THE FINING PERFORMANCE UNDER THE INFLUENCE OF PHYSICO-CHEMICAL PARAMETERS

#MARCELA JEBAVÁ, LUBOMÍR NĚMEC

Laboratory of Inorganic Materials, Joint Workplace of the Institute of Chemical Technology Prague,
Technická 5, 166 28 Prague 6, and the Institute of Rock Structure and Mechanics of the ASCR, v.v.i.,
V Holešovičkách 41, 182 09 Prague 8, Czech Republic

#E-mail: Marcela.Jebava@vscht.cz

Submitted June 26, 2012; accepted September 27, 2012

Keywords: Glass fining, Melting performance, Space utilisation, Bubble growth rate, Physico-chemical parameters, Fining channel

The specific energy consumption and the fining performance of a continuous model fining space were defined for the evaluation of the glass-fining process in the space. A horizontal rectangular channel with a uniform isothermal flow of the molten glass and the experimentally obtained values of the bubble-growth rates − measured under different physico-chemical conditions − were applied to calculate the fining times and, consequently, the fining performance of the channel. The fundamental significance of the temperature and the optimal concentration of the fining agent were confirmed by the calculations. The bubble-growth rate was proved to be a crucial quantity determining the efficiency of the fining process, and its values can be used for a comparison of the fining abilities of different glasses. The application of quantity space utilisation facilitates the comparison of the glass-fining processes, occurring at both different fining kinetics and glass-flow character.

INTRODUCTION

Intensive physico-chemical study of the glass-fining process started in the second half of the last century mostly by laboratory crucible melts focused on the significance of the fundamental melting factors of the glass fining: the glass target composition, the choice of the fining agent and its role in the process, the temperature and the oxidation-reduction conditions of the fining process [1-6]. The physico-chemical examination provided also the fundamentals of the glass-fining kinetics in the form of the mathematical models of glass fining [7-10]. The transfer of the results into the industrial melting process was highly desirable, and there have been many attempts to do that on the basis of state-of-the-art results. However, the scientific effort faced the problem of scarce knowledge of the melting conditions, set up naturally in the continual melting spaces, particularly the temperature and velocity distributions of the melt inside of the melting space. The mathematical modelling provided the needed values and the models of glass fining were developed working under the conditions of the industrial glass-melting spaces [11-14]. The mathematical models of the glass-melting spaces revealed the actual fining conditions in the industrial spaces and helped to solve the fining problems on the technological scale.

Nevertheless, the lack of data needed to enter into the models, particularly gas solubilities, actual concentrations and their diffusion coefficients in the relevant industrial glasses brought a problem to extend the applications of the fining models. The cause of the problem consisted in the absence of relevant experimental methods and in the long-term measurements of the quantities needed for each glass. However, there was always a necessity to have at least a reliable tool for fining assessments available. In [15], the main factors of glass fining were defined in a quiescent glass of model composition and their influence on the bubble-removal process was studied. The specific energy consumption and the fining performance were chosen as the relevant technological quantities. Simplified equations describing the impact of single factors on the above-mentioned quantities were presented.

Recently, the authors of this work and their colleagues have dealt with the impact of the character of glass flow on the fining performance of the model melting space [16-19]. They introduced a quantity designated as space utilisation, which facilitated the separation of the process kinetics (described by the rate of the process or by its duration) from the process spatial distribution in the continual space (described by the space utilisation). Subsequently, the influence of the different glass-flow patterns in the model melting space was examined and the beneficial type of the glass-flow character was described under defined bubble-removal kinetics (given by the constant value of the bubble-growth rate).

The aim of this work is an examination of the impact of the main physico-chemical factors on the kinetics of the fining process under the defined constant glass-flow conditions in a model melting space. The fining performance of the model channel was chosen as a representative of the fining ability of the model space and the experimental values of the bubble growth rates, obtained for several industrial and model glasses under different values of the examined physic-chemical factors, were used for the calculations of the fining performance. It is assumed that the inspection of the process in terms of both the fining kinetics and glass-flow character in the space provides a complex view on the fining process.

THEORETICAL

The main criteria of the evaluation should be specified as the first step of the evaluation of the fining process in a melting space. The specific energy consumption, $H_M{}^0$, and the volume performance of the melting space, $\dot{V}$, were chosen as the relevant quantities. The specific energy consumption required for the melting of a unit of high-quality glass is one of the most considered quantities. The prime reason is its reduction and the subsequent decrease of the ecological burden on the environment.

The specific energy consumption of the melting process, $H_M{}^0$ [kJ/kg], without energy recycling can be defined by the following equation [16-19]:

$$H_M{}^0 = H_M{}^T + \frac{\dot{H}^L \, \tau_{Fref}}{\rho V} \, \frac{1}{u_F} \qquad (1)$$

where the first term on the right side of the equation expresses the theoretical specific-energy consumption needed for the achievement of the phase changes of the raw materials present in a batch, for the achievement of their chemical reactions and for the heating of the entire system to the melting (fining) temperature. The second term on the right side represents the heat losses given by the heat flux through the system boundaries into the surroundings. The value of the heat losses involves the residence time of the molten glass in the melting space.

