SOME CRITICAL POINTS OF THE GLASSMELTING PROCESS

PART I – DISSOLUTION PHENOMENA

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The simple relations expressing the influence of temperature, glass composition, sand granulometry and glass convection on the dissolution time of polydisperse sand have been presented to demonstrate the significance of these factors on the dissolution phenomena in glass melting. The theoretical equations have been compared with available experimental data. The results have shown the primary significance of the initial particle size, temperature and intensity of glass stirring. The applications of optimum conditions faces some critical points of the process as is corrosion of refractory materials at extreme conditions, fast heating the glass batch to the maximum temperature and glass flow arrangement inside of the glass melting space.

INTRODUCTION

When searching for the critical points of the glassmelting process, the corresponding definition of the entire process is needed. From this point of view, the glassmelting process may be characterized as a complex of chemical reactions and phase conversions. As the resulting phase is liquid, the dissolution phenomena seem to play an important role in the process. For the perfect and fast accomplishing the process, the chemical reactions should start far from equilibrium and high values of concentration gradients of transported components must be insured.

Considering the different stages of the glassmelting, the chemical decomposition reactions form the first step of the process. The possible influencing factors of this stage are temperature, pressure, composition, granulometry and hydrodynamic conditions. The general experience shows that especially high temperature insures the fast decomposition, the expected favourable influence of reduced pressure has not been realized up to this time owing to technical problems. The variability of commercial glass composition is usually low to be significant, however, the influence of granulometry of decomposed components (as carbonates, e.g.) has been proved experimentally. The hydrodynamical conditions have only limited significance as the high portion of solid material is present in the mixture during this stage. Generally, the decomposition reactions form only a small part of the time necessary to melt homogeneous glass and high temperature seems to be a sufficient condition for their fast realization.

The following main part of the glassmelting process involves the removing relicts of original phases, i.e. solid particles and bubbles as well as concentration gradients. As the glassmelting process is realized in the melting spaces with real material boundaries, the new generation of solid, gas and liquid inhomogeneities may be expected as the consequence of mutual interactions between melt and boundaries. In a simplified way, the glassmelting process may be considered as the homogenization process of large amount of solid, liquid and gas inhomogeneities coming from the original mixture, from reactions with the material boundaries and from condition variations leading to their arising in a glassmelt. Among these processes, the critical ones have to be sought for. The contemporary and feasible future conditions of inhomogeneity removing are therefore the aim of this work.

Stones and heterogeneities

The separation of solid and liquid inhomogeneities from glass is not feasible and their dissolution in a glass melt is therefore the only possible way of their removing. Under conditions of the glassmelting process, the dissolution controlled by mass transfer is the most usual case. As heterogeneities and stones are almost never in equilibrium with glass melt, the dissolution process proceeds up to their complete disappearing. The mass flow on the inhomogeneity surfaces, $\dot{m}$, may be described by the Nernst-Noyes equation:

$$\dot{m} = - D \, / \, \delta \Delta c \tag{1}$$

where D is the diffusion coefficient, δ is the thickness of diffusion layer and Δc is the concentration difference of transported component between surface and bulk glass. The role of growing temperature is increase in D and Δc while the role of pressure is negligible. The influence of glass composition is complex, however, the general trend tends to slow down dissolution when increasing glass viscosity. The role of inhomogeneity granulometry (or its characteristic size) is hidden in the integration constant, the dissolution times increase with the increasing initial characteristic size of inhomogeneity. The convection of a melt is contributing essentially to the enhancing of dissolution decreasing the thickness of the diffusion layer as well as the characteristic size of heterogeneities. Applying extreme values of temperature, $T > T^{m.p.}$ (melting point), the stones may be removed almost instantly whereas heterogeneities can be instantly dispersed in a glassmelt when applying the extreme intensity of glass convection (dissolution of stones is then controlled by the relatively fast chemical reaction). The application of extreme fine particles for a glass batch is rather technological and economical problem then a physico - chemical one.

The influence of mentioned parameters on the dissolution process under current melting conditions may be demonstrated on the sand dissolution process using semiempirical equations and experimental data.

