# A KINETIC EQUATION FOR INTERACTION BETWEEN GRAIN MATERIAL AND LIQUID WITH APPLICATION TO GLASS MELTING

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## Received 23. 6. 1978

An equation is derived for the kinetics of dissolution or growth of uniform solid grains uniformly dispersed in a liquid. The conditions under which sand dissolves during glass melting are discussed and a simple formula for the pertinent mass transfer coefficient is suggested. Some factors governing the lifetime of silica grains are analyzed.

## INTRODUCTION

A necessary basis for any optimization of glassmaking is a comprehension of the glass melting to a degree where it may be described mathematically. An important part of the overall batch melting process is the dissolution of sand. The purpose of the present contribution is to provide a framework for the description of its kinetics.

The dissolution of silica sand during the melting of glass batch is extremely complex because it may involve a number of processes. For the purpose of further treatment it can be divided into the following stages:

1. the initial stage — controlled by a surface reaction,

2. the transient stage — combined control by surface reaction and non-steady diffusion occurs,

3. the stationary stage — convective diffusion is rate controlling,

4. the grains disappearing stage — the diffusion is accelerated by spherical effect, 5. melt homogenization.

Although we are going to treat of the melting process as general, in this section we shall discuss the case of soda-lime-silica glass.

1. The initial stage. At the first contact of sand with the carbonate melt the material of the grains is being consumed by a chemical reaction. In the presence of sodium sulphate a sulphate-rich liquid is formed and, due to its low surface tension, it readily wets the surfaces of grains [1]. Šašek [2a] has experimentally proved that in the initial period the rate at which sulphate reacts with silica is lower than that of the carbonate (sodium sulphate reacts with silica below its decomposition temperature) and so the rate of sand dissolution decreases with increase of sodium sulphate concentration.

2. The transient stage. The silica-rich melt forms a concentration boundary layer around the grains, the thickness of which increases with time. This increase is limited by

a) free and forced macroscopic convection,

b) free buoyancy convection due to non-uniform density,

c) forced and free convection due to the effect of gas bubbles.

Convection ad c) is the most effective one. It can take place as a result of a number of different mechanisms:

i) Since a bubble attached to a sand grain is situated in a non-uniform concentration field, a non-uniform surface tension arises on its surface so that free surface convection can be induced. Grain dissolution can thus be intensively accelerated at the three phase boundary, similarly to the familiar case of upward drilling of a refractory brick. It is unlikely to apply this mechanism to silica sand for the glass surface tension depends only slightly on silica concentration.

ii) Provided that the concentration of the fining agent as well as temperature are sufficiently high the bubbles grow rapidly. Since the contact angle between a silica grain and the melt is small the bubbles break away easily from the grain surfaces and ascend upwards. Just after breaking away they spheroidize and, at the same time, the concentration of melt at their surfaces becomes uniform due to the effect of surface convection. As a consequence of these two effects the bubbles are driven abruptly away from the grains bringing about a turbulence in their boundary layers. The grain dissolution is thus intensively promoted. This behaviour of bubbles was directly observed by Němec [3]. A protective effect of the bubbles is also imaginable, however, when not increasing bubbles are attached to grains for a given period.

iii) The ascendent bubbles stir the grain-melt mixture thus limiting the boundary layer growth. The bubbles can either destroy the clusters of grains or, on the contrary, add to aglomerate the grains by preferring those paths through the melt at which the viscosity is lower. It seems probable that the latter effect operates at lower temperatures when the bubbles are formed by the decomposition of carbonates while the former one is due to the bubbles resulting from the refining. The flotation of grains by the attached bubbles has been often observed, too.

The shape of grains can change during dissolution. The initially irregular grains can be spheroidized by bubble-free dissolution owing to the fact that dissolution rate increases with increasing surface curvature. The bubbles, however, can produce a geometric instability of grains owing to surface convection or surface protection as explained.

3. The stationary stage. In this stage the effect of diffusion and convection on the dissolution rate are mutually balanced. The more intensive the convection the earlier it sets in. Naturally, the name "stationary" is justified only when the convection pattern does not change with time.

4. The stage of the disappearing of grains. At the very end of dissolution the diffusive resistance drops down to zero owing to the spherical symmetry of a grain [4]. The dissolution is then again governed by the surface reaction.