The meaning of each quantity is as follows: $H_M{}^T$ [kJ/kg] is the theoretical specific energy consumption, $\dot{H}^L$ [kJ/s] is the heat flux through the space boundaries, ρ [kg/m^3] is the density of the molten glass, V [m^3] is the volume of the glass in the melting space, τ_{Fref} [s] is the reference fining time which the bubble of the critical (minimal) size needs to rise from the bottom of the space to the glass level in the quiescent liquid, and, finally, u_F describes the utilisation of the melting space for the fining process.

The performance of the melting space is de facto given by its volume flow rate or by the mass flow rate, $\dot{V}$ [m^3/s]:

$$V = \frac{V}{\tau_{Fref}} \, u_F \qquad (2)$$

Then P is $P = 86.4\rho\dot{V}$ [tons/day]. Thus, the specific energy consumption is inversely proportional to the volume performance of the melting space (see equation (1)).

In the authors' recent articles [18-19], the utilisation of the space for the fining process was defined by the product:

$$u_F = (1 - m_{virt}) \, \frac{\tau_{F\,ref}}{\tau_{F\,crit}} \qquad (3)$$

where m_{virt} is the fraction of the virtual dead space for the bubble-removal process and τ_{Fcrit} is the critical fining time in the glass melt with flow patterns.

The majority of the glass-melting spaces are characterised by horizontal temperature gradients, which cause melt circulations inside of the spaces. The bubble rising to the glass level is mostly hindered by the melt circulations [18-19]; consequently, $u_F < 1$, and the fining process in the circulating melt is characterised by higher specific-energy consumption and lower melting performance in comparison with fining in a quiescent melt. Equations (1-2) thus present separately the influence of the process kinetics, represented here by the value of the reference fining time, τ_{Fref}, and the impact of the melt flow on the space utilisation for the process, represented by the relative value, u_F.

In their recent works [17-19], the authors of this article have dealt with the impact of the different flow patterns, set up in the model melting channel with the help of horizontal linear-temperature gradients, on the melting performance of the channel under the conditions of defined kinetics of the fining process. The fining kinetics were defined in the model TV glass melt by the experimentally measured values of the average growth rates of the critical bubble radii. The beneficial glass-flow patterns were defined along with the temperature gradients under which the desired character of the melt flow had been attained. The spiral character of the melt flow characterised the optimal flow patterns which partially simulated a plug flow and the most favourable values of the space utilisation attained 0.6–0.8.

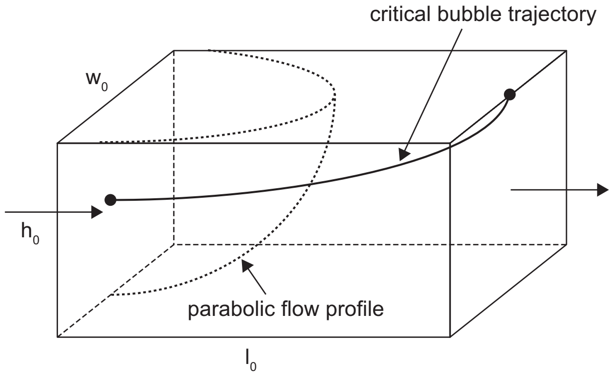

Figure 1. The three-dimensional scheme of the critical-bubble removal from the model horizontal rectangular channel with the uniform isothermal flow (parabolic distribution of glass velocities).

This work is aimed at the impact of the fining kinetics on the bubble removal from the model horizontal rectangular channel. The defined glass-flow character in the channel is represented by the uniform isothermal melt flow, characterised by the parabolic distribution of the melt velocities. The value of the space utilisation in the isothermal channel will be defined.

The fining time of the critical bubble is defined by the bubble which inputs the continual channel in the vertical longitudinal plane of symmetry and near half of the height of the glass layer [18] and reaches the melt level just at the end of the melting space (Figure 1). Thus, the melting facility has no fining reserve and the cases with the different fining kinetics may be relevantly compared.

In the isothermal horizontal channel with free surface, the starting point of the critical growing bubble lies at the vertical position, $h_{crit} = 0.528\ h_0$, where h_0 [m] s the thickness of the glass layer in the channel [20]. The bubble removal from the glass melt, alternatively its velocity of the rise to the glass surface given by Stokes' law, is in this case one of the most important parameters which can decrease the specific energy consumption and increase the performance of the space. The velocity of a single-bubble rise is then given by:

$$\frac{dh}{d\tau} = \frac{2g\rho a^2}{9\eta} \qquad (4)$$

where a [m] is approximately $a = a_0 + \dot{a}\tau$, h [m] is a vertical coordinate in the molten glass, ρ and η [Pa.s] are the density and the viscosity of the glass respectively, a_0 [m] is the initial bubble radius, and, finally, $\dot{a}$ [m/s] is the growth rate of the bubble radius. After the integration, the actual position of the bubble in time is obtained. Since the starting position of the bubble in the channel is at $0.528h_0$ (Figure 1), the critical bubble has to travel the vertical distance $h_0 - h_{crit} = 0.472h_0$:

$$0.472\ h_0 = \frac{2g\rho}{9\eta}\left(a_0^{\,2}\,\tau_{F\,crit} + a_0\dot{a}\tau^2_{F\,crit} + \frac{\dot{a}^2\,\tau^3_{F\,crit}}{3}\right) \qquad (5)$$

When one looks for the reference fining time of the critical bubble, τ_{Fref}, the total vertical distance h_0 instead of $0.472h_0$ should be considered in equation (5), which is valid for bubbles with a constant growth rate, $\dot{a}$. Almost all of the bubbles created by the glass batch decomposition fulfil this assumption, because the steady composition of bubbles in the melt is achieved rapidly at fining temperatures [21].

