Lecture

REFINING AND SAND DISSOLUTION IN THE GLASSMELTING PROCESS*

Lubomír Němec

Institute of the Chemistry of Glass and Ceramic Materials,
Czechoslovak Academy of Sciences,
Sokolská 38, 120 00 Prague 2

In this paper, the theoretical and experimental models of glass refining and sand dissolution are summarized, their ideal conditions are defined and the influence of most important factors on the course of both processes is presented. In the same time, the mutual relations between examinated processes are revealed. From the comparison of attainable optimum conditions of single processes, the alternative or new arrangements of both processes in the melting room are proposed. As is obvious from the results, the space separation of sand dissolution and refining seems to be advantageous as well as application of controlled convection in the melting part and reduced pressure in the refining part of the melting room.

INTRODUCTION

The traditional classification of the whole glass-melting process on the melting (batch reactions and particle dissolution), fining and homogenization may serve as a good initial point for investigation of optimum glass melting conditions, because this classification involves only processes creating glass without those leading to quality deterioration of glass, melting room and of the melting process itself (see Fig. 1). When searching for such a conditions, we are trying

to create experimental or theoretical models of examinated processes, then the ideal state is defined and influence of equilibrium and kinetic factors on the course of single processes is investigated with the aim to approach to ideal conditions as much as possible. In the same time, the mutual relations between examinated processes are revealed. In the following step, the comparison of required optimum conditions for single processes is performed in order to find time and space arrangement of the whole glassmelting process (see Fig. 2). This paper is an attempt to realize the suggested procedure for two of most significant melting processes – particle dissolution in glass and bubble removing (refining).

PARTICLE DISSOLUTION IN GLASS

Theoretical model

The kinetics of sand dissolution is – with rare exceptions – the most significant process here. In order
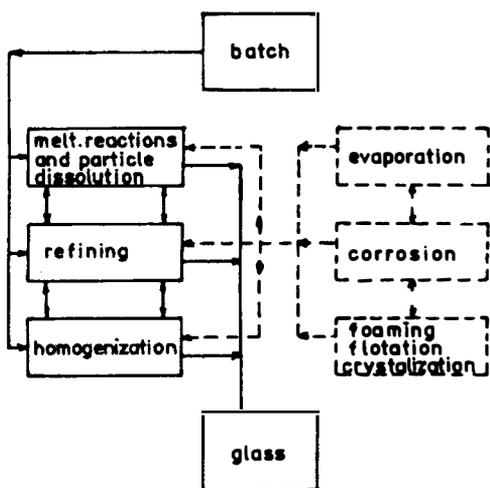
Fig. 1. The schematic way of the course of glassmelting process.
— mutual influences
--- time courses
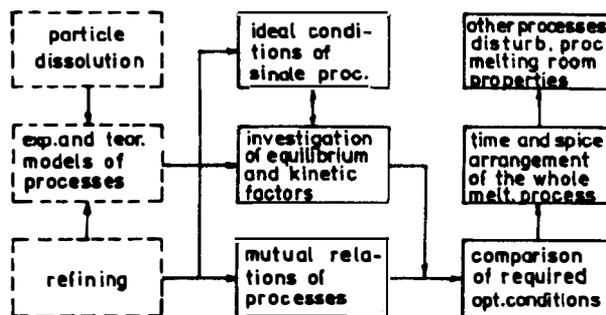
Fig. 2. Searching optimum glassmelting conditions.

to obtain the theoretical model of particle dissolution the polydisperze ensemble of sferical particles is considered dissolving in the melt of changing composition under the control of chemical reaction and diffusion. For the monodisperze particles, the semiempirical equation has been derived by Hrma [1] expressing three stages of sand dissolution – stage of chemical reaction, mixed stage and stage of pure diffusion control – by three coefficients:

$$\frac{1-w_s}{w_s(w_e-1)+w_t-w_e}dr =$$

$$= \frac{\alpha_0\alpha_f}{\alpha_0+(\alpha_f-\alpha_0)\exp(-\kappa\tau)}d\tau \qquad (1)$$

where w_s is mass fraction of undissolved SiO_2 in the mixture melt – sand, w_e solubility of SiO_2 in the glass under given conditions, w_t mass fraction of the entire SiO_2 in the mixture, r radius of the particle, α_0 constant expressing the rate of chemical reaction on the particle surface, κ constant expressing the rate of mechanism change from the chemical reaction control to the diffusion control, α_f constant expressing the rate of dissolution controlled by diffusion and τ is time.

If at given time the rate of dissolution of different sand particles is supposed to be independent from their instantaneous size – which fact has been satisfactorily proved by experiments [2] – the quantity w_s may be expressed using probability density function of particle size distribution of sand. The value of w_s is then given by [3]:

$$w_s = \frac{4}{3}\pi\frac{\rho_s}{\rho}N_{S_0}\int_0^{r_{max}} f(r+r_{0max}-r_{max})r^3\,dr \qquad (2)$$

where ρ_s and ρ are sand and glass melt densities respectively, N_S initial number of sand particles in volume unit of mixture melt – sand, $f(r+r_{0max}-r_{max})$ probability density function in time τ, r_{0max} and r_{max} are initial and instantaneous radii of the maximum sand particle respectively. The course of dissolution is schematically demonstrated in Fig. 3.

The simultaneous solution of equations (1) and (2) gives the course of polydisperze sand dissolution in form of dependence between maximum particle size and time $r_{max}=f(\tau)$ or in the form $w_s=f(\tau)$, the dependences for another particle sizes being similar.