5. The stage of melt homogenization. After complete dissolution of all grains the melt refines for the bubbles can no longer be nucleated. The non-uniformity in the melt composition is gradually smoothed by diffusion as analyzed by Cooper [5]. <sup>\*</sup> It is interesting to note that the effect of bubbles can be very different — they can both accelerate and retard or even stop the dissolution of the sand grains. Which effect prevails depends on the melting conditions, particularly on the temperature. It is obvious that the dissolution process can become more complex when the temperature changes with time in an intricate way as in the case of glass-melting in both classical and electric tank furnaces.

The following section deals with the growth or dissolution of a grain material in a liquid in a more general way. It is only assumed that the grains are uniform in sizes and shapes and uniformly dispersed in the mixture. As the mechanism of the mass transfer in such a mixture can be very complicated or even unknown, the approach to the problem is not based on field equations of continua but rather on defining a mass transfer coefficient subject only to the requirement that it must be reduced to the rate constant of a chemical reaction or  $D/\delta$  (*D* is diffusion coefficient and  $\delta$  boundary layer thickness) in trivial cases. As a result of this section a differential equation is established which enables to calculate the grain size as a function of time, if the mass transfer coefficient as a function of time is known.

In the last two sections the mass transfer coefficient for the case of the sand dissolution in a melt is being discussed. In the first of them a relation correlating the results of crucible experiments is suggested. In the last section the batch-free time, e.i. the lifetime of sand grains is discussed regarding possibilities of accelerating the sand dissolution.

# KINETIC EQUATION FOR THE INTERACTION BETWEEN GRAINS , AND A LIQUID

Let us consider such a mixture of solid grains and a liquid where the grains of uniform sizes and shapes are uniformly distributed in space and soluble in the liquid, thus forming one of the liquid components (component A). If the liquid is oversaturated with A, the grains are increasing in size; in the opposite case the dissolution of the grains proceeds.

An effective radius r of a grain can be defined by

$$w_s = \frac{4}{3} \pi r^3 n \varrho_s, \tag{1}$$

where  $w_s$  is the mass fraction of solid in the mixture, n the number of grains in a unit mass of the mixture and  $\varrho_s$  the solid density. The rate of change of the solid concentration can be measured as the rate of change of r. It seems useful to define the mass transfer coefficient  $\alpha$  by the equation

$$d_t r = \alpha (w_m - w_e), \tag{2}$$

where  $w_m$  is the mean and  $w_e$  the saturated mass fraction of A in the liquid and  $d_t$  denotes the time derivative.  $w_m$  can be expressed from the mass balance of A

$$w_d = w_s + (1 - w_s) w_m, (3)$$

where  $w_d$  is the mass fraction of A in the mixture.

Denoting by  $w_0$  the mass fraction of solid in the mixture at time t = 0, it follows from (1) that

$$r = r_0 (w_s/w_0)^{1/3},$$
 (4)

where  $r_0$  is the effective grain radius at t = 0. Equation (4) rests upon the assumption that the number of grains is constant during the process.

The mass fraction  $w_f$  of the solid in the equilibrium mixture is given by the relation

$$w_f = (w_d - w_e)/(1 - w_e);$$
 (5)

indeed, if  $w_s = w_f$ , it follows from (3) and (5) that  $w_m = w_e$ . The corresponding effective grain radius is

$$r_f = r_0 (w_f / w_0)^{1/3}. (6)$$

According to the value of  $w_f$  the mixtures may be divided into the following classes:

- (i)  $w_f > w_0$ , the grains increase in sizes,
- (ii)  $w_f = w_0$ , the grains do not change, the mixture is at equilibrium.
- (iii)  $w_f < w_0$ , the grains decrease in sizes,
- (a)  $w_f \in (0, w_0)$ , the grains never disappear,
- (b)  $w_f = 0$ , the grains disappear and a saturated solution results,
- (c)  $w_f < 0$ , the grains diappear and the liquid remains unsaturated.

In clases (i)—(iiib) the process leads to a mixture of liquid saturated with A and solid of the mass fraction  $w_f$ . In class (iiic) it would be necessary to add the mass  $|w_f|$  of A to every unit mass of the mixture to saturate it.