If the initial bubble size is small and the fining times are sufficiently long, the first two terms in the brackets of equation (5) may be neglected and the critical fining time of the bubble can be explicitly expressed:

$$\tau_{F\,crit} = \left(\frac{27\eta h_0}{2g\rho\dot{a}^2}\right)^{1/3} \qquad (6)$$

Taking into account equation (5), the ratio between τ_{Fref} and τ_{Fcrit} in equation (3), is equivalent to 1.3. The value of m_{virt} is given by the ratio τ_{Fcrit}/τ_G [18-19], where τ_G is the mean residence time of the melt in the channel. τ_G is calculated from the velocity distribution of the channel in the critical case (the critical bubble reaches the glass level just at the end of the channel). The value of the m_{virt} in the case of the isothermal rectangular channel is then 0.482 and the space utilisation of the channel according to equation (3) is 0.67.

If the system is non-isothermal, the space utilisation has to be calculated by using the mathematical model, which takes into account the distribution of the temperatures and velocities in the melting space and also the temperature dependence of the bubble-growth rate along its trace [13].

The basic physico-chemical quantities which influence the specific energy consumption and the performance are as follows: temperature, pressure, and the composition of the glass melt (major and minor components of the glass), as well as the oxidation-reduction state of the glass. The constant homogeneous temperature field in the channel with a uniform melt flow is considered.

EXPERIMENTAL AND CALCULATION CONDITIONS

The bubble-growth rate has to be measured if the fining performance is to be calculated (see equations 5 and 6). The laboratory measurement is conducted using the method of the high-temperature observation [22], which is demonstrated in Figure 2.

A silica glass cell filled with cullet is placed into a vertical laboratory furnace heated from above to the required temperature. After the cullet has been melted, a silica-glass tube connected with a source of gas is immersed into the molten glass and a small bubble with the defined initial composition is blown in the melt. The

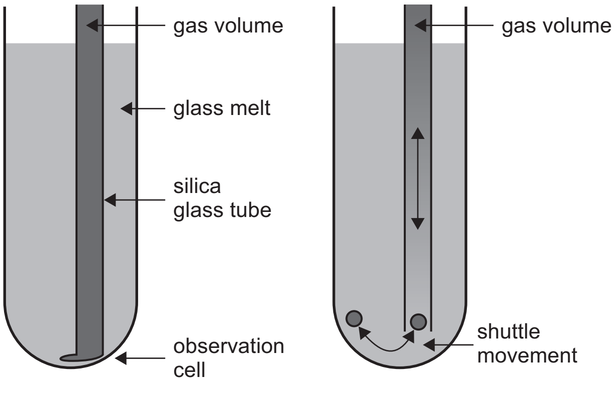

Figure 2. The scheme of the 'shuttle' method for the bubble long-term observation in the melt.

bubble is then forced to make the vertical shuttle-like motions (see Figure 2) by applying small variations of pressure inside the silica glass-tube and remains kept in this way inside the molten glass for the needed time. The bubble images are recorded in the course of the observation experiment using a camera installed in front of the furnace with an observation window. The recorded images (see Figure 3) are processed and the development of the bubble radius in time is obtained. The bubble-growth rate is read from the linear part of the dependence between the bubble radius and time. If demanded, the bubble can be pulled out of the melt, cooled, and used for the determination of the final composition at the end of the measurement. The size-versus-time dependences can be obtained alternatively from the bubbles formed naturally by the melting of a relevant glass batch (e.g. for the examination of the impact of pressure and oxidation-reduction state of glass).

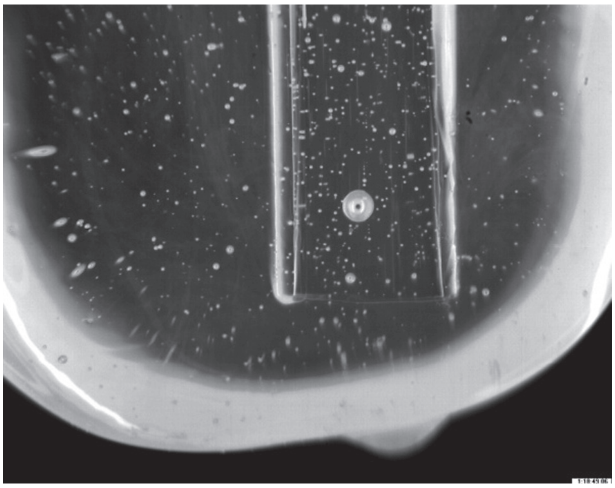

Figure 3. The image of the high-temperature observation of a bubble in the laboratory furnace.