Temperature influence

For the dissolution time of polydisperze sand, following simplified equation may be applied [1, 2] using the coefficient of mass transfer:

$$\tau_D = \frac{\varphi}{\alpha} = - \frac{1}{\kappa} \ln \frac{\alpha_{ch}}{\alpha_f} - \frac{\psi}{\alpha_f} \qquad (2)$$

where α_{ch}, α_f and κ, respectively, are three temperature coefficients expressing the stage of chemical reaction (α_{ch}), stationary dissolution controlled by diffusion (α_f) and the rate of transition of the dissolution process from the control by chemical reaction to the control by diffusion (κ). The quantity ψ is value of integral involving the concentration gradient on the sand particle boundary.

Assuming an exponential increase of all three coefficients, α_{ch}, α_f and κ, the temperature dependence of τ_D may be approximated by the relation:

$$\tau_D = K_{D1}^T \exp \left(\frac{K_{D2}^T}{T} \right) \qquad (3)$$

where K_{D1}^T a K_{D2}^T are temperature independent constants and T is temperature in K. The subscripts in the constant

K designate the controlling process (D - dissolution, R - refining), the superscripts the influencing factor (T - temperature, P - pressure, MaC - major component, MiC - minor component, D - distribution of particles, C - glass convection). The comparison between experimental results and Equation (3) is presented in Figure 1 and shows good agreement between theory and experiment. As temperature $T \rightarrow \infty$, τ_D in Equation (3) tends to a very low value, however, the process will be controlled by sand melting starting from 1717 °C; thus, temperature appears to be a very strong intensification factor.
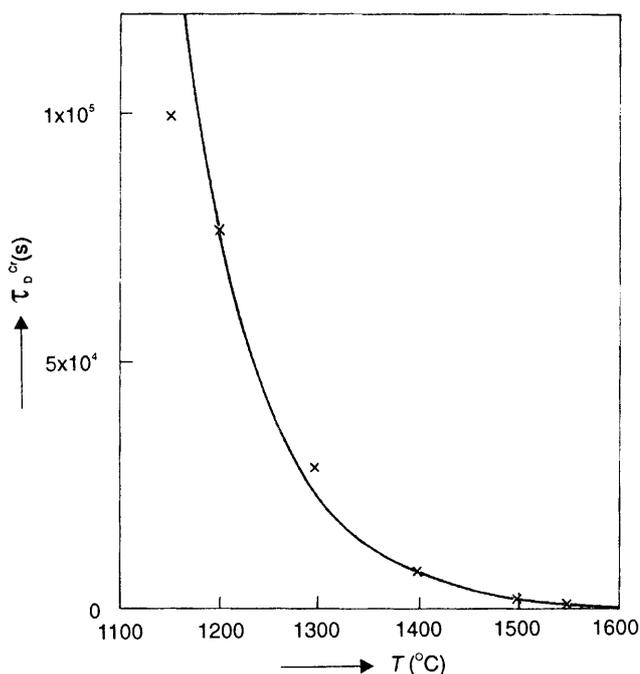

Figure 1. Temperature influence. The dependence of the sand dissolution time, τ_D, on temperature for the model glass (74 SiO_2, 16 Na_2O, 10 CaO, wt.%) refined, by 0.7 % of Na_2O as Na_2SO_4, $r_{max\,o} = 2.5 \times 10^{-4}$ m
—— the proposed Equation (3); × - exp. values

Influence of major components of glass

The function expressing the time dependence of undissolved mass fraction of sand, w_s, can be usually expressed by a simple power function, $w_s = Kr_{max}^{n'}$, where exponent n' for the industrial sand is about 6 - 8 and r_{max} is the instantaneous size of maximum sand particle. Using the simplified integrated form of quantity ψ from Equation (2) and rearranging gives for τ_D:

$$\tau_D \quad \frac{K_{D1}^{MaC}}{\alpha} + \frac{K_{D2}^{MaC}}{\alpha(w_{eq}-w_t)^{p'}} \qquad (4)$$

where $p' = (n'-1)/n'$, $\bar{\alpha}$ is the average value of the entire coefficient of mass transfer, α, w_{eq} is the equilibrium mass fraction of SiO_2 in the glass melt, w_t is the total mass fraction of SiO_2 in the mixture of glass and sand and K_{D1}^{MaC} as well as K_{D2}^{MaC} are composition independent constants. Equation (4) is valid under simplifying conditions and in a narrow interval of w_t. The hyperbolic dependence between τ_D and w_t goes to infinity

