

THE MEASUREMENT OF OXYGEN PARTIAL PRESSURE AND CHARACTERISATION OF OXIDATION-REDUCTION EQUILIBRIA IN GLASS MELTS

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Submitted May 7, 1999; accepted June 13, 1999.

The measurement of oxygen partial pressure in glass melts by the method of reference glass melt is presented. The experimental procedure completed by the wet chemical analysis of the ratio Fe^{2+}/Fe^{3+} is used for the determination of equilibrium constant of iron in soda-lime-silica glass melt. Experimentally obtained values of oxygen partial pressure bring input data for the calculation procedure of redox equilibria in glass melt containing sulphate and iron. In addition, calculated temperature dependencies of oxygen partial pressure are verified by experimental values. The calculation example showing positive effect of Calumite addition in glass batch to the efficiency of bubble refining process is discussed.

INTRODUCTION

Redox state of glass melt is of great interest of glass research and technology. Progress in laboratory development has brought the improvement in defining the redox state from the systems of redox numbers or the redox ratio of iron to the measurement of important thermodynamic quantity - partial pressure of physically dissolved oxygen. The knowledge of this quantity allows the characterisation of redox equilibria of polyvalent elements in glass melts having fundamental significance for many practical problems, such as glass colour change or bubble refining process.

The principle of the determination of oxygen partial pressure in glass melt is the measurement of electromotive force between platinum electrode placed in the measured glass melt and that in the reference medium with known value of oxygen partial pressure.

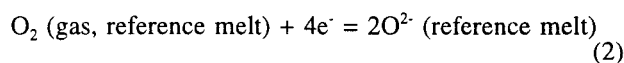
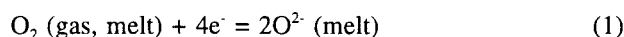
Among several hand-made measuring systems [1-3], there are two commercial apparatus. The system of Kühnreich&Meixner [4] has been developed for the "in-situ" measurement in working part of industrial furnaces. The RAPIDOX system [5] is used for the measurement of redox state of industrial cullet. The amount of the sample 500g and the small dimension of measuring cell make possible the measurement in laboratory scale.

The aim of this work is to present several applications of the oxygen partial pressure measurement by the method of reference glass melt and to compare experimental data with calculation of oxidation-reduction equilibria in glass melt containing sulphate and iron.

EXPERIMENTAL PART

The experimental method

The principle of the method is the measurement of the electromotive force between the couple of platinum electrodes. The reference electrode is immersed in the silica test tube containing the reference glass melt with known value of the oxygen partial pressure. The test tube is provided by the slot making the liquid junction between both glass melts. The set of both electrodes is located in a platinum crucible with the measured glass melt (figure 1). The following electrode reactions take place:



Equation (3) gives the electromotive force of the galvanic cell constructed (reference melt on the left side as a negative pole):

$$E_p = -t_+ \nu \frac{RT}{4F} \ln \frac{a_{O^{2-}}(\text{melt})}{a_{O^{2-}}(\text{reference melt})} + \frac{RT}{4F} \ln \frac{a_{O_2}(\text{gas, melt})}{a_{O_2}(\text{gas, reference melt})} \quad (3)$$

Paper presented at the 5th Conference of European Society of Glass Science and Technology "Glass Science and Technology for the 21st Century", Prague, June 21 – 24, 1999.

where R is gas constant, T is the temperature (K), F is Faraday constant, t_+ is cation transport number and ν is the number of ions formed by the dissociation of the electrolyte molecule. As the oxygen ion activity is equal in both melts and the ideal behaviour of the oxygen is supposed, the following relation is used for the calculation of oxygen partial pressure in the melt:

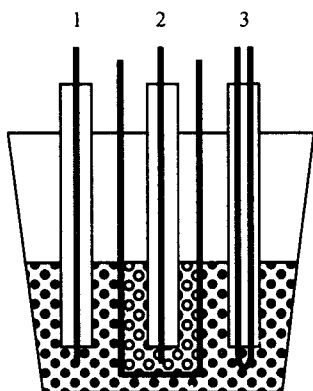


Figure 1. The experimental arrangement of the measurement by the method of reference glass melt.
1 - the measuring electrode, 2 - the reference electrode, 3 - the thermocouple

$$\ln p_{O_2}(\text{melt}) = \frac{4E_p F}{RT} \ln p_{O_2}(\text{reference melt}) \quad (4)$$

The value of p_{O_2} (reference melt) has been obtained by the RAPIDOX measuring system.