A rectangular horizontal channel (length $l_0 = 1\ m$, the thickness of the glass layer $h_0 = 0.5\ m$, width $w_0 = 0.5\ m$) with the assumed uniform isothermal flow of the molten glass was chosen as the relevant model melting space. The channel was identical with the space which was applied for the examination of the impact of the melt-flow character on its melting and fining performance [18-20]. The reference fining time, τ_{Fref}, of the critical bubble having the initial radius 5×10^{-5} m and starting at the bottom of the channel was obtained according to equation (5); subsequently, equation (2b) was used for the calculation of the fining performance with the obtained value of the space utilisation, $u_F = 0.67$.

RESULTS

The extensive measurements of the bubble growth rates in the various types of industrial glasses and at different levels of the above-mentioned physico-chemical quantities have been accomplished in the authors' laboratory over the last several years. Consequently, the mentioned data and the data measured for the purpose of this article were applied in order to evaluate the individual factors having an impact on the fining efficiency of the glass melt. The time which the critical bubble needs to be removed from the melt by rising to the level appeared a proper quantity for the evaluation of the fining efficiency of the given space – its fining performance and specific energy consumption.

The influence of the temperature on the fining performance of the model channel is demonstrated by Figure 4. Figure 5 then describes how the fining performance is dependent on the external pressure, i.e. the pressure dominating above the glass surface.

The type of fining agent and its concentration are the next important factors of the bubble-removal process [6, 23]. Figure 6 summarises the dependence of the fining performance on the increasing concentration of several commonly used fining agents. The maxima are obvious on the dependences valid for the arsenic oxide and sodium chloride, which signalise the existence of the optimal concentrations of both compounds for the process under given conditions. Whereas the fining agents belong to the minor components of the glass composition, the alkali oxides represent the major components in most of the industrial glasses. The decrease of the fining performance with the increasing content of sodium oxide in the soda-lime-silica glass melt is shown in Figure 7. The literary data are applied involving the use of sodium sulphate as the fining agent [1].

The initial oxidation-reduction state of a glass melt predetermines the glass-fining ability, particularly when

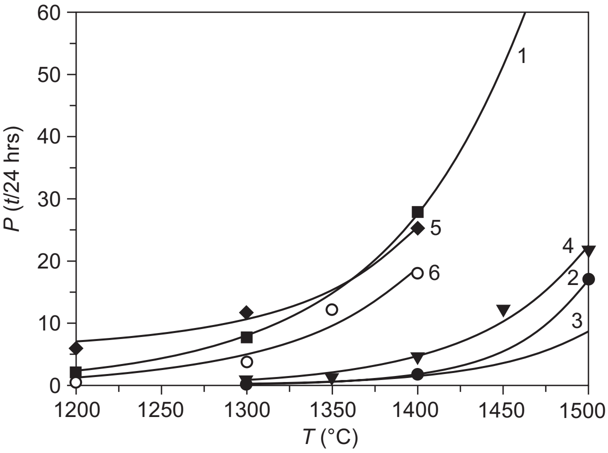

Figure 4. The dependence of the fining performance of the channel (in tons per day) on the temperature for the various industrial glasses. 1 - the Czech float glass with the higher content of Na_2SO_4, 2 - the float glass G1 with the lower content of Na_2SO_4, 3 – the ion-exchange glass, 4 - the TV-panel glass with Sb_2O_3 as the fining agent, 5 - the lead-silica glass at pressure 50 kPa with As_2O_3 as the fining agent, 6 - the TV-panel glass at pressure 16 kPa and without any fining agent.

using sodium sulphate as the fining agent. This is obvious from Figure 8, in which the decreasing initial redox state of glass is represented by the increasing carbon/sulphate ratio in the glass batch.

Considering equation (4), the glass density, viscosity, the instant bubble size and the bubble-growth rate determine the bubble rising velocity and consequently the bubble fining time and the fining performance of the fining channel. However, when all of the calculated values of the channel-melting performance are plotted against the average growth rate of the bubble radius for the bubbles of the critical radius, the typical smooth, progressively growing dependence in Figure 9, curve 1, is obtained, which shows that the fining performance of the model channel is determined mostly by the bubble-growth rate in a broad range of bubble-growth rates.

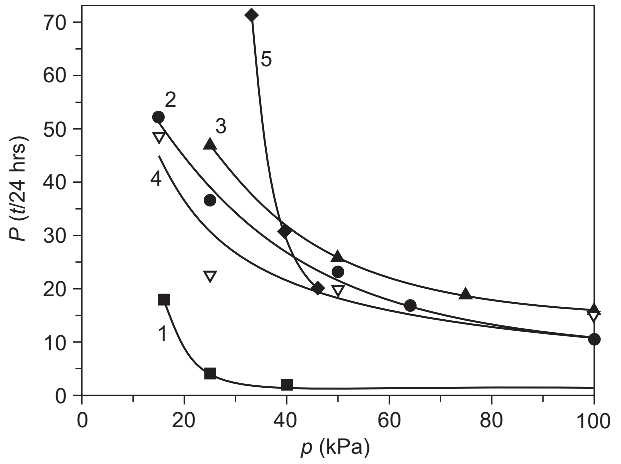

Figure 5. The dependence of the fining performance of the channel on the external pressure for the various industrial glasses. 1 - the TV-panel glass at 1300°C and with Sb_2O_3 as the fining agent, 2 - the lead-silica glass at 1300°C and with As_2O_3 as the fining agent, 3 - the lead-silica glass at 1400°C and with As_2O_3 as the fining agent, 4 - the lead-silica glass at 1400°C and without any fining agent, 5 - the E-glass at 1350°C and with Na_2SO_4 as the fining agent.