when $w_t \rightarrow w_{eq}$. The comparison between experimental values of τ_D versus SiO_2 concentration and Equation (4) for two glasses is presented in Figures (2a, b). The changes of other major components cause more complicated behaviour, however, τ_D grows usually with increasing glass viscosity (see in Figure 2c) For industrial glasses, only small changes of major glass composition are allowed.
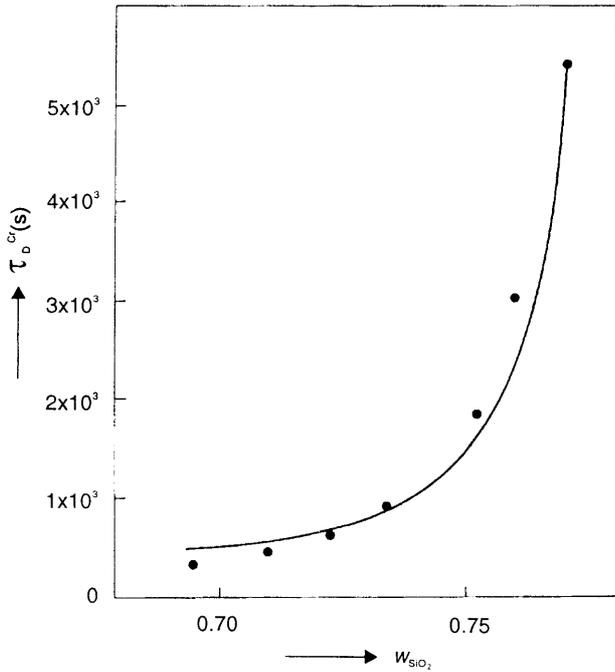
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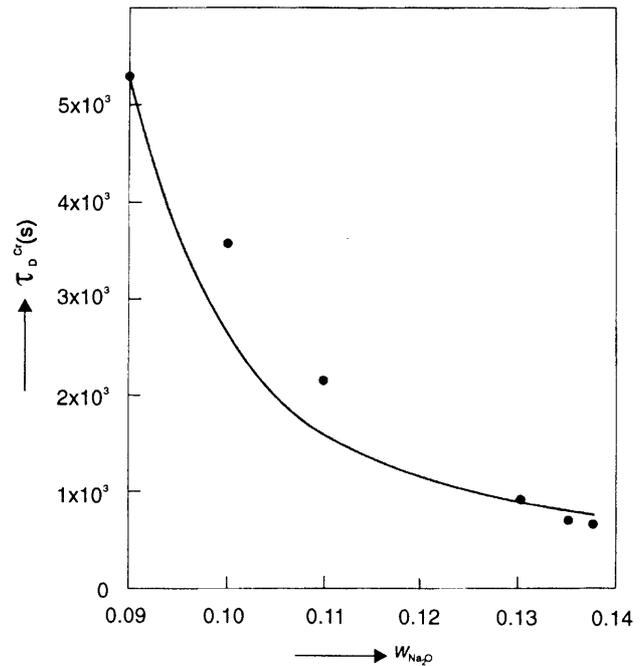
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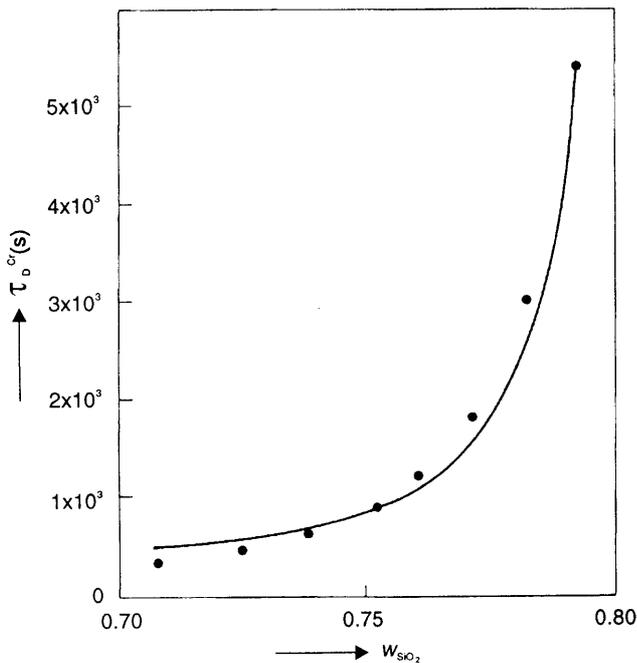
b)