Using (3) and (5) equation (2) can be rewritten

$$d_t r = \alpha (1 - w_e) (w_f - w_s) / (1 - w_s).$$
(7)

By (4) and (6) we have

$$d_t r = \alpha (w_d - w_e) (r_f^3 - r^3) / (r_f^3 - w_f r^3).$$
(8)

Introducing a substitution

$$\varphi = (1 - w_e)^{-1}(\hat{r}^{-2}/2w_0 + \hat{r})$$
 for  $r_f = 0$ , (9a)

$$\varphi = (r_f/r_0) \left(1 - w_e\right)^{-1} (\tilde{r} + (1/w_f - 1) \left(\frac{1}{6} \ln \left((1 - \tilde{r}^3)/(1 - \tilde{r})^3\right) + 3^{-1/2} \tan^{-1}(3^{-1/2}(2\tilde{r} + 1)))\right) \qquad \text{for } r_f \neq 0, \quad (9b)$$

where  $\hat{r} = r/r_0$  and  $\tilde{r} = r/r_f$ , equation (8) becomes

$$d_t \varphi = \alpha / r_0. \tag{10}$$

Substitutions (9a) and (9b) eliminate effects of changes of boundary surface, liquid volume and liquid composition on the rate of dissolution or crystalization. Coefficient  $\alpha$  describes only the effects of diffusion, convection, surface reaction, and the change of grain shapes during the process. A similar substitution was introduced by Hixson and Crowell [6] in 1931. Their analysis, however, was based on a different starting point, because they have considered the liquid volume as a constant.

Integration of (10) yields

$$\varphi(\hat{r}) - \varphi(1) = \int_{0}^{t} \alpha \, \mathrm{d}t / r_0 \tag{11a}$$

or

$$\varphi(\tilde{r}) - \varphi(r_0) = \int_0^t \alpha \, \mathrm{d}t / r_0.$$
 (11b)

For large t we can deduce from (11), (9) and (5) the approximations

$$r = kt^{-1/2}, \quad \text{for } r_f = 0,$$
 (12a)

$$r = r_f (1 \pm \exp\left(-bt\right)), \quad \text{for } r_f \neq 0, \tag{12b}$$

where  $k = r_0^{3/2} (2w_0(1 - w_e) \alpha_{\infty})^{-1/2}$ ,  $b = 3(\alpha_{\infty}/r_f) (w_d - w_e) (1 - w_e)/(1 - w_d)$ , and  $\alpha_{\infty} = \lim_{t \to \infty} \alpha_{\infty}$ .

In the mixtures of class (iiic) the solid is completely dissolved in a finite time  $t_f$ . Developing (9b) into a Taylor series in the neighbourhood of r = 0, we get

$$\varphi = \varphi(0) - (w_e - w_d)^{-1} r_0^{-1} \left( r + (1 - w_f) r_f \left( \frac{1}{4} \, \hat{r}^4 + \frac{1}{7} \, \tilde{r}^7 + \dots \right) \right) \tag{13}$$

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where

$$\varphi(0) = -(\pi/6 \sqrt{3}) (r_f/r_0) (1 - w_f)/(w_e - w_d).$$

If  $t_f - t = o(t_f)$ , then

$$r = \alpha (w_e - w_d) (t_f - t) + o(\tilde{r}^4). \tag{14}$$

For a constant  $\alpha$  equation (14) represents the model of a sphere shrinking with a constant rate. As seen from the last term it holds up to the relatively large values of  $\tilde{r}$ . For very small r, however,  $\alpha$  is not constant as will be discussed in the following sections. Relation (14) without its last term also results from the equation

$$d_t r = -\alpha (w_e - w_d), \tag{15}$$

which follows from (7) or (8) for  $w_s = o(1)$  or  $r = o(r_0)$ . If, moreover,  $w_0 = o(1)$ , (15) describes the whole dissolution process.