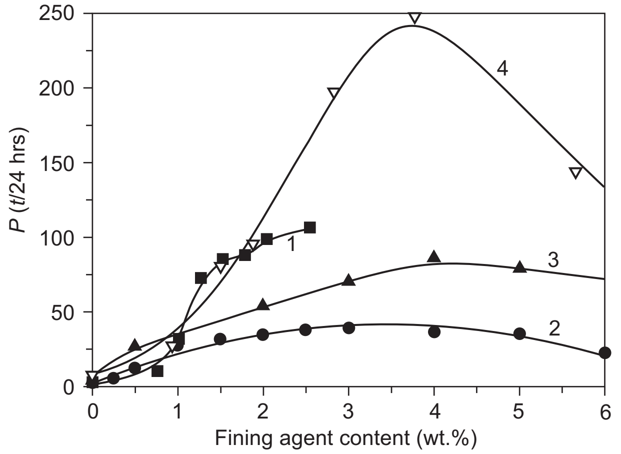

Figure 6. The dependence of the fining performance of the model channel on the concentration of the fining agent added to the batch in the model soda-lime-silica glass (16 wt. % of Na_2O, 10 wt. % of CaO, 74 wt. % of SiO_2) at the atmospheric pressure. 1 - Na_2SO_4 (1470°C), 2 - As_2O_3 with $NaNO_3$ (1400°C), 3 - As_2O_3 with $NaNO_3$ (1450°C), 4 - NaCl (1530°C).

DISCUSSION

All of the parameters examined in this work play their irreplaceable role in the course of the glass-fining process. Good knowledge helps in the assessment of the optimal conditions of the process in terms of the heat consumption and performance of the fining process.

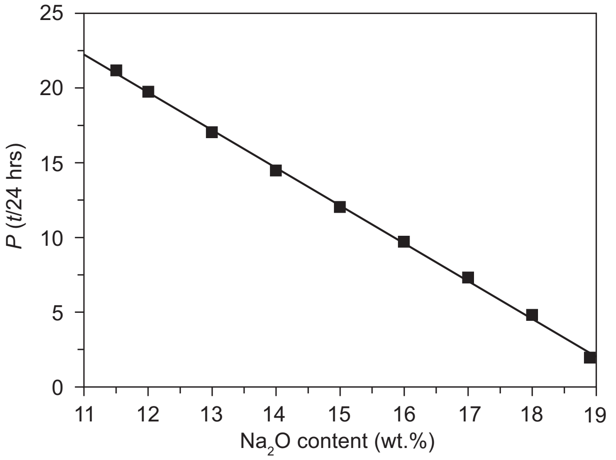

Figure 7. The dependence of the fining performance of the model channel on the Na_2O content in the model soda-lime-silica glass at 1475°C, Na_2SO_4 was used as the fining agent [1].

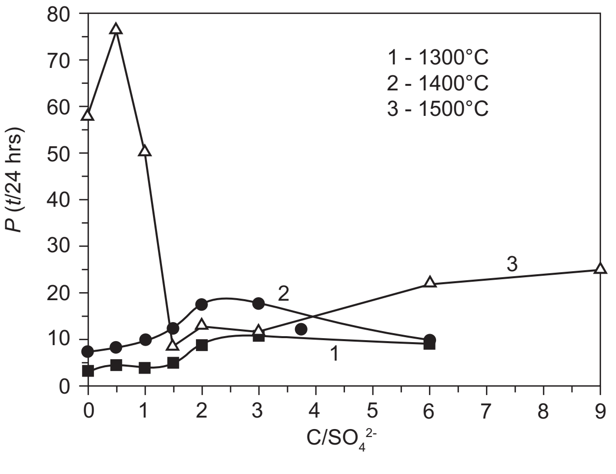

Figure 8. The dependence of the fining performance of the model channel on the molar ratio carbon/sulphate added to the glass batch of the soda-lime-silica glass at temperatures 1300°C, 1400°C and 1500°C. The reducing agent was dosed in the form of the fine-grounded coke containing 85 wt. % of C, the initial content of the SO_3 as the sodium sulphate in the melt was 0.5 wt. % [24].

