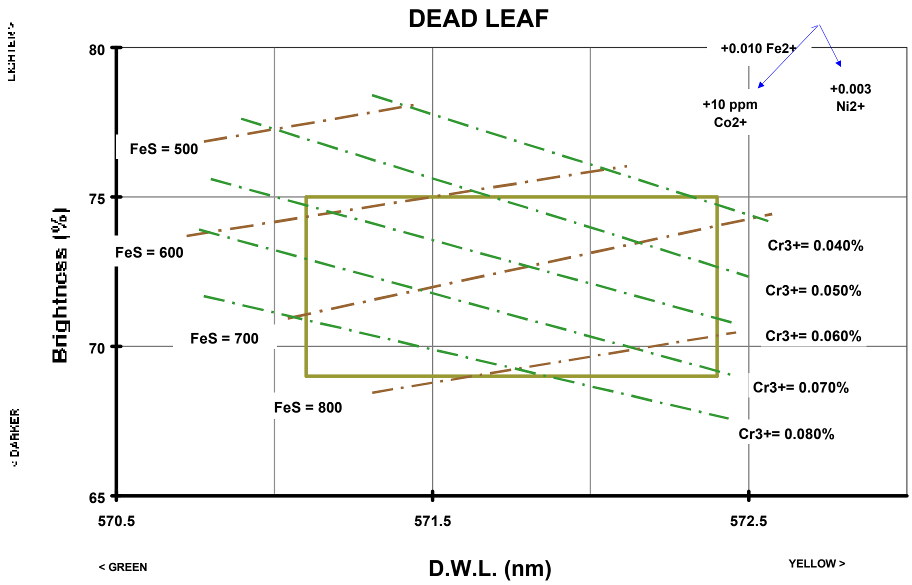
$$D(\lambda) = \Sigma_i\, \varepsilon_i(\lambda).c_i$$

With ci : concentration by coloring i
$\varepsilon i(\lambda)$: extinction coefficient of the coloring agent in the wavelength

It is then possible by mathematical resolution to appreciate the nature and concentration of the various coloring species of the glass. Some statistical tests are also added giving an indication of the validity of the model. The knowledge of the extinction coefficients of coloring agents is indispensable and remains the key element of the system. They result from own work and are established for the following ions: Fe2+, Fe3+, Cr3+, Cr6+, Ni2+, Co2+, Mn3+, Cu2+, Se° and the iron polysulfides. About 200 industrial glasses served as a base to establish these figures requiring to know the weight concentration of each colouring agent present and the measurement of transmission value ranging from 300 to 1500 nm every 5 nm.

The choice to establish by ourselves these data rather than to use those of the literature [2] was dictated by the necessity of resources of coefficients more close to our glass matrix and to obtain information about missing data concerning the iron polysulfides.

The amber chromophor is the main coloring element of most industrial glass. For this reason, it must be appreciated quantitatively like other "normal" polyvalent ions to assist in color adjustment and control. In this way, It is possible to represent the influence of every ion with regard to the colorimetric diagram defined by the Dominant Wave Lenght and Brightness.



Redox control

The appreciation of %Fe2+, %Fe3+, iron polysulfides and sulfides (by deduction) allows us to obtain precious indications on the glass redox state in order to access the batch redox number and thus to achieve the proper redox correction to be applied to the batch (by coke or sulfate …).

Redox is fully correlated with the ratio Fe2+ / Fe2O3 but in case of reduced glass this information has proven rather inaccurate to make fine tune redox correction. The appreciation of the level of iron polysulfide makes possible to improve the use of this information. Within a "normal" redox range, the percent of iron polysulfide can be translated into quantities of oxidizing or reducing components to adjust in the batch.

Because the redox of the final glass is not only due to the batch but resulting from combined the effect of the melting process, the redox management requires high frequency control only permitted by fast color monitoring tool.

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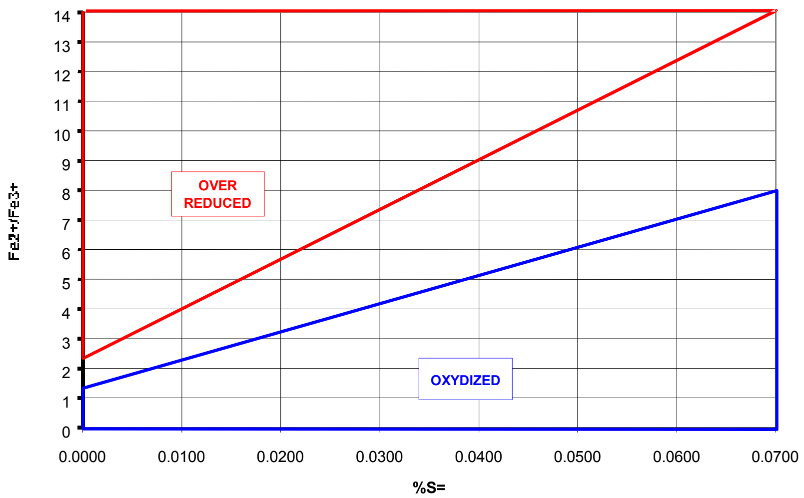
Over reduction warning

The amber colouring is due to the combination of oxidized specie, the ferric iron (Fe3+) with reduced specie, the sulfide (S2-). The amount of iron polysulfide increases with that of reducing state of glass until a certain limit. Too much reduction can lead to a complete shift of the iron equilibrium toward ferrous form making a sharp decrease of residual ferric iron. When the glass is reduced too much, there is not enough ferric iron to develop the amber complex and the phenomenon is reversed.