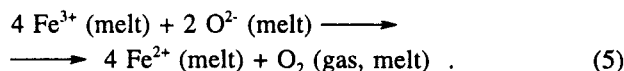
Table 1 summarises the measured oxygen partial pressures [kPa] in industrial soda-lime-silica glass melt and compares these values with measurement by RAPIDOX system. The last column in the table presents the average standard deviation of both methods calculated from measurements on three samples.

Table 1. The values of oxygen partial pressure measured by both methods (kPa).

	1200 °C	1300 °C	1400 °C	σ (rel.%)
RAPIDOX system	4.4	12.8	37.3	7.7
The method of reference glass melt	3.7	10.2	32.6	11.1

The determination of equilibrium constant of iron in glass

Redox behaviour of iron in glass can be described by the reaction:



The equilibrium constant of the reaction has the form:

$$K'_{\text{Fe}} = \frac{[\text{Fe}^{2+}]^4 p_{O_2}^r}{[\text{Fe}^{3+}]^4} \quad (6)$$

where $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$ are molar concentrations related to standard concentration 1 mol m^{-3} and $p_{O_2}^r$ is partial pressure of oxygen related to standard pressure 101.325 kPa supposing ideal behaviour of the gas. The measurement was made in soda-lime-silica glass melt containing 0.1 wt.% Fe_2O_3 without any other polyvalent elements. The glasses were melted at temperatures 1200, 1300 and 1400 °C. After cooling the sample to the room temperature, the content of redox species Fe^{2+} and Fe^{3+} was analysed by wet chemical method. The procedure was completed by the electrochemical measurement of oxygen partial pressure. Figure 2 makes a comparison of the measured temperature dependence of iron equilibrium constant (T in K):

$$K'_{\text{Fe}} = \exp(2.4633 - 3579.3/T) \quad (7)$$

with literary data [6-8].

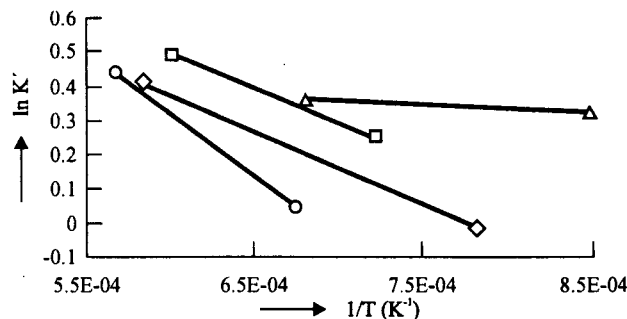
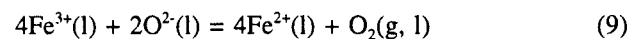
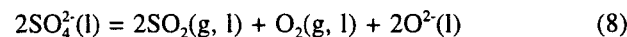


Figure 2. Comparison of measured K'_{Fe} values with literary data. Δ - Baak (1961), \square - Johnson (1964), \diamond - Ortman (1996), \circ - this work

REDOX EQUILIBRIA CALCULATION

Physically dissolved oxygen enters the equilibrium of polyvalent elements in glass melt. In case of sulphate refined glass melts, the oxygen is shared by oxidation-reduction reactions of sulphate and iron:



Equilibrium concentrations of individual redox species at chosen reference temperature $T_0 = 1473$ K are obtained with the knowledge of temperature dependences of equilibrium constants. The determination of physically dissolved oxygen and the chemical analysis of dissolved sulphate and total iron bring sufficient input data. The shift of oxidation-reduction equilibria with the temperature is calculated using the equations:

$$K_{\text{SO}_4}^{(T)} = \frac{(c_{\text{SO}_4}^0 + 2x_1)^2 (c_{\text{O}_2}^0 + x_1 + x_2)}{(c_{\text{SO}_4}^0 - 2x_1)^2} \quad (10)$$

$$K_{\text{Fe}}^{(T)} = \frac{(c_{\text{Fe}^{2+}}^0 + 4x_2)^4 (c_{\text{O}_2}^0 + x_1 + x_2)}{(c_{\text{Fe}^{3+}}^0 - 4x_2)^4} \quad (11)$$

where superscript (Fe^{3+}) indicates equilibrium concentrations at reference temperature and x_i are the changes of the component concentrations connected with the temperature variation. The temperature dependence of sulphate equilibrium constant was obtained by using the experimental data of equilibrium partial pressures of O_2 and SO_2 in soda-lime-silica glass melt [9]. The values of physical solubilities of both gases were taken from [10].

RESULTS AND DISCUSSION

The temperature dependence of oxygen partial pressure

Figure 3 presents the measurement of oxygen partial pressure in soda-lime-silica glass melt containing 0.1 wt.% SO_3 as sulphate and 0.05 wt.% Fe_2O_3 . The glass sample was held at 1400 °C, then it was cooled to 1200 °C and stepwise heated to 1300 °C and again to 1400 °C. The temperature variation was connected with

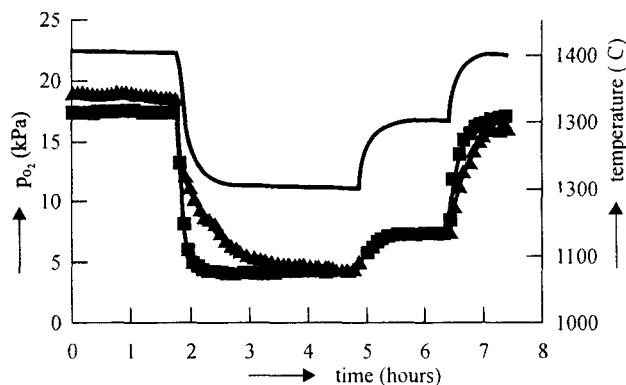


Figure 3. The oxygen partial pressure vs. time-temperature history of the melt.

▲ - experimental, ■ - calculated, — - temperature

the shift of p_{O_2} value in the interval 5 - 19 kPa. The square-connecting line in the figure presents results of the redox equilibria calculation. As can be seen, the values measured and calculated are acceptable agreement having relative difference up to 20 rel.%.

The effect of reducing agent addition to the glass batch

The composition of soda-lime-silica glass batch containing 0.2 wt.% SO_3 and 0.1 wt.% Fe_2O_3 was modified by the addition of 5 and 7 wt.% of Calumite having the composition: 35 - 37 SiO_2 , 10 - 12 Al_2O_3 , 42 - 47 CaO , 4 - 6 MgO , 1 S, 0.6 MnO , TiO_2 , Fe_2O_3 (wt.%). The samples of glass batches were melted in laboratory furnace for 120 minutes at temperature 1450 °C. Figure 4 illustrates the influence of Calumite addition on the value of oxygen partial pressure.

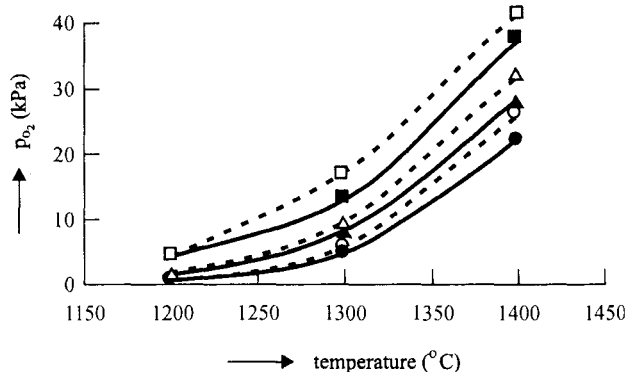


Figure 4. Comparison of calculated and experimental p_{O_2} values. ■ - 0 wt.%, ▲ - 5 wt.%, ● - 7 wt.%, □ - 0 wt.% calculated, △ - 5 wt.% calculated, ○ - 7 wt.% calculated