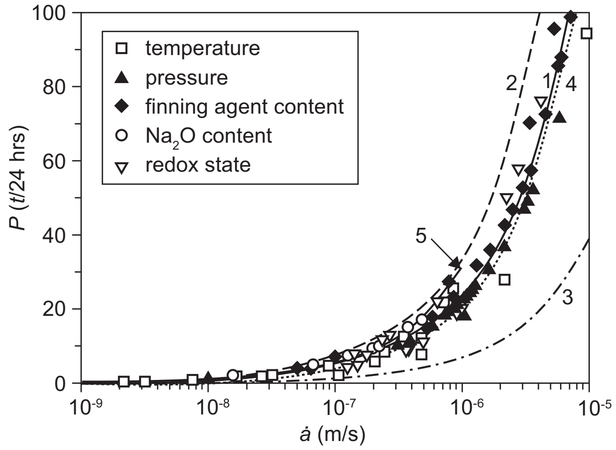

Figure 9. The overall view on the dependence between the fining performance of the model channel and the average growth rate of bubble radius with respect to 5 basic physico-chemical factors of the fining process. The thickness of the glass layer is 0.5 m, the initial bubble radius is 5×10^{-5} m, parabolic profile of the glass flow in the channel (curve 1). 1 - the isothermal model channel with a uniform (parabolic) flow of melt, 2 - the melting pot with a quiescent liquid, 3 - the model channel with the character of the melt flow corresponding to the current industrial melting facility [19], 4 - the model channel with the optimised character of the glass flow [18, 20], 5 - the melting pot with glass without any fining agents and with melt circulations [26], temperature gradient in the pot was 50°C/m, heated from the top.

Therefore, let us appreciate the impact of each parameter.

A progressively growing dependence between P and $\dot{a}$ is obvious from Figure 4 at all temperatures, corresponding approximately to the exponential one [15]. At higher temperatures, the decomposition of the fining complex proceeds in favour of the fining-gas release into the molten glass. The rising concentration of the dissolved gas in the glass melt enhances diffusion of the fining gas into bubbles and increases the bubbles sizes, which leads to the acceleration of the bubble rise to the glass surface. The suitable temperature interval of the fining-agent activity can be found in the area where the internal partial pressure of the fining gas or the mixture of fining gases (evolved by the fining-agent decomposition) corresponds roughly with the external pressure.

Temperature is certainly the most powerful accelerator of the fining process. On the other hand, the application of a higher fining temperature leads to a higher theoretical energy consumption of the process. That is why the relation between the increase of theoretical-energy consumption and decrease of the heat losses owing to sinking theoretical fining time should be considered when increasing the fining temperature.

The external pressure has an enhancing effect on the volume of the released gases and consequently on the mass transport of the released gases into bubbles. The internal partial pressures of the mentioned fining gases dissolved in the melt naturally aim at the equilibrium with the pressure of gases in the atmosphere above the melt and in the bubbles. The pressure changes can thus bring about both responses – bubble dissolution and bubble growth. The increased external pressure leads to the compression of the bubbles and to their dissolution, i.e. to the mass transport from the bubbles into the molten glass. Nevertheless, the complete dissolution of bubbles in a technologically acceptable time of about 10^4 s occurs at external pressures attaining as much as tens of MPa and at temperatures around 1500°C, as estimated in [27]. Thus, the mentioned conditions are not feasible for practical use. On the contrary, the decrease of the external pressure brings about the expansion of the gases in the bubbles, and the total, as well as partial, pressures of gases in the bubbles drop, which supports the diffusion of gases from the molten glass into the bubbles. As a consequence of the mentioned phenomenon, a progressive (approximately hyperbolic, see [15]) increase of the bubble-growth rate as well as the fining performance is achieved with declining external pressure, as can be seen from Figure 5. A significant rise of the bubble-removal rate appears under a pressure of around 50 kPa, and the pressure area around 30 kPa can be quoted as an efficient area for the process of the bubble removal in practice [25].

As obvious from Figure 6, the 'optimal' concentration of the fining agent in the melt can be discussed. The bubble-growth rates – and as well the fining performance – initially increase with the increasing concentration of the fining agent, because a larger amount of the refining agent is able to release a larger volume of the gas which then enters the bubbles under given conditions. When moving to the even higher concentrations of the fining agents, the growing basicity of the melt increases the stability of the fining complexes [1] and a smaller volume of the fining gas is released into the molten glass. In addition, the maximal concentration of the fining agent in the case of the sodium sulphate is limited by its solubility in the melt [28 - 29].

The high concentrations of fining agents can also slow the dissolution of sand grains at medium and lower temperatures, probably due to an inhibition of the chemical reaction on the sand-particle surfaces. At high temperatures, however, the undissolved grains serve as nucleation centres for the formation of new bubbles. This phenomenon leads, on the contrary, to an acceleration of the sand-dissolution process [30], but the newly nucleated bubbles can prolong the fining process. The optimal concentration of the fining agent here represents a compromise between the effect accelerating the sand dissolution and inhibiting fining owing to bubble nucleation. Its value usually decreases with a decrease of the melting temperature.

The impact of the variations of the major glass components on the fining process is primarily significant from the point of view of the basicity changes. The basicity of a molten glass is determined by the concentration of the free oxygen ions in the glass structure, which increases particularly with the content of alkali oxides in the glass. As already mentioned, the basicity supports the stability of fining complexes chemically binding fining gases. On the contrary, the increasing content of alkali oxides provides a glass melt of a lower viscosity, which facilitates the bubble ascent to the glass surface. The result of both counteracting effects is presented in Figure 7. As is evident from the graph, the fining performance almost linearly declines with the increasing content of the sodium oxide in the glass melt, i.e. the increasing stability of the fining complex is dominant. Consequently, either higher content of the fining agent, a fining agent with a fining effect at lower temperatures or higher fining temperatures are required for glasses of high basicity.