Figure 2. Influence of major components of glass

a) The dependence between batch free times [3] of the SiO_2 - CaO - MgO - Na_2O glass (CaO + MgO = 14 wt.%) and mass fraction of SiO_2, w_{SiO_2}, at 1427 °C
——— Equation (4); ● - exp. values

b) The dependence between batch free times [3] of the SiO_2 - CaO - Na_2O glass (CaO = 10 wt.%) and the mass fraction of SiO_2, w_{SiO_2}, at 1427 °C
——— Equation (4); ● - exp. values

c) The dependence between batch free times [4] of glass with substitution B_2O_3 for Na_2O and the mass fraction of Na_2O, w_{Na_2O}, at 1427 °C.
——— Equation (4); ● - exp. values

Influence of minor components of glass

The discussion will be restricted to refining agents as there is lack of information about other minor components. Some experimental results show that refining agents may inhibit sand dissolution at low temperatures [5], however, they accelerate the process at their high values [6]. If the explanation of this behaviour is restricted to the supposed inhibition of chemical reaction by refining agents and to the assumed acceleration of sand dissolution due to the convection by bubbles nucleated and growing on sand particles at high temperatures, following equation may be written for τ_D:

$$\tau_D = - \frac{1}{\kappa} \ln \frac{\alpha_{ch0} \exp (-K_{D1}^{MiC} w_R)}{\alpha_{f0}(1 - K_{D3}^{MiC} + K_{D4}^{MiC} w_R)} +$$

$$+ \frac{\psi}{\alpha_{f0}(1 - K_{D3}^{MiC} + K_{D4}^{MiC} w_R)} \qquad (5)$$

where w_R is the mass fraction of refining agent and K_{D3}^{MiC} as well as K_{D4}^{MiC} are composition independent constants. Subscript o designates a standard value.

At low temperatures, the influence of refining agents on bubble behaviour is negligible $[(K_{D4}^{MiC} w_R - K_{D3}^{MiC}) \rightarrow 0]$ and Equation (5) can be simplified into form:

$$\tau_D = K_{D5}^{MiC} + K_{D6}^{MiC} w_R \qquad (6)$$

where $K_{D5}^{MiC} = \psi/\alpha_{f0} - 1/\kappa \ln(\alpha_{ch0}/\alpha_{f0})$ and $K_{D6}^{MiC} = 1/\kappa K_{D1}^{MiC}$ are composition independent constants. As is obvious from Figure 3a, Equation (6) is in an acceptable agreement with experimental results [5].

At high refining temperatures, the second term in Equation (5) considerably decreases with growing w_R and the first one decreases only slightly. As a result, there is a slight decrease in τ_D with growing refining agent concentration (see Figure 3b). At medium temperatures, both influences mutually compensate. Even though refining agents can considerably influence the sand dissolution especially at very low and very high temperatures, their effect on sand dissolution is not decisive.

Influence of sand granulometry

Laboratory experiments show a roughly linear dependence between the maximum particle size and dissolution time of sand [7]. When searching for the theoretical proof of this fact, Equation (2) can be applied. After rearranging the integral designated as ψ in Equation (2) and obtaining its solution for the polydisperse sand with a small amount of coarse particles, following equation is valid:

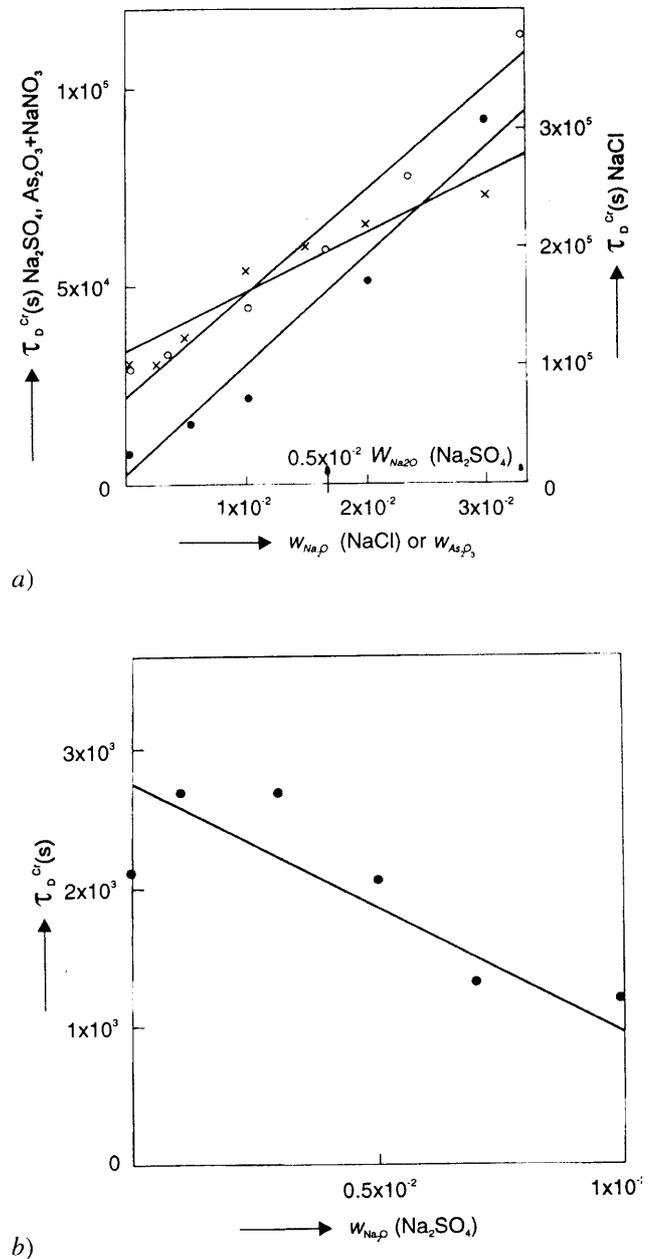$$\tau_D = \frac{B}{\alpha} + \frac{r_{max_0} - \Delta}{\alpha(w_{eq} - w_t)} \qquad (7)$$

a)

b)

Figure 3. Influence of minor components of glass

a) The dependence between the sand dissolution time, τ_D, and the mass fraction of refining agents in the model glass (74 SiO_2, 16 Na_2O, 10 CaO, wt %); $r_{max\,0} = 2.5 \times 10^{-4}$ m, $t = 1200$ °C
1: Na_2O as Na_2SO_4; ——— Equation (6); O - exp. values
2: Na_2O as $NaCl$; ——— Equation (6); ● - exp. values
3: As_2O_3 as $NaNO_3$; ——— Equation (6); × - exp. values

b) The dependence between the sand dissolution time, τ_D, and mass frastion of Na_2O added as Na_2SO_4 in the model glass, $r_{max\,0} = 2.5 \times 10^{-4}$ m, $t = 1500$ °C
——— simplified Equation (5); ● - exp. values

where B is constant value of integral, Δ is constant difference of sand particle sizes and r_{max_0} is initial effective radius of maximum sand particle. As $\bar{\alpha}$ and the difference $w_{eq} - w_t$ are constant too, Equation (7) expresses the linear dependence between τ_D and r_{max_0}. Its graphical form taken from literature [7] is obvious in Figure 4.

The effect of the shape of sand distribution function may be described in a simplified form by the equation:

$$\tau_D = K_{D1}^D - K_{D2}^D \qquad (8)$$

where K_{D1}^D and K_{D2}^D are constants independent from the distribution curve and r_{io} is the effective radius of sand particle corresponding to the maximum on the sand distribution function. The influence of the shape of sand distribution function (at constant value of r_{max_0}) is not very significant; in addition, there is only a small chance to influence considerably the size distribution of industrial sands.

Influence of glass stirring

The influence of glass stirring can be expressed by the growth of the coefficient of mass transfer in the later melting stages, α_f, with growing value of glass velocity gradient, grad v. Equation (2) may be rewritten as:

$$\tau_D = - \frac{1}{\kappa} \ln \frac{\alpha_{ch}}{\alpha_{f0}(1 + K_D^C \text{ grad } v)} +$$

$$+ \frac{\psi}{\alpha_{f0}(1 + K_D^C \text{ grad } v)} \qquad (9)$$

Where α_{f0} is the value of α_f for grad $v = 0$ and K_D^C is constant independent from grad v. Since the first term changes much less than the second one, Equation (9) may be rewritten as:

$$\tau_D = \frac{K_{D1}^C}{1 + K_{D2}^C \text{ grad } v} - K_{D3}^C \qquad (10)$$

where K_{D1}^C, K_{D2}^C and K_{D3}^C are independent from grad v.