The decrease of measured values with increasing content of reducing agent in the batch corresponds with calculated results within 15 rel.%. This experimental verification of the calculation procedure makes possible its quantitative application. Figure 5 shows an example of calculated temperature dependencies of partial pressures of refining gases O_2 and SO_2 and the redox ratio of iron in the glass melt without Calumite addition in the batch. The knowledge of these quantities at high temperatures is important when evaluating the efficiency of refining process. Figure 6 presents calculated partial pressures of refining gases and the redox ratio of iron at temperature 1400 °C. The decrease in oxygen partial pressure brings about the increase in appropriate SO_2 value. In addition, the sum of both partial pressures giving the driving force for their mass transfer from glass melt to bubbles is slightly gaining with reducing agent addition. This tendency corresponds with experimental values of bubble growth rates measured in the glass melt [11].

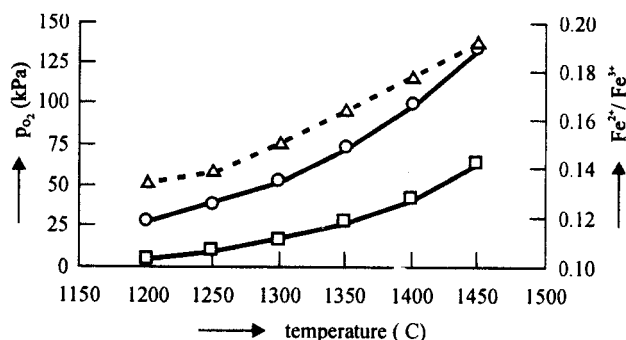


Figure 5. Calculated temperature dependencies of partial pressures of refining gases O_2 and SO_2 and of the redox ratio Fe^{2+}/Fe^{3+} .
 \circ - p_{SO_2} , \square - p_{O_2} , Δ - Fe^{2+}/Fe^{3+}

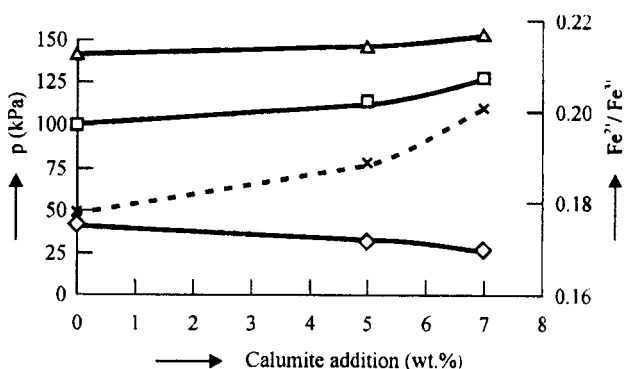


Figure 6. Calculated partial pressures of O_2 and SO_2 and the redox ratio Fe^{2+}/Fe^{3+} vs. Calumite addition in the glass batch.
 Δ - $p_{O_2} + p_{SO_2}$, \square - p_{SO_2} , \times - Fe^{2+}/Fe^{3+} , \diamond - p_{O_2}

CONCLUSION

The values of oxygen partial pressure in glass melt measured by the method of reference glass melt were compared with those given by the commercially available RAPIDOX system. The data obtained by both methods are in acceptable agreement with relative difference up to 20 rel. %.

The measurement of oxygen partial pressure completed by the chemical analysis of quenches glass sample was used for the determination of equilibrium constant of iron in soda-lime-silica glass melt. The temperature dependence of equilibrium constant shows sufficient consent with literary data.

Measured value of oxygen partial pressure being very often the only one quantity obtained in glass melt at high temperatures bring realistic input data into the calculation procedure of redox equilibria making thus possible its quantitative applications. Calculation example showing positive effect of the addition of reducing agent in the glass batch on the efficiency of

the refining process was experimentally confirmed by the measurement of the bubble growth rate in the glass melt.

Acknowledgement

This work was supplied with the subvention by The Ministry of Education, Youth and Sports of The Czech Republic, Project No. VS 96065.