The initial oxidation-reduction state of the glass melt affects the starting equilibrium between the input and output components of the chemical reaction producing a fining gas or gases. The initial oxidation-reduction conditions of the melt are set up using batch components having either an oxidation or reduction character. The oxide fining agents in combination with the nitrates and the sulphates in combination with carbon or another reducing agent may serve as an example. The combination of the alkali sulphates with a reducing agent – mostly carbon, organic material, sulphides pyrite or silicon – is commonly used in the production of flat and container glasses. The presence of the reducing component pushes the reaction of the sulphate in favour of the release of the sulphur dioxide and shifts the gas-releasing reaction to lower temperatures [30-31].

Figure 8 represents the dependence of the channel performance on the increasing molar ratio of the carbon to the sulphate added to the glass batch. The increasing ratio illustrates the decreasing redox state of the glass. The molar ratios $C/SO_4^{2-} \in <0; 9>$ involve a region between oxidised and reduced glasses. According to [30 - 31], two main temperature areas of sulphur-compound reactions can be observed during the heating of the glass melt. When adding the reducing agent to a glass batch containing sulphates, the partial or total reduction of the sulphide and sulphur dioxide occurs. The ratio between the sulphate and sulphide ions sets up in the melt according to the initial ratio of the reducing agent to the sulphate in the batch. The remaining sulphate (if still present) reacts with the sulphide distinctly from about 1200°C and the reaction produces a considerable amount of sulphur dioxide which oversaturates the molten glass and brings about a bubble nucleation in the more reduced glasses. The released bubbles grow and support the homogenisation of the glass melt owing to micro-convection. At a lower initial ratio of the reducing agent to the sulphate added to the batch, a part of the sulphate ions remains in the glass melt even after the accomplished reaction with sulphides. These residual sulphate ions dissociate at temperatures above 1450°C, causing a typical fining effect.

The fining process thus falls into two regions. The first one, active in medium-reduced and reduced glasses particularly around the temperature 1300°C, is driven by sulphur dioxide as the only fining gas and shows both the homogenisation effect due to melt micro-convection by nucleated and growing bubbles and the low-temperature fining effect. The latter effect is reflected by the relatively high fining performances of the model channel in the case of medium reduced glasses (the C/SO_4^{2-} interval is 2–3) at 1300 and 1400°C in Figure 8. The second – well-known − region of the intensive fining sets in the oxidised glasses ($C/SO_4^{2-} = 0 – 1$) above the temperature 1450°C when sulphates spontaneously decompose and release both sulphur dioxide and oxygen. This fact is reflected by the high fining performance of the model channel at 1500°C as is obvious from curve 3 in Figure 8.

The resulting almost smooth summary functional dependence of the fining performance of the model channel on the bubble-growth rate in Figure 9 indicates that the bubble growth rate is a dominant quantity for the given process and the glass density and viscosity play a minor role for bubble rising in a broad interval of the bubble-growth rates. Consequently, the ability of various glasses to remove bubbles can be assessed only using the experimentally obtained values of the bubble-growth rates. The average value $\dot{a} > 1\times10^{-6}$ m/s indicates mostly an effective industrial fining process. The summary dependence presented in Figure 9 provides a chance to compare the efficiency of different ways of glass fining as a function of the bubble-growth rate. The different arrangements of the fining process are mostly characterised by the flow patterns of the melt set up in the melting space. The melting of glass in a laboratory crucible may be in most cases simulated by the fining of a quiescent liquid, where the space utilisation in equation (2) is equivalent to 1 [20]. The dependence of the fining performance of the melting pot with a quiescent melt is given by curve 2 in Figure 9. The melting in the contemporary continual melting space provides values of u_F mostly around 0.2 [19], which is reflected by curve 3 in Figure 9. The results of modelling at the optimal melt flow-patterns in the model channel showed, however, values of u_F up to 0.8 [18, 20], which is demonstrated by curve 4 in Figure 9. The melting in pot furnaces shows values of u_F close to 1 when the average value of the growth rate of bubble radius is greater than about 5×10^{-5} m/s [32] and is approximately simulated by curve 2 in Figure 9. An interesting case is the fining of glasses without any fining agent in the pot-melting furnace with relatively intensive circulations [26]. The bubbles can utilise the lift effect of the circulating melt and the space utilisation attains values greater than 1: the bubbles are removed from the circulating melt more easily than from the quiescent one. This case is represented by the square point for the value u_F of 1.8 at $\dot{a} = 1\times10^{-8}$ m/s.

CONCLUSION

The basic physico-chemical parameters showing an impact on the bubble removal (fining) of the glass-melting process were tested with respect to the values of the fining performance of the model space. The dependences of the fining performance of the horizontal model channel with the uniform isothermal flow of the molten glass on the temperature, the subatmospheric pressure, the glass minor and major components and on the redox state of glass were obtained with the help of the average values of the bubble-growth rates for several model and industrial glasses. For this purpose, some recently and earlier measured data of the bubble-growth rates were applied.