In Figure 5, there is the graphical form of this dependence for soda - lime glass stirred in the laboratory scale by bubbling of oxygen [5]. The linear dependence between the amount of bubbled gas, $\dot{V}$, and grad v is assumed. Unfortunately, there is lack of experimental data to prove unambiguously validity of Equation (10). Nevertheless, the strong positive influence of glass stirring on the sand dissolution time is indicated by the available results.

Summarizing of particle and heterogeneity removing

When evaluating the significance of single melting parameters for the dissolution process, three factors seem
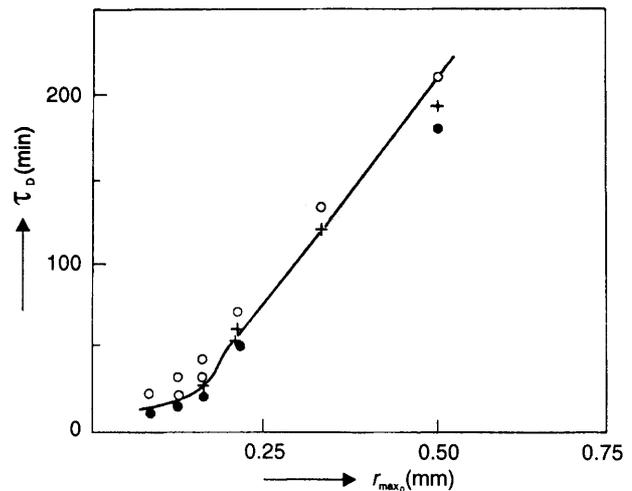
Figure 4. Influence of maximum sand particle size on the melting time, temperature 1470 °C, 73.8 SiO_2, 0.2 R_2O_3, 11.9 CaO, 0.1 MgO, 14.0 Na_2O (wt.%) [7]

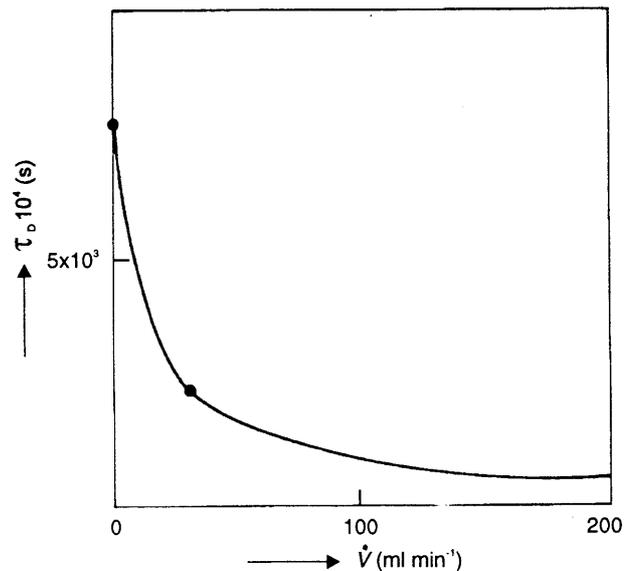O - no undissolved particles; ● - 1-12 undissolved particles

Figure 5. Influence of glass stirring
The dependence between the sand dissolution time, τ_D, and intensity of glass stirring by bubbling oxygen. Soda-lime-silica glass (74 SiO_2, 16 Na_2O, 10 CaO, wt.%), 0.7 Na_2O as Na_2SO_4, $r_{max_0} = 2.5 \times 10^{-4}$ m, $t = 1400$ °C

to be most important: the initial size of inhomogeneity, temperature, and intensity of glass stirring. As for particle dissolution, the further decrease in r_{max_0} is restricted by the natural size distribution of sand particles depending on the finding place. The crushing of original sand faces the problems with processing large amounts of material. As for heterogeneities, arising of some of their kinds is independent from the batch granulometry. The application

of extreme temperatures seems to be most significant for particle dissolution. Problems are arising, however, with corresponding furnace refractory materials showing at these conditions an acceptable corrosion and consequently the low level of secondary inhomogeneities in glass. The second difficulty involves the rapid heating of the large amount of material to the extreme temperatures in a relatively small furnace space. The application of glass stirring does not demand extreme temperatures, however, the corrosion problems are arising too. Both dissolution of sand and heterogeneity removing are in this case highly accelerated.The joint problem of effective glass stirring in a real melting space is soluble by the mathematical modelling. Separation of refining process seems to be necessary when applying forced convection.