References

1. Tran T., Brungs M.P.: Phys. Chem. Glasses 21, 133, 178, 184 (1980).
2. El Harfoui M., Hilger J.P.: Glastechn. Ber. 64, 253, 281, 299 (1980).
3. Tamashita M., Yamanaka: Glastechn. Ber. Glass Sci. Technol. 70, 371 (1997).
4. Müller-Simon H., Mergler K.W.: Glastechn. Ber. 61, 293 (1988).
5. Plessers J., Faber A.J., Tonthat T., Laimbock P.: Proc. of the 55th Conference on glass problems, p.340, Chicago, October 13 - 15, 1997.
6. Baak T., Hornyak E.J.: J.Am.Ceram.Soc. 44, 541 (1961).
7. Johnson W.D.: J.Am.Ceram.Soc. 47, 198 (1964).
8. Ortmann L., Hohne D., Nolle G.: Glastechn. Ber. Glass Sci. Technol. 69, 235 (1996).
9. Kloužek J., Černá M.: Proc. of the 3rd Int. Seminar on Mathematical Simulation in the Glass Melting, p.108-112, Horní Bečva, May 26 - 27 (1995).
10. Kloužek J., Němec L.: Glastechn. Ber. Glass Sci. Technol. 68CZ, 128 (1995).
11. Ullrich J., Kloužek J.: Unpublished results.

Submitted in English by the authors.

MĚŘENÍ PARCIÁLNÍHO KYSLÍKU A CHARAKTERIZACE ROVNOVÁH V ROZTAVENÝCH SKLECH

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V práci je popsána metoda stanovení parciálního tlaku kyslíku metodou referenční skloviny. Principem metody je měření napětí mezi dvěma platinovými elektrodami, z nichž jedna je umístěna v měřené sklovině a druhá v referenční sklovině se známým parciálním tlakem kyslíku.

Měření parciálního tlaku kyslíku spojené s chemickou analýzou redox poměru Fe^{2+}/Fe^{3+} bylo použito ke stanovení teplotní závislosti rovnovážné konstanty reakce iontů železa v sodno-vápenato-křemičité sklovině:

$$K = \frac{[\text{Fe}^{2+}]^4 p_{\text{O}_2}^r}{[\text{Fe}^{3+}]^4}, \quad K_{\text{Fe}}^r = \exp(2.4633 - 3579.3/T)$$

Stanovené hodnoty parciálního tlaku kyslíku byly použity jako vstupní data pro výpočty oxidačně redukčních rovnováh ve sklovině obsahující síranové ionty a ionty železa. Rovnovážné koncentrace jednotlivých složek byly vypočítány s použitím vztahů:

$$K_{\text{SO}_2}^{(T)} = \frac{(c_{\text{SO}_2}^0 + 2x_1)^2 (c_{\text{O}_2}^0 + x_1 + x_2)}{(c_{\text{SO}_4}^0 - 2x_1)^2},$$

$$K_{\text{Fe}}^{(T)} = \frac{(c_{\text{Fe}^{2+}}^0 + 4x_2)^4 (c_{\text{O}_2}^0 + x_1 + x_2)}{(c_{\text{Fe}^{3+}}^0 - 4x_2)^4}.$$

Uvedený výpočetní postup byl použit k hodnocení vlivu přídavku redukujících látek do sklářského kmene. Složení kmenů sodno-vápenato-křemičitého skla obsahující 0,2 hmot.% SO_3 a 0,1 hmot.% Fe_2O_3 bylo modifikováno přídavkem 5 a 7 hmot.% Calumitu. Obr. 4 ilustruje vliv přídavku redukovadla na hodnotu parciálního tlaku kyslíku ve sklovině v teplotním rozmezí 1200 – 1500 °C. Pokles hodnoty parciálního tlaku s rostoucím obsahem redukujících látek byl ověřen experimentálním měřením. Uvedený pokles způsobuje růst odpovídající hodnoty oxidu siřičitého. Součet parciálních tlaků obou plynů ve sklovině určující hnací sílu jejich transportu do bublin, a tím i účinnost čeřícího procesu, také roste s obsahem redukujících látek v kmeni. Tato závislost byla experimentálně potvrzena měřením rychlosti růstu bublin v dané sklovině.