Temperature evidently proved to be the most powerful accelerator of the fining process, whose upper limit is determined by the increasing value of the theoretical energy consumption of the process and by undesirable processes such as volatilisation or corrosion. The search for fining agents active at medium temperatures is therefore profitable as shown by the results of glass fining by the combination of sodium sulphate and a reducing agent. The reduced external pressure can serve as an accelerator of the fining process as well, where external pressures having values around or under 30 kPa ensure the fast diffusion of gases into bubbles, speed up the process of bubble removal and make the fining process efficient. The optimal concentrations of the chemical accelerators in the form of fining agents haves been shown to be the second fundamental factor of the fining process, but the relevant optimal-concentration values depend considerably on the time-temperature regime of the process. The initial redox state of glass shows a particularly remarkable effect on glass fining by the combination of oxidising and reducing components as represented by sodium sulphate and a reducing agent. Two temperature regions of the fining activities are obvious in the case of the medium-reduced glasses, which are reflected by the increased values of the fining performances of the model space.

A summary of the fining results provides evidence in favour of the bubble-growth rate as the fundamental quantity suitable for the overall evaluation of the glass-fining process of different glasses. The quantity is relatively easily measurable in the laboratory. The use of the quantity utilisation of the space makes it possible to compare the efficiency of different arrangements of the glass-fining process. This is also significant for designing new concepts of the process.

Acknowledgement

This work has been supported by the project of the Technology Agency of the Czech Republic, No. TA01010844, "*New glasses and their technologies*" *and by the project of the Ministry of Industry and Trade of the Czech Republic, No. 2A-1TP1/063, "New glass and ceramic materials and new concepts of their preparation and manufacturing".*

References

1. Lyle A.K.: In: Travaux IV^e Congress International du Verre, Paris 1956, p. 93-102.
2. Pearce M. L.: J. Am. Ceram. Soc. *48*, 611 (1965).
3. Cable M., Evans D.J.: J. Appl. Phys. *38*, 2899 (1967).
4. Cable M.: Glass Technol. *1*, 139, 144 (1960), *ibid. 2*, 151 (1961).
5. Mulfinger H.O.: Glastechn. Ber. *45*, 238 (1972).
6. Němec L: Glass Technol. *15*, 153 (1974).
7. Němec L.: Glass Technol. *21*, 134 (1980).
8. Onorato P.I.K, Weinberg M.C.: J. Am. Ceram. Soc. *64,* 676 (1981).
9. Cable M., Frade J.R.: Glastechn. Ber. *60*, 355 (1987).
10. Ungan A.: Glastechn. Ber. *63K*, 19 (1990).
11. Beerkens R.: 7th Int. Conf. On Advances in Fusion and Processing of Glass III, Rochester, July 27-31, 2003.
12. Balkanli B., Ungan A.: Glass Technol. *37*, 101 (1996).
13. Matyáš J., Němec L.: Glass Sci. Technol. *76,* 71 (2003).
14. Oda K., Kaminoyama M.: J. Cer. Soc. Japan *117*, 736 (2009).
15. Němec L.: Glastechn. Ber. Glass Sci.Technol. *68*, 1 (1995).
16. Němec L., Jebavá M.: Glass Technol.: Eur. J. Glass Sci. Technol. A *47*, 68 (2006).
17. Němec L., Jebavá M., Cincibusová P.: Ceramics − Silikáty *50,* 140 (2006).
18. Němec L., Cincibusová P.: Ceramics − Silikáty *52*, 240 (2008).
19. Polák M., Němec L.: J. of Non-Cryst. Sol. *357*, 3108 (2011).
20. Cincibusová P.: Ph.D. Thesis, Prague (2011).
21. Němec L., Mühlbauer M.: Glastechn. Ber. *54*, 99 (1981).
22. Jebavá M., Němec L., Kloužek J.: Ceramics − Silikáty *48*, 121 (2004).
23. Němec L.: J. Am. Ceram. Soc. *60*, 436 (1977).
24. Kloužek J., Arkosiová M., Němec L., Cincibusová P.: Glass Technol.: Eur. J. Glass Sci. Technol. A *48*, 176 (2007).
25. Němec L., Schill P., Chmelař J.: Glastechn. Ber. *65*, 135 (1992).
26. Jebavá M., Němec L.: J. Non-Cryst. Sol. (2012). (in print).
27. Bartuška M. et coll.: Glass defects. Bubbles in glass, Glass Service, Inc., Vsetín, and Práh, Prague, 2008, p. 465.
28. Holmquist S.: J. Am. Ceram. Soc. *49*, 467 (1966).
29. Beerkens R.G.C.: J. Am. Ceram. Soc. *86*, 1893 (2003).
30. Kloužek J., Arkosiová M., Němec L., Cincibusová P.: Glass Technol.: Eur. J. Glass Sci. Technol. A *48*, 176 (2007).
31. Kloužek J., Arkosiová M., Němec L.: Ceramics − Silikáty *50*, 134 (2006).
32. Jebavá M., Němec L.: Ceramics – Silikáty *55*, 232 (2011).