# THE ISOTHERMAL DISSOLUTION

It follows from above given reamarks that the sand dissolution during the glass melting is too complicated for exact analysis. On the other hand the semiempirical approach based on the mass transfer coefficient defined by equation (2) is relatively easy. The dissolution of grains is then described by a simple equation (11b). It does not suffice to determine the overall dissolution kinetics alone and it must be supplemented by a relation for  $\alpha$  appropriate to the given mixture. It is also possible to determine  $\alpha$  experimentally as a function of time and temperature. Typical plots of  $\psi = (\varphi(\tilde{r}) - \varphi(\tilde{r}_0)) r_0$  vs. t established by isothermal melting experiments [2] are shown in Fig. 1. According to (10) the mass transfer coefficient  $\alpha(t) = d_t \psi$  is equal to the slope of the curve correlating the experimental points. At t = 0, the mass transfer coefficient  $\alpha_0$  represents the rate of the surface reaction between a grain and the ambient melt. For t > 0 the total resistance  $\alpha^{-1}$  can be given as the sum of resistance due to surface reaction and that due to diffusion:

$$\alpha^{-1} = \alpha_c^{-1} + \alpha_d^{-1}. \tag{16}$$

The value of  $\alpha_d^{-1}$  gradually increases in the transient stage. This behaviour can be described by

$$\alpha_d^{-1} = \alpha_D^{-1}(1 - \exp\left(-\varkappa t\right)),\tag{17}$$

where  $\varkappa$  and  $\alpha_D$  are constants. In the stationary stage the slope of the curve in Fig. 1 is  $\alpha_f = (\alpha_0^{-1} + \alpha_D^{-1})^{-1}$ . The introduction of (16) and (17) into (11b) gives after integration

$$\psi = \alpha_f t + (\alpha_f/\varkappa) \ln (\alpha_0/\alpha_f - (\alpha_0/\alpha_f - 1) \exp (-\varkappa t)).$$
(18)

This equation correlates the experimental data using only three coefficients,  $\alpha_0$ ,  $\varkappa$ , and  $\alpha_f$ , each of them is related to one of the melting stages, i.e. initial, transient, and stationary, respectively. For a cursory estimation of these coefficients the following relations may be useful

$$\psi_0 = (\alpha_f/\varkappa) \ln (\alpha_0/\alpha_f), \tag{19}$$

$$\varkappa = t_1^{-1} \ln \left( 2 - \exp \left( - \varkappa \psi_0 / \alpha_f \right) \right), \tag{20}$$

where  $\psi_0$  and  $t_1$  are defined in Fig. 1.

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If segregation or aglomeration phenomena occur, the sand dissolution can be retarded or even suppresed as it is shown by curve 3 in Fig. 1. If no such phenomena take place,  $\alpha$  remains constant during the stationary stage until the grain size becomes comparable to the concentration boundary layer thickness,  $\delta$ . Then the final stage sets in and

$$\alpha_d^{-1} = \alpha_D^{-1} r / (r + \delta). \tag{21}$$

The substitution of (21) into (15) and integration leads to the equation

$$\mathbf{r} - (1 - \alpha_f/\alpha_0) \,\delta \ln \left(1 + r/\delta\right) = \alpha_f(w_e - w_d) \,(t_f - t), \tag{22}$$

which for  $r = o(r_0)$  is simplified to

$$r = \alpha_0 (w_e - w_d) (t_f - t). \tag{23}$$

By (13) we can see that  $d_t \psi |_{r=0} = \alpha_0$ , thus at its very end the dissolution is again controlled by the surface reaction.



Fig. 1. The time-dependence of  $\psi$  for isothermal crucible melting. In the final stage the dissolution rate of silica particles is accelerated due to the spherical effect as it is shown by curve 2. However, a retardation of dissolution is also possible under some circumstances—see curve 3. It can result from segregation or aglomeration of grains or from the lowering the convection efficiency (due to viscosity increase, bubbles disappearing etc.). Line 1 is an extrapolation from the stationary stage and does not correspond to any real situation.

Since the initial heating rate of a sample is limited by heat conduction (and also due to endothermal effect of chemical reactions), the initial dissolution rate of grains is controlled by heat supply into the mixture. An isothermal melting is, therefore, not possible at the very beginning of the process. For slightly nonisothermal melting, where the sequence of dissolution mechanisms remains unchanged, equation (18) can be generalized to

$$\psi = \int_{0}^{t} (\alpha_{f}(T)^{-1} + (\alpha_{f}(T)^{-1} - \alpha_{0}(T)^{-1}) \exp(-\kappa(T)t))^{-1} dt.$$
(24)

This equation rests upon the assumption that  $\alpha_0$ ,  $\alpha_f$ , and  $\varkappa$  are known functions of temperature which depends on time.