Experimental model

The dissolution of single sand particles cannot be usually followed experimentally. In laboratory experiments, the relations between the number of undissolved sand particles and time are currently obtained: $N_s=f(\tau)$. Applying the suggested assumption about the independence between the dissolution rate of different particles and their instantaneous size, the mentioned experimental dependence may be transferred
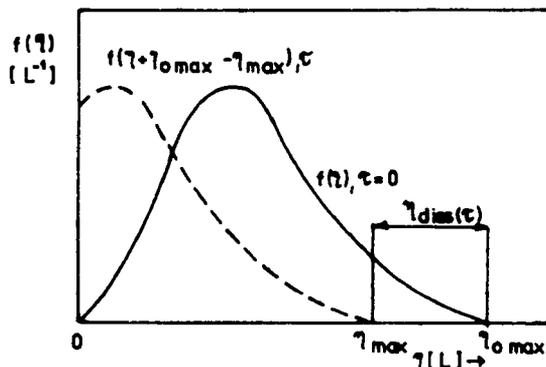
Fig. 3. The shift of the probability density function of particle size distribution with time. f(r)- the probability density function, r_{max} the maximum particle radius.

into the dependence $r_{max}=f(\tau)$ from the theoretical model in a following way [3]:

$$N_{diss}=N_{S_0}-N_S(\tau)=N_{S_0}\int_0^{r_{diss}} f(r)\,dr \qquad (3)$$

where N_{diss} is number of dissolved particles in time τ in volume unit. The value of r_{max} is then given by:

$$r_{max}(\tau)=r_{0max}-r_{diss}(\tau) \qquad (4)$$

The experimental model is especially important for evaluation of constants α_0, α_f and κ respectively when examining the influence of different factors on the particle dissolution, however it plays also important role in evaluation of factors not being explicitly expressed in equations (1) and (2) – f.e. factors influencing the mass transfer coefficient.

Ideal conditions

The ideal conditions may be classified into two groups.
a) Melting temperature is higher then the particle melting point. In this case, temperature is the only significant factor and the entire dissolution time of sand – $\tau_D\to 0$. This apparently favourable situation is however strongly restricted by other processes as is glass volatilization, melting room corrosion and heat supply.
b) Melting temperature is lower than the particle melting point. The temperature is from bellow limited by liquidus temperature of the melt where $w_t\to w_e$ and consequently $dr/d\tau\to 0$. At higher temperatures, especially the values of maximum size r_{0max} and value of mass transfer coefficient play fundamental roles. If $r_{0max}\to 0$, then also $\tau_D\to 0$, but this process is limited economically and by other disturbing processes as is unfavourable course of refining (see refining), foaming and flotation.

If glass is stirred sufficiently intensively, i.e. if $\kappa \rightarrow$ 0, then the whole mass transfer coefficient $\alpha \rightarrow \alpha_0$ – the sand dissolution is controlled by the chemical reaction only and the value τ_D is reduced to the time necessary for accomplishing of chemical reaction – $\tau_D \rightarrow \tau_{CH}$.

The influence of equilibrium and kinetic factors on the course of sand dissolution.

a) The value of the mass transfer coefficient α is only little influenced.

Under this assumption, the integral on the left side of eq. (1) is the measure of the melting time τ_D. The analytical solution of eqs. (1–2) for the case $f(r) =$ const has the following form (after simplification):

$$\tau_D = k \frac{r_{0max}}{\bar{\alpha}} \tag{5}$$

The relation (5) confirmes repeatedly experimentally obtained linear dependence between τ_D of polydisperze sand and initial size of maximum sand particle. In fact however, the dependence is not valid for very little values of r_{0max} as is obvious from Fig. 4 [4].
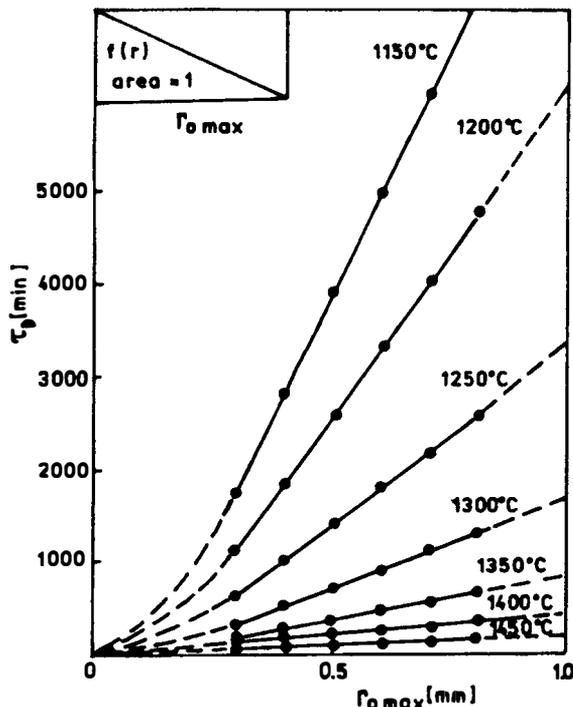
Fig. 4. The dependence of the polydisperze sand dissolution time τ_D in flat glass on the maximum initial size of sand particle.

The influence of another factors is obvious from Fig. 5 [5], where the surface under the single curves is proportional to τ_D. The values are valid for flat glass, $r \in \langle 0; 1mm \rangle$ and $f(r) =$ const. The reference

Table I

The influence of the shape of probability density function $f(r)$ expressing sand granulometry on the sand dissolution time, $r_{0max} = 1$ mm

The shape of probability density function $f(r)$	The value of $\int_0^{r_D} \alpha\, dr$ being proportional to τ_D
industr. glass sand	15.00
monodispersion	11.42
◺	12.52
▭	12.71
◿	13.51
◺	13.61
two stage dissol. starting from $r \in \langle \frac{r_{0max}}{2}; r_{0max} \rangle$	11.12
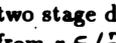
case is designated by number 1. The influence of sand granulometry is seen from comparison between curves 1 and $r = r_{max}$ (monodispersion); this influence is better obvious from Table I showing that dissolving time for given value of r_{0max} is growing with increasing portion of fine particles. From this table is also obvious the favourable effect of two (or more) stage dissolution where dissolution is started with addition of coarser sand particles.

