Investigations on selenium decolorization of industrially melted flint glasses

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Introduction

Selenium pink is the most suitable decolorizing agent for the green tint, which is introduced into flint glass through iron contaminations. However, the profit of the positive decolorizing properties is limited by the poor reproducibility of selenium decolorization. According to the general opinion this is caused by two problems: 80 to 90 % of the selenium, which is introduced with the batch, evaporates during melting, while only 10 to 20 % of the integrated selenium are in the elemental state which is used for decolorization.

Electrochemical selenium sensor

Electrochemical methods are sensitive to selenium.[1] This enables the measurement of the selenium concentration online under industrial conditions by means of a formerly developed voltammetric sensor[23]. Figure 1 shows the results of such a sensor measurement in a flint glass.

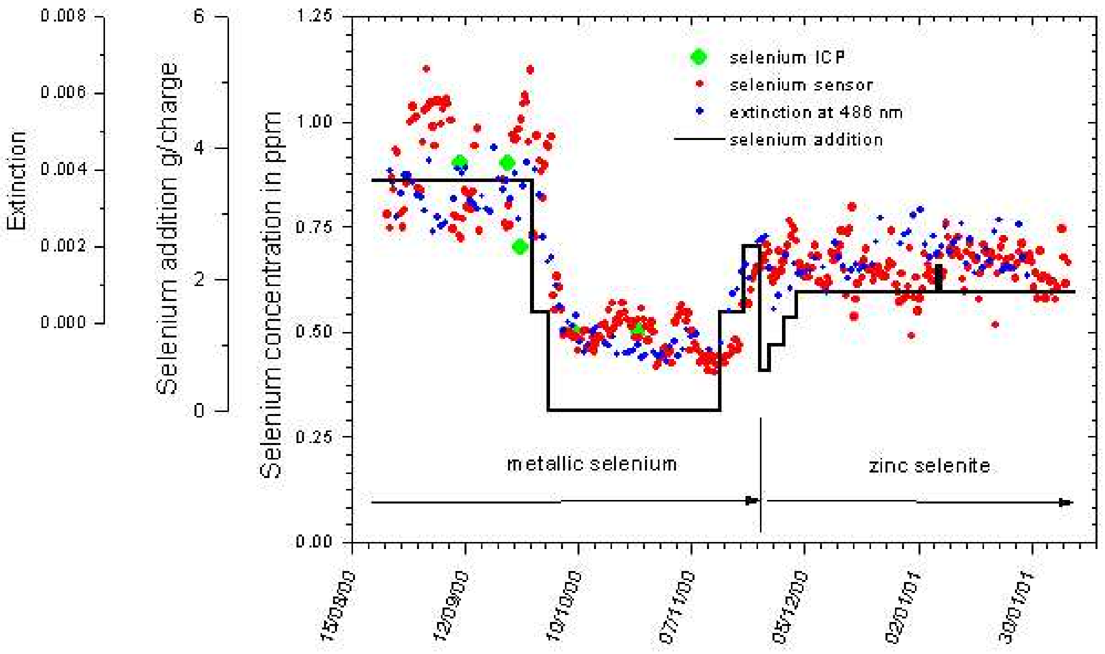

Figure 1: Selenium concentration in a flint glass measured by means of an electrochemical sensor and ICP-AES. Additionally, the extinction at the selenium band at 486 nm are included.

The most crucial point of electrochemical online measuements is the calibration. Since production quality must not be affected considerable variations of the concentrations of coloring elements as in usual calibration procedures are not allowed. Thus, calibration is only possible by observing a melt over a sufficient long period. In case of figure 1 advantageously noticeable variations of the selenium additions took place. The observed selenium concentrations are in the range of the detection limit of normal analysing methods like ICP-AES. However, calibration by means of the ICP analysis results in an excellent agreement with optical measurements. After omitting the selenium addition in the batch, the selenium concentration decreases very slowly mostly due to cullet recycling. Figure 1 makes clear that the mostly used raw materials metallic selenium and zinc selenite do not differ in their decolorizing power. Obviously, in industrial glass melting the selenium retention is mainly governed by the furnace settings.

Influence of redox state

The decolorization behavior of selenium depends primarily on its oxidation state. Selenium exists in oxidic glass melts in four valence states: Se^{6+}, Se^{4+}, Se^{0} and Se^{2-}. $Se^{6+}$and Se^{4+} provide no color while Se^{0} exhibits the typical selenium pink and the combination of iron and Se^{2-} forms an amber chromophore. The distribution into the four valence states depends on the oxygen partial pressure of the glass melt. However, if other polyvalent elements as iron and sulfur are present in the glass melt, the oxidation state distribution additionally shifts due to electron exchange reactions. The redox distribution of selenium in a sulfur refined glass with iron contamination has been calculated by means of a thermodynamic calculation model which is based on the balance of chemically bonded oxygen in glass melts.[4] The model has been checked by comparison with wet-chemical analyses of the selenium oxidation states.