# THE LIFETIME OF GRAINS

When segregation or aglomeration does not take place, then, neglecting the acceleration of dissolution at very small r, the isothermal lifetime of grains can be expressed by (18) as

$$t_f = \kappa^{-1} \ln \left( 1 + (\alpha_f / \alpha_0) \left( \exp \left( \kappa \alpha_f^{-1} r_0 \omega \right) - 1 \right) \right), \tag{25}$$

where  $\omega = \varphi(0) - \varphi(\tilde{r}_0)$ . At glass melting temperatures  $\alpha_0 \gg \alpha_f$ . Further simplifications result for small and large  $r_0\omega$ . In the former case

$$t_f = \alpha_0^{-1} r_0 \omega, \tag{26}$$

which is equivalent the grains being completely dissolved in the initial stage by chemical reaction alone. In the latter case, by (19), we obtain

$$t_f = \alpha_f^{-1}(r_0\omega - \psi_0). \tag{27}$$

This represents the most frequent case, an illustration of which is shown in Fig. 1 (curve 1).

Assuming that  $\alpha$  does not depend on  $r_0$ , in both cases, the lifetime increases with  $r_0$  linearly. This assumption, however, can be violated in practise for the initial surface reactivity and the hydrodynamic interaction among grains, melt and bubbles (especially in the presence of refining agents) can be affected by the initial grain size.

Equation (27) is appropriate to show the effect of fining agents. Below its decomposition temperature a fining agent (particularly sulphate) can inhibit the surface reaction and so increase  $t_f$ . Above its decomposition temperature it enhances the diffusive mass transfer thus reducing  $t_f$ .

The quantity  $\omega$  depends only on the composition of the mixture and can be expressed using (9b), (14), (5) and (6) as

$$\omega = (1 - w_e)^{-1} \left( \left( (1 - w_d) / (w_e - w_d) \right) \mathcal{L}(W) - 1 \right), \tag{28}$$

where

$$\begin{aligned} \mathscr{L}(W) &= W^{-1/3} \left( \frac{1}{6} \ln \left( (1 + W^{1/3})^3 / (1 + W) \right) + 3^{-1/2} \pi \zeta \right. \\ &+ 3^{-1/2} \tan^{-1} \left( W^{1/3} \, 3^{1/2} \, (2 - W^{1/3})^{-1} \right) \right) \\ &= 1 - \frac{1}{4} \, W + \frac{1}{7} \, W^2 - \dots, \end{aligned}$$

$$\begin{aligned} W &= w_0 (1 - w_e) / (w_e - w_d), \\ \zeta &= \begin{cases} 1 \text{ for } W > 8, \\ 0 \text{ for } W < 8. \end{cases} \end{aligned}$$

$$(30)$$

Definitely, the inequality  $w_0 \leq w_d < w_e$  must be satisfied.

Holding  $w_d$  and  $w_e$  constant,  $\omega$  depends only on  $w_0$  as a variable. It can be seen from (28) that  $\omega$  increases as  $w_0$  decreases and at  $w_0 = 0$  reaches its maximum value  $\omega_{\max} = (w_e - w_d)^{-1}$ . This means that, for  $w_e$  and  $w_d$  given, the lifetime of grains increases as the portion of SiO<sub>2</sub> introduced by sand decreases. The lifetime is shortest when the entire content of silica is introduced only by sand and longest for an isolated grain in a melt of ultimate composition.

It is usual that the entire amount of  $SiO_2$  is introduced into the glass only by sand. In such a case  $w_0 = w_d$  and

$$\omega = w_e^{-1} (1 - w_e)^{-1} \mathcal{H}(W) - w_e), \tag{28a}$$

where  $\mathscr{K}(W) = (1 + W) \mathscr{L}(W)$ . In this case, holding  $w_e$  constant,  $\omega$ , and consequently  $t_f$ , increases to infinity as the difference  $w_e - w_d$  is nearing zero. The functions  $\mathscr{L}(W)$  and  $\mathscr{K}(W)$  are plotted in Fig. 2.