The change of glass composition has distinct influence on τ_D as is obvious from comparison of curves for different values of w_t. For $w_t \rightarrow w_e$, $\tau_D \rightarrow \infty$ as already mentioned (see Fig. 5).

The impact of temperature is complex, the influence of values w_e only being obvious from Fig. 5. In addition, the value of α is influenced, however, this influence is distinct only at higher temperatures characterized by intensive convection (see following part).

The value of w_0 (initial concentration of SiO_2 in solid phase) expresses the influence of cullet addition. For $w_0 = w_t$ (no cullet), the dissolving time τ_D has the lowest value, in practice however, also heat conductivity of glass batch plays an important role (see Fig. 5).

b) The value of the mass transport coefficient α is distinctly influenced.

For sand dissolution, especially the last period characterized by the diffusion control is significant. In this period, the simple equation may be written:

$$\frac{dr}{d\tau} = \alpha(w_b - w_e) = \frac{D}{\delta}(w_e - w_b), \tag{6}$$

where w_b is mass portion of SiO_2 dissolved in glass, D diffusion coefficient of SiO_2 and δ thickness of diffusion layer. In later stadium $w_b \rightarrow w_t$ and $\frac{dr}{d\tau} =$ const. As already said, the influence of temperature on the

Fig. 7. The dependence of the sand dissolution time τ_D on the Na_2SO_4 concentration in the soda-lime glass at different temperatures. The lower line: bubbled by 30ml O_2/min.
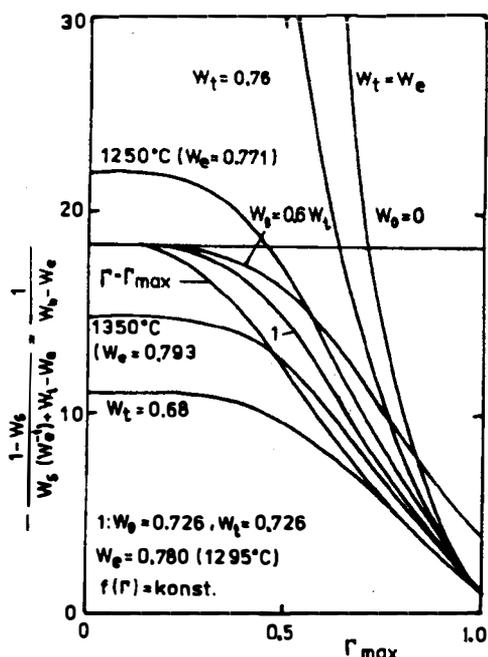
Fig. 5. The dependence between reciprocal value of concentration difference-surface of sand particle – glass melt-on the maximum radius of sand particle for different values of parameters.

α value need not be significant, however the value of δ may be distinctly reduced by convection. At very high temperatures, the convection in the vinicity of sand particles may be enhanced by nucleation of bubbles (see following part) and by bubble rising through the melt. This effect is restricted to the cases with refining agent as is obvious from example in Fig. 6. In this figure, the minimum dissolving time τ_D has been found for the most intensive convection by bubbles,

i.e. for the highest value of bubble growth rate $\Delta a/\Delta \tau$ (a – radius of bubble) [6]. At medium and lower temperatures, the glass stirring may play similar role as refining bubbles. Especially bubbling seems to be very effective. In Fig. 7, the lower in couple of lines corresponding to the same temperature designates the experimental values of τ_D when gas is bubbled through the melt. The distinct decrease of dissolution time is obvious especially at lower temperatures [7].

Another fact obvious from Fig. 7 is distinct inhibition influence of refining agent (also arsenic and NaCl) on the sand dissolution at lower and medium temperatures. The cause of this effect is probably slowing down of chemical reaction or observed agglomeration of sand particles under the influence of refining agents.

Summarizing the favourable influences of factors, the main verified results may be presented as follows:
1. Reducing of maximum sand particle sizes;
2. Application of refining temperatures (if ref. agent is present);
3. Application of forced convection and low ref. agent concentration if lower and medium temperatures are applied.

REFINING

Theoretical model

Experimental studies have shown that intensive diffusion of gases between bubbles and glass melt [8] must take part during melting and refining. This problem has been subject of several theoretical studies [9-12] leading to the derivation of sets of differential equations less or more reasonably describing

Fig. 6. The experimental dependence between the average value of bubble growth rate and sand dissolution time τ_D and the As_2O_3 concentration in the glass batch (soda-lime glass) at 1400° C.
1 – τ_D; 2 – $\Delta a/\Delta \tau$

behaviour of multicomponent bubble in glass melt. Schematically, the set of differential equation has the form:

$$\frac{dp_i}{d\tau} = F_i(D_i, \Delta m_i \ldots); \quad i = 1, 2, \ldots, n-1 \qquad (7)$$

$$\frac{da}{d\tau} = F_a(D_i, \sum_{i=1}^{n} \Delta m_i \ldots) \qquad (8)$$

where F_i and F_a are functions describing the partial pressure of i-th gas in the bubble and bubble radius a respectively, D_i is diffusion coefficient of i-th gas, Δm_i the concentration difference of diffusing gas between bulk glass and bubble boundary.