When summarizing the main features of the dissolution process, the intensive glass stirring seems to be the most advantageous factor accelerating considerably both important processes by the relatively cheep mechanical energy. The critical points remain the choice of a corrosion resistant refractory material and the rapid heating of glass batch.

The rapid heating of the glass batch being necessary for attaining high outputs from the glass melting furnace may be in a simplified way described by the expression $\dot{M} = A\lambda / \delta(T^h - T^p) / H_M^G$ where $\dot{M}$ is the output, A is the surface, λ is the coefficient of heat conductivity, δ is the thickness of heating layer, T is temperature, the superscripts h and p designate heating medium and product (reacting glass batch, glass), respectively, and H_M^G is the specific theoretical energy consumption of the glass melting process. Generally, the product may be heated in form of continuous or dispersed phase. When the product is heated as a continuous phase, onesided (all electric melting) or bothsided heating (classical heating by gas or oil) is applied. The preheating of glass batch decreases the value of H_M^G. The increase in interface area A is limited by the furnace size and by construction feasibilities. The amount of heat accepted by glass batch from the glassmelt may be enhanced by increasing maximum temperature and by the convection of glass under the glass batch (decrease in δ). The value T^p can be favourably influenced by decarbonization during preheating.

The heating of the product may be also realized with the product being a dispersed phase while the heating medium is gas or glassmelt. In both cases, the value of the interface area grows considerably. The value of δ decreases at high intensity of mutual mixing of product and medium. The construction and ecological problems accompany the dispersing and heating the product in gas phase while there arise troubles with rapid batch dispersing in the glassmelt and with introducing there the required amount of energy.

CONCLUSION

The considerable acceleration of the glass melting process involves especially the enhanced removing remaining inhomogeneities from the glass melt As the dissolution process plays here an important role, the influence of internal melting factors on sand dissolution process has been examined in this part. Using derived simplified equations and experimental data, the influence of single factors may be quantitatively evaluated. This evaluation has shown the prior significance of inhomogeneity size, temperature and glass stirring. The glass stirring procedure seems to be especially advantageous for the future glassmelting, however, the mathematical modelling of stirring arrangement in the melting space will be necessary. Both in the case of extremely high temperatures and glass stirring, the corrosion resistant refractory materials are critical items of the process. The second critical process seems to be the rapid heating of the glass batch to the melting temperature; the dispersing of the glass batch in the heating medium - combustion gases or glassmelt - seems to be suitable procedure in future. The critical items of the refining process must be treated separately.

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Submitted in English by the author

NĚKTERÉ KRITICKÉ STRÁNKY TAVICÍHO PROCESU SKEL - ČÁST 1: PROCESY ROZPOUŠTĚNÍ

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Vliv základních vnitřních faktorů jako je teplota, složení, granulometrie a konvekce skloviny na procesy rozpouštění při tavení skel může být demonstrován na případu rozpouštění polydisperzních částic SiO_2. Byly odvozeny zjednodušené rovnice vyjadřující vliv uvedených faktorů a jejich průběh porovnán s dostupnými experimentálními daty. Za nejdůležitější parametry lze považovat počáteční charakteristický rozměr částice, teplotu a intenzitu konvekce skloviny. Aplikace optimálních podmínek - nevylučujíce podmínky extrémní - naráží na nejmenší problém při aplikaci nucené konvekce. Kritickými stránkami této části tavicího procesu se jeví výběr vhodných žárovzdorných materiálů pro rozhraní tavicího prostoru a rychlý ohřev většího množství sklářské vsázky na tavicí teplotu v malém objemu. Problém uspořádání proudění v tavicím prostoru při aplikaci nucené konvekce lze řešit matematickými modely proudění.