The value of  $w_e - w_d$  is very sensitive to the batch homogeneity. If the density of grains increases in some place, an increase of  $w_d$ ,  $\omega$  and  $t_f$  results in the same place. When in some place  $w_d$  reaches or even exceeds  $w_e$ , the mixture passes from class (iiic) into (iiib) or (iiia) in which the grains cannot be dissolved at any finite time. The situation can be improved by the increase of temperature, for  $w_e$  and  $\alpha$  increase.



Fig. 2. Plot of the functions  $\mathscr{L}(W)$  defined by (29) and  $\mathscr{K}(W) = (1 + W) \mathscr{L}(W)$ .

What happens when the sand contains grains of different sizes? Let N be the number of classes containing identical grains. If  $\alpha$  is independent of  $r_0$ , equation (7) remains valid with  $w_s = \sum w_{st}$ , where  $w_{si}$  is the mass fraction of class *i* relative to the mixture. We can see from this equation that until some grains do not disappear, the rate of dissolution is the same for each class. If the small grains do not begin to disappear before reaching the stationary stage, then, by (15), the dissolution rate does not depend any longer on  $w_s$  which means that the grains dissolve independently of each other. The lifetime of the large grains is thus not affected by the presence of the small ones and the batch-free time is the same as if it would contain only the largest grains. When very fine grains which can be dissolved even in the initial period (see equation (26)) are present, the remaining grains are then dissolved in a melt containing already a part of the entire amount of SiO<sub>2</sub> and, as it has been explained above, their lifetime increases to a certain extent. The influence of the melt composition on transport properties (diffusion coefficient and viscosity) should also be taken into account.

In summary, the lifetime of sand grains can be reduced by

- a) adding fining agents,
- b) raising temperature,
- c) increasing batch homogeneity,
- d) removing the largest and the smallest grains.

#### Acknowledgements

The author would like to thank Dr. J. Beneš, Professor A. R. Cooper, Professor J. Hlaváč, Dr. L. Němec, and Professor L. Šašek for helpful contribution.

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# KINETICKÁ ROVNICE PRO INTERAKCI MEZI ZRNITÝM MATERIÁLEM A KAPALINOU S APLIKACÍ NA TAVENÍ SKLA

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V článku jsou diskutovány děje, které se podílejí na řízení rozpouštění pískových zrn při tavení skla. Pozornost je věnována vlivu čeřiv (speciálně síranu sodného), bublin a různých typů proudění skloviny (nucené proudění, volné proudění, povrchové proudění v okolí bublin přichycených k zrnům). Byla odvozena rovnice (10), která popisuje obecný děj rozpouštění nebo růstu zrn rovnoměrně rozptýlených v kapalině:  $\varphi$  je proměnná definovaná rovnicemí (4), (5), (6) a (9),  $w_{s}(t)$  je hmotnostní podíl zrn (např. písku) ve směsi v čase  $t, w_{0} = w_{s}(0)$  je počáteční hmotnostní podíl zrn ve směsi,  $w_a$  je hmotnostní podíl složky odpovídající materiálu zrn (např. SiO<sub>2</sub>) ve směsi a  $w_e$  je rovnovážný hmotnostní podíl této složky v kapalině. Je li známa závislost koeficientu přestupu hmotnosti  $\alpha$  na čase, lze integrací rovnice (10) vypočítat průběh rozpouštění. Jsou-lí  $\hat{\mathbf{k}}$  dispozici experimentální data o průběhu rozpouštění, lze z nich pomocí (10) určit lpha jako funkcí času. Aproximační funkce  $\alpha(t)$  pro rozpouštění písku při tavení skla je vyjádřena rovnicemí (16) a (17), kde  $\alpha_0$ ,  $\alpha_D$  a  $\varkappa$  jsou koeficienty závislé na teplotě a složení skloviny;  $\alpha_0$  odpovídá rychlostnímu koeficientu povrchové chemické reakce,  $\alpha_D$  podílu  $D/\delta$  (D je difúzní koeficient a  $\delta$  tloušťka koncentrační vrstvy) a z charakterizuje rychlost přechodu z reakčního na difúzní režim. Kinetickou rovnici pro rozpouštění písku lze potom psát ve tvaru (24) nebo pro izotermní podmínky

ve tvaru (18). Technologicky důležitou veličinou je celková doba rozpouštění pískových zrn. Lze jí počítat ze vztahu (27) (pro izotermní situací), v němž  $\alpha_f$  a  $\psi_0$  jsou definovány na obr. 1 a  $\omega$  je definováno vztahy (28) až (30). Závěrem je diskutován vliv různých faktorů na dobu rozpouštění. Lze ji zkrátit vyšším přídavkem čeřiv, zvýšením teploty, zvýšením homogenity vsázky a odstraněním největších a nejmenších zrn písku.