In some cases the refining agent may be excluded on the phase boundary and additional equation considering the growth or dissolution of the refining agent layer is suggested [11]. The set of equations is completed by the pressure balance in the bubble and by the formula for bubble rising velocity.

Among quantities influencing bubble behaviour, the difference $\Delta m_i = m_{ii} - m_{0i}$, where m_{ii} is concentration of diffusing gas on the bubble boundary and m_{0i} its concentration in the bulk glass, plays the crucial role.

The presence of refining agent in the glass melt brings about that at least one values of Δm_i is high at proper conditions, thus accelerating or bubble growth and their rising to the level or bubble dissolution. The value of Δm_i is determined by the solubility of appropriate gas and thus connected with the equilibrium concentration of appropriate complex ion of refining agent [12], therefore the knowledge of chemical equilibria of refining agents in the melt at given conditions may answer the question of actual refining mechanism. Unfortunately these values are very often lacking.

From the qualitative point of view, following criteria for the growth or dissolution of multicomponent bubbles are valid [13].
If

$$\sum_{i=1}^{n} p_{i\text{Glass}} - \sum_{i=1}^{m} p_{i\text{Glass}} > p_{\text{ex}} \qquad (9)$$

– where n is the number of present gases, m the number of non diffusing gases, p_{ex} external pressure, $p_{i\text{Glass}}$ equilibrium partial pressure of i-th gas in the glass melt – the bubble will steadily grow and may be removed only by rising to the level.
If, on the contrary:

$$\sum_{i=1}^{n} p_{i\text{Glass}} - \sum_{i=1}^{m} p_{i\text{Glass}} < p_{\text{ex}} \qquad (10)$$

the bubble will initially dissolve, however the dissolution will be stopped as soon as the diffusing

gases reach their equilibrium partial pressures in bubbles. In fact industrially melted glasses contain always small quantities almost non–diffusing gases (N_2), therefore the complete bubble dissolution may not play role of refining mechanism.

Experimental model

The laboratory refining studies usually followed the decrease of bubble amount in glass with time [8]. These results did not however provide unambiguous picture of refining mechanism because of complicated bubble behaviour. The application of high temperature photography [14] has shown that the role of refining agent at refining temperatures is to release gas which diffuses into bubbles and enhances rising of growing bubbles to the level. As well the predicted mechanism of uncomplete bubble dissolution at lower temperatures has been confirmed by this method. The example of bubble behaviour in soda-lime glass with $As_2O_3+NaNO_3$ are in Fig. 8 and 9. In early stages, the bubble coalescence occurred. For every glass batch composition and temperature, the average value of bubble growth rate $\Delta a/\Delta \tau$ could be defined being measure of refining efficiency of glass melt. Several experimental values for soda-lime glass are in Table II. The distinct influence of bubble growth rate on the refining efficiency expresses simple equation describing bubble removing from isothermal layer of glass melt [6]:

$$\omega a_0^2 \tau_R + \omega a_0 k \tau_R^2 + \frac{k^2}{3}\tau_R^3 = h_0 \qquad (11)$$

where $\omega = 2g\rho/9\eta$, a_0 initial bubble radius, τ_R refining time of glass layer of thickness h_0, $k = \overline{\Delta a/\Delta \tau}$ is average bubble growth rate.
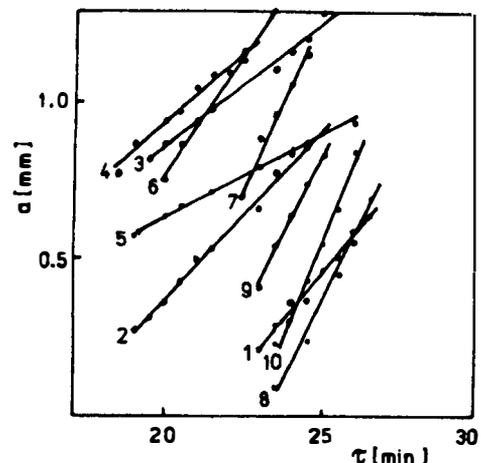
Fig. 8. Bubble growth at 1400° C in the glass melt with 2% As₂O₃ and 1% Na₂O added to the batch as NaNO₃. 1–10: bubble number.

t [°C]
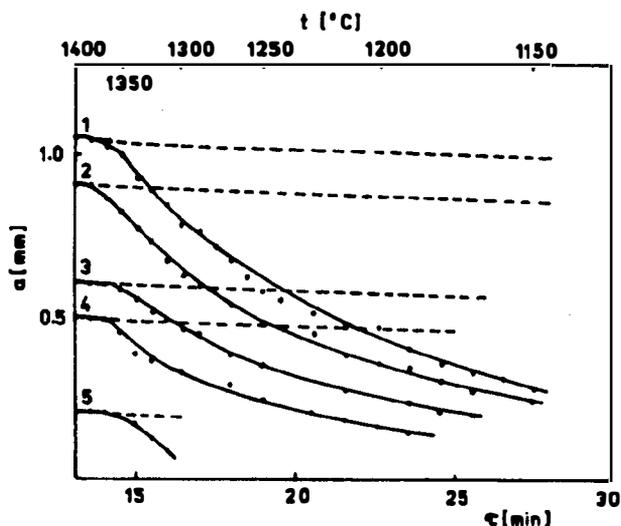
Fig. 9. Bubble dissolving in the glass melt with 2% As_2O_3 and 1% Na_2O added to the batch as $NaNO_3$ on a drop in temperature from 1400 to 1150°C. 1-5: bubble number.