In industrially melted flint glass selenium is reduced during cooling by iron as well as by sulfur. In sulfur refined flint glass the main reaction is caused by sulfur. Figure 2 shows the effect of sulfur on the Se^{0} and figure 3 on Se^{2-} assuming various selenium/sulfur ratios. The smaller the selenium/sulfur ratio, the higher is the share of Se^{2-}. Thus, in typical flint glasses selenium is completely reduced to the selenide state. Obviously, in industrially melted flint glasses selenium decolorization is not provided by the pink color of elemental selenium as assumed so far but by the amber color of iron selenide. These findings agree with optical measurements. Figure 4 shows the CIELAB values of two selenium containing glasses. Selenium addition always causes an additional yellow tint beside the required red tint.

In order to illustrate the influence of oxygen partial pressure and selenium/sulfur interaction on the coloration of a flint glass figure 5 shows the absorption of the elemental selenium and iron selenide based on literature data of the absorption coefficients[5]. An increasing iron content shifts the point where the selenium pink becomes dominant in the direction of higher oxygen partial pressures. Experience with oxygen sensors in the glass melt showed that under industrial conditions flint glass is melted at an oxygen partial pressure of approximately 0.01 bar. According to figure 5 iron selenide coloring predominates in this oxygen partial pressure range. Due to the organic contamination of recycled cullet and the poorer refining behavior of sulfur under oxidizing conditions a decolorization by means of selenium pink is impossible under industrial conditions.

Summary

The selenium content in industrially melted flint glass can be detected by means of electrochemical sensors down to concentrations of 1 ppm and below. Results of investigations based on such sensor measurements showed that the type of selenium rawmaterial has no measurable influence on the selenium retention. The oxidation state of selenium is governed by the interaction between sulfur and selenium. Industrially melted flint glasses are primarily decolorized by the iron selenide chromophore.

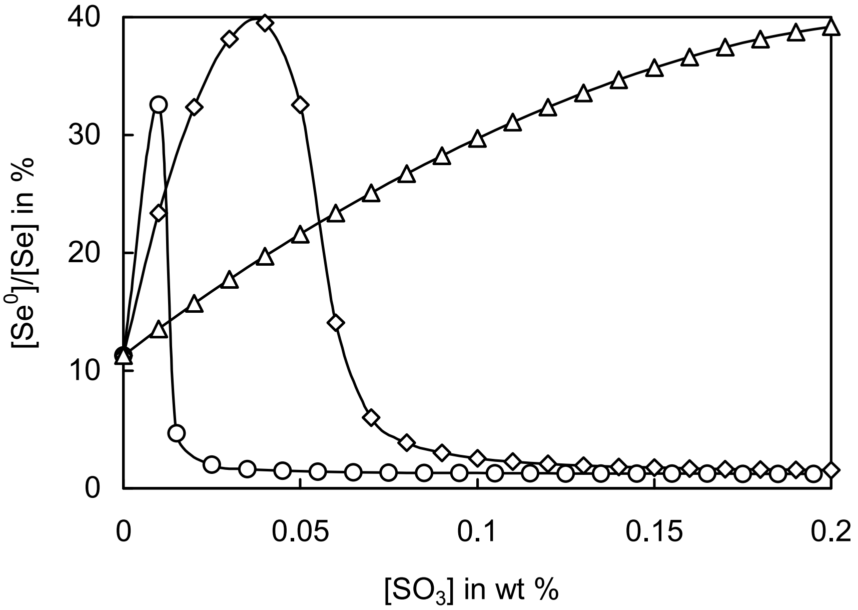

Figure 2: Calculated Se^0 concentrations in soda-lime-silica glasses with different total selenium concentrations as a function of sulfur concentration. ○ : 10 ppm, ◇ : 50 ppm, Δ : 300 ppm.

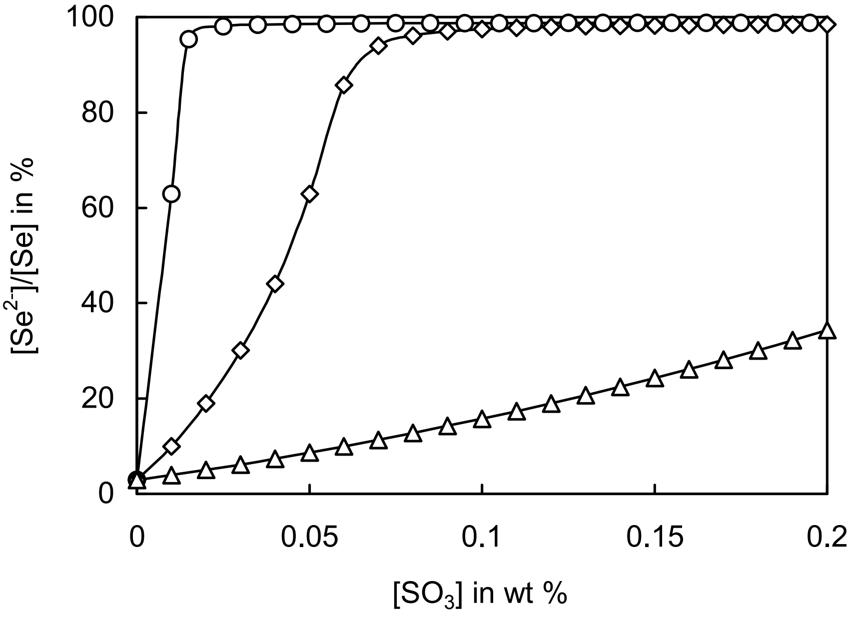

Figure 3: Calculated Se^{2-} concentrations in soda-lime-silica glasses with different total selenium concentrations as a function of sulfur concentration. ○ : 10 ppm, ◇ : 50 ppm, Δ : 300 ppm.