In reduced glass, the phenomenon of over reduction is a trap, which is difficult to apprehend and could lead to a wrong decision. In case of losses of iron poysulfides, it is important to know if the phenomenon is due to a lack or an excess of reduction. The critical point depends on rates of iron, chromium and sulfur dissolved in the glass. Careful control of redox melt is essential to reveal if the glass is over reduced.

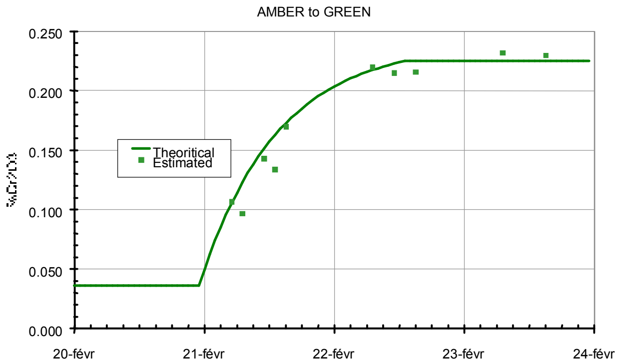
We showed that the appreciation of the glass redox could be appreciated on the basis of the knowledge of two parameters coming from the results of the spectral deconvolution. According to the levels of the ratio Fe3+ / Fe2+ and of the rate of S=, a synthetic redox index has been developed. This gives a clear indication of how the glass redox evolved and provides an early warning for deviations of the target in order to make the right redox correction.



Color change

Some furnaces are periodically dedicated to this operation consisting in changing the colour in the mass. Generally method employed is referred to as an on-the-fly conversion rather than the technique of drain and fill. This involves scheduling the operation to convert composition and to monitor the color evolution so as to be able to make correction if necessary.

Many methods of evaluation for the colourings evolution on furnace exist based on knowledge of dwell-time behavior of the furnace [3]. Evolution can be described by combining the different models of behavior such plug flow and mixer models. The calculation supplies information about how colourings agents will evolve themselves and also serves of guideline.



The operation has to be conducted in a minimum of time while preserving glass quality. The challenge is to switch from the old color range in scheduled time to the new target with a minimum of time. This involves an appropriate boosting of the coloration or discoloration. The operation must be carried out carefully and must be neither too slowly or too fast in order to avoid stopping before reaching the target or going through it.

By comparing the coloring trend given by the color measurements with the expected evolution, possibility is given to know if transition runs well and to react in time.

Another problem is that the coloring is not always homogeneous in the mass during certain transitions. This making it delicate to appreciate the evolution of the situation. The inhomogeneity is not always perceptible to the naked eye and the control of color from one piece of glass cannot be really representative. Only results based on the average of several points of measurement take on all around the article allow us to obtain a more objective idea of the glass coloring. This is particularly true in forehearth coloring.

Forehearth coloring

This technic offers greater flexibility than in a furnace and possibilities of coloring are more numerous and more diversified. The issue is how to manage a wide variety of polyvalent ions present in various combinations and concentrations. The different species redox couple can interact themself. If various metal oxides are introduced together into a glass melt, mutual interaction of the various ions may occur. Some redox species don't give a coloring effect. Color can't be managed by the quantities of metallic oxides introduced but by the knowledge of the concentration of ions present under their coloring form.

In case of drift of color or to match a new color, the operator has really no time and the means to obtain the elements of analyses. The residence times of glass in coloring forehearth are very short generally lower at one o'clock. Directly to obtain useful and pertinant data from an article even if the coloring is far to be perfect gives an advantage to anticipate the required correction.

Identification of colored streaks

Dark or light streak is a common aspect defect occuring sometimes and sporadicaly on few lines of production. Streak, a small glass color inhomogeneity, is a familiar problem in glass container. This defect is usually the result of redox fluctuations, metal contamination or glass coming from stagnant zone. Chemical analysis of these streaks is usually difficult because the streak cannot be easely be separated from the matrix and it occurs at a low level. Qualitative method is the only way of investigation due to the slight variation in composition. FGCM is an effective device to investigate the streak by setting the scan over the inhomogeneity and to compare the result with the healthy glass. By comparing or subtracting two transmission curves it is then possible to identify the nature of the element in cause and to pinpoint the most likely origin of the problem.

Conclusions

The process of glass of containers with the increasing of performances of furnace and machine and requirements in terms of quality and stability require more ability to react in case of glass color variation or glass redox deviation. This implies to have quickly and very frequently access to reliable information about the glass chemistry. Furthermore, the system must be able to assist the operator in quickly identifying and correcting the source of these problems. Our device has been developed in this spirit with the challenge to build a system reliable and easy to use for monitoring the color.

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[2] Bamford, Colour generation and control in glass (1977) Elsevier Scientific Publishers Amsterdam

[3] C. Philips Ross: Changing colors in containers furnaces. Glass Industry / October 1992, p.17- 20