Ideal conditions

As is obvious from equation (11), the refining time is especially dependent on the value of bubble growth rate $k = \overline{\Delta a/\Delta \tau}$ the remaining quantities can play only less important role. The value of $\Delta a/\Delta \tau$ is then given mainly by the sum $\sum_{i=1}^{n} p_{iGlass} - \sum_{i=1}^{m} p_{iGlass}$ in relation (9), i.e. by the sum of equilibrium partial pressures of diffusing gases in the glass melt. Thus, the increase of this value predominantly increases the refining rate. However, in order to define more pre-
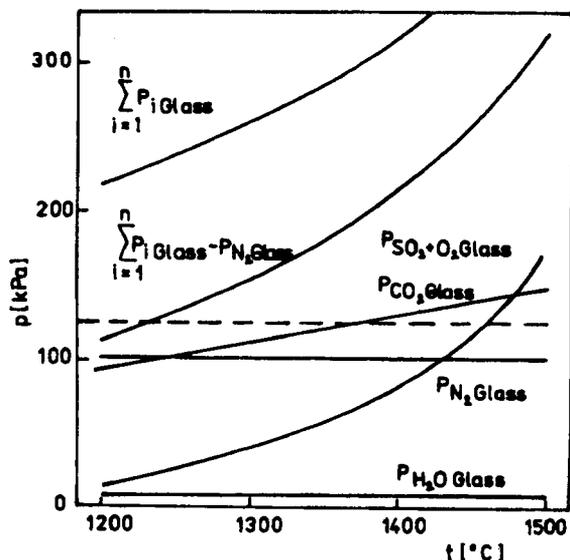
Fig. 10. The dependence of values of p_{iGlass} on temperature in flat glass.

Table II

The values of average bubble growth rates in soda-lime glass at constant temperature

Refining agent combination	Temperature [°C]	$\overline{\Delta a/\Delta \tau}$ [ms^{-1}]
without ref. agent	1400	3.3×10^{-9}
1% Na_2O as $NaNO_3$	1400	3.8×10^{-8}
0.25% As_2O_3	1400	4.8×10^{-8}
0.50% As_2O_3	1400	9.2×10^{-8}
0.25% As_2O_3, 1% Na_2O as $NaNO_3$	1400	6.3×10^{-8}
0.5% As_2O_3, 1% Na_2O as $NaNO_3$	1400	2.1×10^{-7}
0.5% As_2O_3, 1% Na_2O as $NaNO_3$	1450	5.8×10^{-7}
1% As_2O_3, 1% Na_2O as $NaNO_3$	1400	7.3×10^{-7}
2% As_2O_3, 1% Na_2O as $NaNO_3$	1400	1.4×10^{-6}
0.74% Sb_2O_3, 1% Na_2O as $NaNO_3$	1450	8.0×10^{-8}
0.43% CeO_2	1450	8.0×10^{-8}
0.5% Na_2O as Na_2SO_4	1450	4.4×10^{-6}
1% Na_2O as $NaCl$	1500	1.3×10^{-7}
borosil. glass (1% Na_2O as $NaCl$)	1560	2.8×10^{-7}

cisely the ideal conditions, the more detailed knowledge about influencing factors is necessary.

The influence of most important factors on the course of refining

The influence of temperature

Refining agents are characterized by the high values of p_{iGlass} of refining gas at refining temperatures and by a steep temperature dependence of refining gas evolution in this temperature region (Arrhenius type of dependence). This is obvious from Fig. 10 where the values of p_{iGlass} are plotted against temperature for the flat glass with Na_2SO_4 [13]. Thus, the distinct favourable influence of increasing temperature on the refining rate may be expected. Fig. 11 confirmes this assumption for the flat glass with refining agent Na_2SO_4; similar dependences are valid for other glasses and refining agents.

The influence of pressure

The pressure decrease strengthens inequality (9) and accelerates bubble growth rate, i.e. the refining rate by bubble rising. The increasing pressure
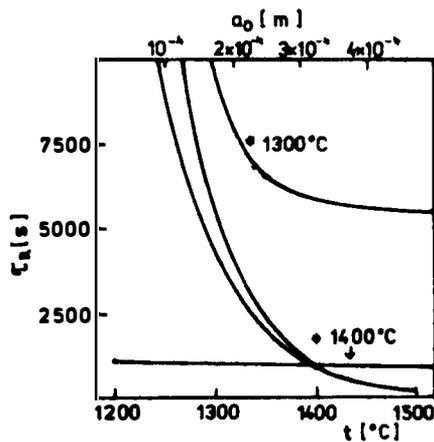
Fig. 11. The dependence between calculated value of refining time τ_R and temperature (resp. initial bubble radius a_0) in the isothermal glass layer of thickness 1m.
$1 - p_{0CO_2} = 1.013 \times 10^5$, $p_{0SO_2+O_2} = \sum p_i - p_{0CO_2}$
$2 - p_{0N_2} = \sum p_i$
$* -$ the dependence of τ_R on a_0

Fig. 12. The semilogarithmic dependence between the calculated and experimental values of bubble growth rates $\Delta a/\Delta \tau$ and external pressure p_{ex}. $a_0 = 0.1mm$; $h_0 = 0.25m$, glass melt for coloured TV screens, refining agent $Sb_2O_3 + KNO_3$.

strengthens on the contrary inequality (10), but the complete bubble dissolution cannot be reached in real time if some non-diffusing gas is presented. Thus, the low pressure refining seems to be more promising. As is obvious from mathematical modelling of bubbles and their direct laboratory observations at lowered pressures about 20kPa, the efficient refining may be accomplished at relatively low temperatures (1300 – 1350°C instead of 1480°C at normal pressure for TV glass) [15]. The calculated dependence of τ_R on external pressure confirming that fact is in Fig. 12, the validity of calculation results has been verified experimentally. At lowered pressures, as well another gases may play significant role in bubble growth as CO_2, H_2O f.e. In some cases, no classical refining agent is necessary and the role of refining gas is entirely shifted to the mentioned gases CO_2 or H_2O which fact has favourable ecological effect.