Obr. 1. Závislost w na čase pro izotermické tavení v kelímku. V konečném období se rozpouštění křemenných zrn urychlí následkem sférického efektu (křivka 2). Segregace a aglomerace zrn nebo snížení intenzity proudění (zvýšením viskozity, vymizením bublin apod.) mohou naopak zpomalit rozpouštění (křivka 3). Přímka 1 je extrapolací z období ustáleného rozpouštění a neodpovídá skutečné situaci.

Obr. 2. Graf funkce  $\mathscr{L}(W)$  definované vztahem (29) a  $\mathscr{K}(W) = (1 + W) \mathscr{L}(W)$ .

# КИНЕТИЧЕСКОЕ УРАВНЕНИЕ ДЛЯ ВЗАИМОДЕЙСТВИЯ МЕЖДУ ЗЕРНИСТЫМ МАТЕРИАЛОМ И ЖИДКОСТЬЮ С ПРИМЕНЕНИЕМ ДЛЯ ВАРКИ СТЕКЛА

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В предлагаемой работе рассматриваются процессы, принимающие участие на управлении растворением песочных зерен при варке стекла. Особое внипание уделяется влиянию осветлителей (именно сульфату натрия), пузырков и разных типов протока стекломассы (вынужденное течение, свободное течение, поверхностное течение в близости пузырков, прилипшихся к зернам). Было выведено уравнение (10), которое описывает общий процесс растворения или роста зерен, равномерно распределенных в жидкости, где  $\varphi$  — переменная, определяемая уравнениями (4), (5), (6) и (9),  $w_s(t)$  — доля веса зерен (напр. песка) в смеси во времени  $t, w_0 = w_s(0)$  — исходная доля зерен в смеси, wa — доля веса компонента, отвечающая материалу зерен (напр. SiO<sub>2</sub>) в смеси и we равновесная доля веса этого компонента в жидкости. Если известна зависимость коэффициента массопередачи « от времени, то интеграцией уравнения (10) можно расчитать ход растворения. Располагая экспериментальными данными относительно хода растворения, можно на их основании и с помощью (10) определять а как функцию времени. Функция аппроксимации а (t) для растворения песка при варке стекла выражается уравненияпи (16) и (17), где «о, «о и « — коэффициенты, зависимые от температуры и состава стекломассы; «о отвечает коэффициенту скорости химической реакции на поверхности,  $\alpha_D$  доле D/ $\delta$  (D — коэффициент диффузии и  $\delta$  — толщина концентрационного слоя) и « характеризует скорость перехода от режима реакции к режиму диффузии. В таком случае кинетическое уравнение можно записать в виде (24) или для изотермических условий в виде (18). С технологической точки зрения важной величиной является общее время растворения песочных зерен. Можно его определить на основании отнотения (27) (для изотермического гоположения), в котороп ат и уо определяются на рис. 1 и со определяется отношениями (28)-(30). В заключение рассматривается влияние разных факторов на время растворения. Его можно уменьшить большей добавкой осветлителей, повышением температуры, повышением гомогенности шихты и устранением наибольших и наименьших зерен песка.

Рис. 1. Зависимость у от времени для изотермической варки в тигле. В окончательной фазе растворение кварцевых зерен ускоряется в результате сферического эффекта (кривая 2). Сегрегация и агломерация верен или понижение интенсивности течения (повышением вязкости, удалением пузырков и т. д.) могут наоборот замедлить растворение (кривая 3). Прямая 1 является экстраполяцией, относящейся к времени постоянного растворения и не отвечает действительному положению.

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Рис. 2. График функции  $\mathscr{L}$  (W), определяемой отношением (29) и  $\mathscr{K}$  (W) = (1 + W)  $\mathscr{L}$  (W).