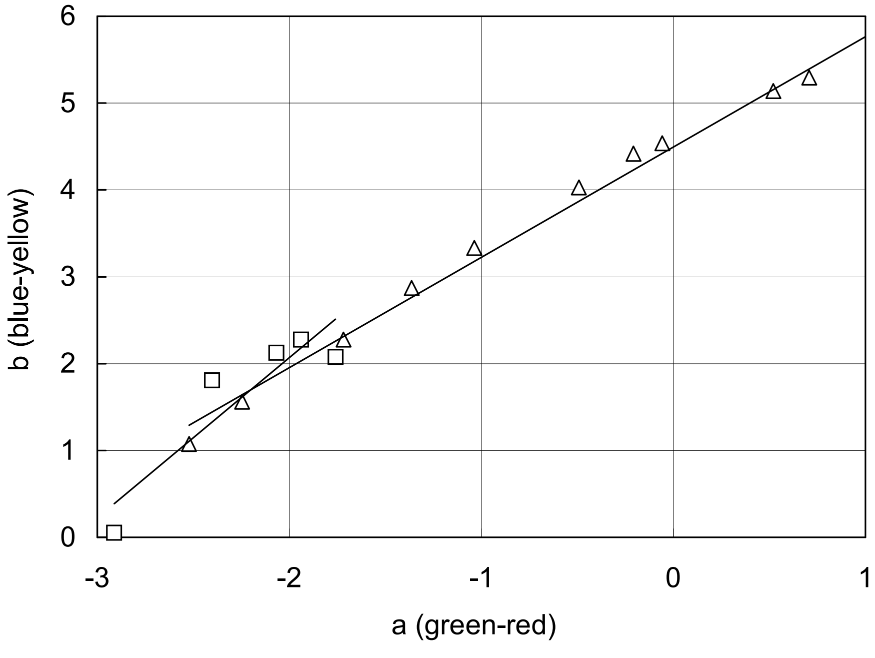

Figure 4: CIELab color coordinates of industrially melted flint glasses with varying selenium contents.

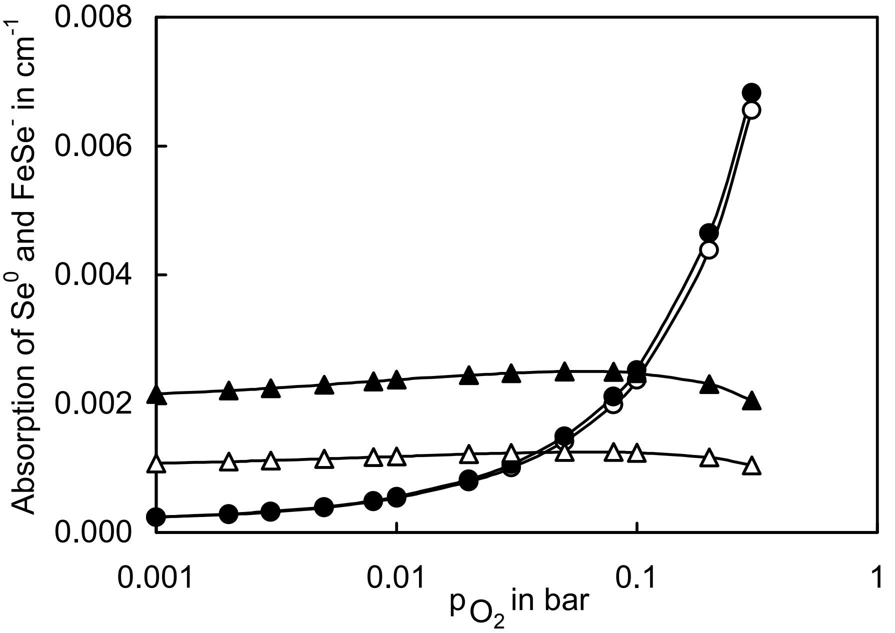

Figure 5: Concentrations of the coloring components elemental selenium and iron selenide weighted with the respective absorption coefficients in glasses with different iron contents. ○: Se^0 with 100 ppm Fe, ●: Se^0 with 200 ppm Fe, △: Se^{2-} with 100 ppm Fe and ▲: Se^0 with 200 ppm Fe.

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[5] C. R. Bamford, in *Colour generation and control in glass.* (Elsevier, Amsterdam-Oxford-New York, 1977).