The influence of composition

The fundamental equation may be written in a following way:

$$SO^{2-}_{4(melt)} \rightleftharpoons SO_{2(gas)} + \frac{1}{2}O_{2(gas)} + O^{2-}_{(melt)} \qquad (12)$$

$$4(MO_x)^{(m-2x)+}_{(melt)} \rightleftharpoons$$

$$\rightleftharpoons 4M^{(m-n)+}_{(melt)} + 2(2x - n)O^{2-}_{(melt)} + nO_{2(gas)} \qquad (13)$$
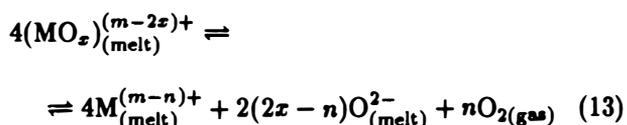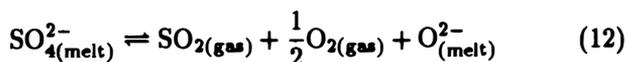
Thus, the base glass composition influences signifi-

cantly refining efficiency through the glass basicity (the activity of free oxygen ions). The majority of gases important from the point of view of refining are chemically bonded in glass melt and their solubility at given conditions increases with the glass basicity thus giving more favourable conditions for the refining (see eqs. 12–13). The significance of the type of refining agent is also connected with the chemical bond of refining agent in the glass structure. As is obvious from Fig. 13 [16], the redox pairs on the right side are more readily reduced at given condition (releasing oxygen) then those on the left side which fact can be related to the relative reduction potential of the appropriate redox couple. The increase of total refining agent concentration in the glass melt accelerates refining at lower refining agent concentrations (see Table II) which fact is in connection with glass saturation by the refining gas [17], however, at very high concentrations of refining agent, the extremes or stagnation of refining rate has been found (see Fig. 14 and 6, [6]). The stagnation or decrease of refining efficiency at very high concentrations of refining agents may be explained by their limited solubility in glass (sulphate) or by the change of glass basicity caused by refining agent.

The efficiency of refining process is also influenced by the kinetics of evaporation of refining agent and diffusion kinetics of refining gas [21] or by accumulation of refining agent in glass melting rooms with covered level [19] during melting process.
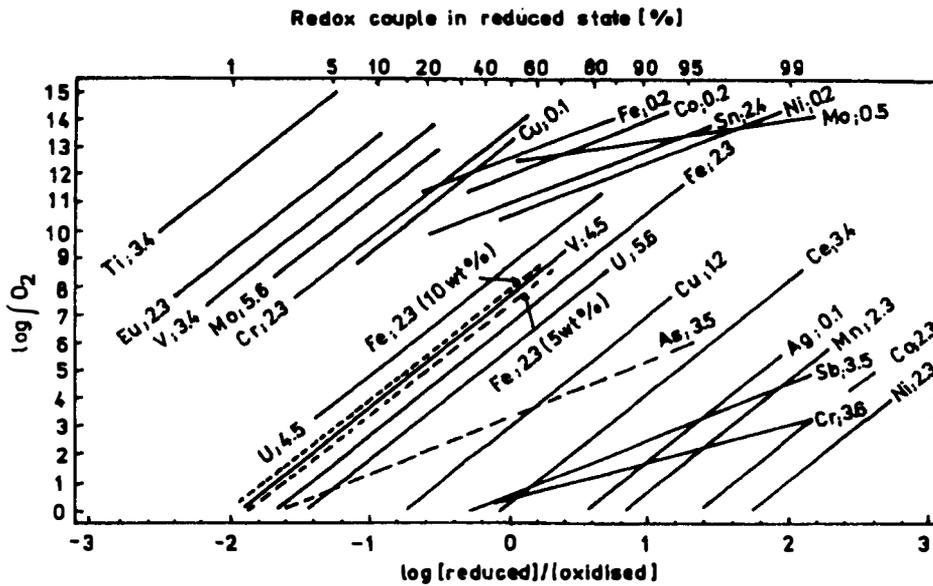
Fig. 13. Redox equilibria of various multivalent elements with respect to the imposed oxygen fugacity in a SRL-131 glass melt at 1150° C. The redox equilibrium is expressed as the concentration ratio of reduced to oxidised ions of the redox couple. Nominal concentration of the multivalent element in the melt is about 1 wt.%, except where noted.

The generalization of refining process

The summarizing of results involving favourable conditions of refining process makes it possible to search for general conditions of efficient refining [15]. In Table III, there are the couples of temperature and pressure and calculated values of $\overline{\Delta a/\Delta \tau}$ insuring effective refining of TV glass with or without refining agents in the rectangular refining room. In following Table IV, there are the experimental values of

$\Delta a/\Delta \tau$ insuring effective refining of laboratory melts of soda-lime glass with different refining agents at normal pressure and temperatures 1400–1530 °C [6]. As is obvious from both tables, the value of $\overline{\Delta a/\Delta \tau}$ moving from about 5×10^{-7} to about 1×10^{-6} ms^{-1} seems to be the general requirement of successful refining. This value is little dependent on the type of glass, refining agent, geometrical factors and tem-
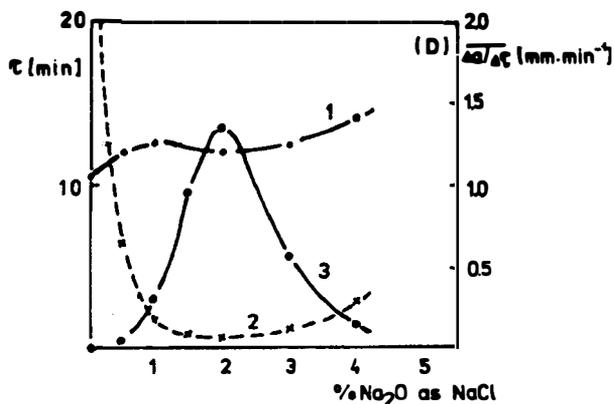
Fig. 14. Experimental comparison of (curve 1) τ_D, (curve 2) τ_{RN} – refining time of nucleated bubbles – and (curve 3) $\Delta a/\Delta \tau$ for soda-lime glass at 1530° C when NaCl is added.

Table IV

The experimental values of average bubble growth rate corresponding to effective refining (τ_R is about 10 min) of soda lime glass (74 wt. % SiO$_2$, 16 wt.% Na$_2$O, 10 wt.% CaO) refined by several combinations of refining agents

	Refining agent	Temperature [°C]	$\Delta a/\Delta \tau$ exp. [ms^{-1}]
1	1% As$_2$O$_3$ + 1% NaNO$_3$	1400	7.3×10^{-7}
2	1% As$_2$O$_3$ + 1% NaNO$_3$	1450	8.5×10^{-7}
3	0.4% Na$_2$O as Na$_2$SO$_4$	1470	1.2×10^{-6}
4	0.5% Na$_2$O as NaCl	1530	7.0×10^{-7}

Table III

The values of temperatures and pressures insuring bubble removing from the refining room and respective values of
bubble growth rates obtained from isothermal calculations

Average temperature of refining [°C]	p_{ex} [Pa] With ref. agent	$\Delta a/\Delta \tau$ [ms^{-1}] With ref. agent	p_{ex} [Pa] Without ref. agent	$\Delta a/\Delta \tau$ [ms^{-1}] Without ref. agent
1275	5000	5.8×10^{-7}	< 1	–
1325	20000	4.7×10^{-7}	3000	4.8×10^{-7}
1375	40000	4.7×10^{-7}	15000	3.8×10^{-7}
1425	85000	4.8×10^{-7}	20000	5.3×10^{-7}
1500	135000	6.2×10^{-7}	30000	5.5×10^{-7}

perature or pressure. The analysis of single cases has
shown that such a favourable case occurs whenever
the equilibrium partial pressure p_{iGlass} of at least one
of released gases reaches or overcomes the value of
given external pressure (gas saturation and supersat-
uration respectively). The mentioned fact is demon-
strated by Fig. 15, where the values of $p_{O_2 Glass} - p_{ex}$
and $p_{CO_2 Glass} - p_{ex}$ are plotted against temperature
for TV glass. This knowledge confirms the suggestion
about the dominating role of concentration difference
of refining gas connected with glass supersaturation
in refining process. Generally, not only classical refin-
ing agent can be succesful but also every component

present in glass and being able to produce quickly
diffusing gas or vapour of partial pressure compara-
ble with external pressure at given conditions. The
previous sentence is also the generalized condition of
succesful refining.

Mutual relations between sand dissolution and refining

The possible relations between both processes are
resulting from two phenomena:

1. Bubble nucleation on the solid particles (sand)
when melt near the particle surface is oversatu-
rated by gas.
2. Collecting surface active refining agent (sul-
phates, oxides, chlorides) on the surfaces (bub-
bles, sand particles).

Thus, four relations have been revealed when investi-
gating melting process:

a) Bubble nucleation on sand particles. This phe-
nomena has been directly observed [6], being caused
by temperature reboil at refining temperatures and
most probably by the low basicity of glass melt near
the sand boundary at lower temperatures. This fact
results in additive relation between sand dissolution
time and time for refining of nucleated bubbles:

$$\tau_M = \tau_D + \tau_{RN}, \qquad (14)$$

where τ_M is the entire melting and refining time, τ_{RN}
– time for refining of nucleated bubbles. Example of
experimental prove of equation (14) for refining agent
$As_2O_3 + NaNO_3$ in soda-lime glass at 1400°C is in
Fig. 16. At reduced pressures, the equation (14) may
hold even in absence of refining agent.

b) Acceleration of sand dissolution by the convection
evoked by bubbles nucleated on sand particles. The
experimental prove of this fact is in Fig. 6. At re-
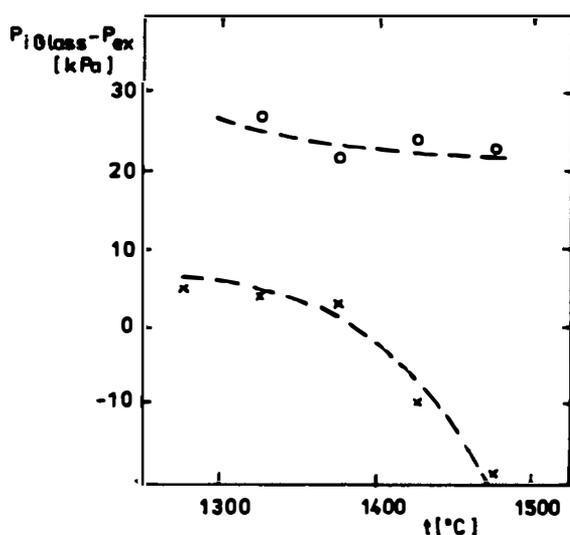
*Fig. 15. The difference of the equilibrium partial pressure
of refining gas and external pressure $p_{iGlass} - p_{ex}$ versus
temperature.*

× – for oxygen (TV glass with refining agent);

○ – for carbon dioxide (glass without refining agent).

Table V

Several favourable combinations of the melting and refining conditions, recommended arrangements of melting and refining room and related problems

Particle dissolution	Refining	Melting room	Problems to be solved
high temp., ref. agent	high temp.	electrically heated	corrosion
low, medium temp., controlled convection, refining agent	high temp.	gas or el. heated, one or two rooms	heating to ref. temp., volatil., flow control
low, medium temp., controlled convection, no classic. ref. agent	low, medium temp., reduced pressure	gas and el. heated, (ref. no heating?), two rooms	flow control, reduced pressure instalation
⇑			
medium temp., very low value of r_{0max}, ref. agent	high temp.	gas or el. heated	foaming, refining, sand price
low, medium temp., reduced pressure, no classic. ref. agent	low, medium temp., reduced pressure	electrically heated	batch reactions, reduced pressure instalation
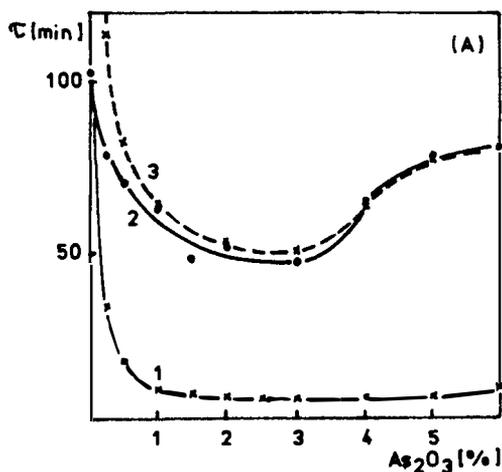
Fig. 16. Proof of validity of eq. (14) for soda-lime glass at 1400°C when As_2O_3 and $NaNO_3$ are added. Curve 1 – τ_{RN}, curve 2 – τ_M, curve 3 – $\tau_D + \tau_{RN}$.

duced pressures, this phenomenon may occur even in absence of refining agent.

c) Inhibition of sand dissolution at lower temperatures by refining agents collected on sand particle surface or caused by sand particle aggregation (the example of experimental prove see Fig. 7).

d) Increased glass foaming melted from fine sand particles in early melting states [20] and subsequent slow refining (possibly low retention of refining agent [21]).

Possible arrangements of the glass melting process

The necessary conditions for successful course of sand dissolution and refining are summarized at the end of appropriate chapters. In addition, the mutual relations must be taken into account for possible arrangements. As is f.e. obvious, the presence of refining agent could be substituted by lowered pressure. The absence of classical refining agent has favourable ecological consequences (toxicity of refining agents) and favourably influences sand dissolution at lower temperatures as well as glass foaming. However, these promising results are compensated by technical troubles with realization of low pressure refining or melting. Using mentioned conclusions, several possible arrangements of glass melting from the point of view of sand dissolution and refining may be suggested in Table V.

CONCLUSION

The sufficient knowledge of both melting processes and their mutual relations completed by analysis of their optimum conditions may lead to suggestions of

new or optimalized arrangements of glass melting process. To realize such suggestions, several other tasks must be however fulfilled:

1. The related processes being potentially controlling steps of the whole melting process must be examined and analysed (batch reactions, foaming, homogenization).

2. The reliable mathematical models of melting phenomena and melting rooms must be prepared for verification of suggested arrangements.

3. The technical problems connected with suggested arrangements must be solved.

References

[1] Hrma P.: Silikáty *27* (1), 7 (1980).

[2] Němec L., Freivolt Š.: Silikáty *29* (3), 215 (1985).

[3] Němec L., Mühlbauer M.: Glastechn. Ber. *56K*, 82 (1983).

[4] Mühlbauer M., Němec L.: Amer. Ceram. Soc. Bull. *64* (11), 1471 (1985).

[5] Němec L.: Sklář a keramik *33* (11), 285 (1983).

[6] Němec L.: Jour. Am. Ceram. Soc. *60* (9–10), 436 (1977).

[7] Němec L.: Sklář a keramik *29* (4), 103 (1979).

[8] Cable M.: Glass Technol. *2* (2), 60 (1960).

[9] Onorato P. I. K., Weinberg M. C.: Jour. Am. Ceram. Soc. *64* (11), 676 (1981).

[10] Cable M., Frade J. R.: Glastechn. Ber. *60* (11), 355 (1987).

[11] Němec L.: Glass Technol. *21* (3), 134, 139 (1980).

[12] Beerkens R. C. G.: Glastechn. Ber. *63K*, 222 (1990).

[13] Němec L., Mühlbauer M.: Glastechn. Ber. *54* (4), 99 (1981).

[14] Němec L.: Glass Technol. *15* (6), 153 (1974).

[15] Němec L., Schill P., Chmelař J.: Submitted for publication to Glastechn. Ber.

[16] Schreiber H. D., Korak S. J., Fritchman A. L., Goldman D. S., Schaeffer H. A.: Phys. Chem. Glasses *27* (4), 152 (1986).

[17] Němec L.: Sklář a keramik *23* (8), 232 (1973).

[18] Kloužek J.: Proceedings of I. Internat. Seminar on Mathematical Simulation in the Glass Melting, Val. Meziříčí, May 1991, p. 107.

[19] Němec L., Lubas J.: Poster Abstracts of 2. International Conference "Advances in the Fusion and Processing of Glass", Düsseldorf, October 1990, p. 41.

[20] Kim, Don-Sang, Hrma P.: Jour. Am. Ceram. Soc. *74* (3), 551 (1991).

[21] Kloužek J.: Unpublished results.