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Overheating of the Cryolite–Alumina Melt Caused by a Change in Its Velocity

A. A. Vlasov*, R. Yu. Feshchenko, V. Yu. Bazhin, V. M. Sizyakov, and M. A. Nevskaya
*National Mineral Resources University (Mining University), Vasilievskii Ostrov,
21st Line 2, Saint Petersburg, 199106 Russia*
**e-mail: wlasow87@mail.ru*

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Abstract—The influence of the melt velocity in commercial electrolysis cells on the overheating is discussed

Keywords: electrolyte overheating, cryolite-alumina melt, electrolysis, flowing rate of melt
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INTRODUCTION

Haupin, Solheim, Moxnes and other researchers consider the operation of commercial electrolysis cells at a negative overheating of an electrolyte, which is known as the "liquidus enigma." Numerous variants of its explanation have been proposed, and none of them has been commonly approved.

Practical experience of implementation of high-power electrolysis cells with prebaked anodes reveals that their efficient operation is possible upon constant control of scheduled parameters, such as the electric current, the anode to cathode distance, the heights of metal and electrolyte, the cryolite ratio, the alumina concentration, and the melt temperature. The implementation of such operation sequence is impossible without automated control systems, and their algorithms should be based on the modern concepts of heat and mass transfer and the dissolution of alumina [1].

High-current electrolysis is based on a set of engineering solutions, one of which is the application of acid modified electrolytes, enabling technological process at low temperatures (940—955°C) [2–4]. Thus, the solution of the "liquidus enigma" becomes a challenging problem for the implementation of high-power electrolysis.

THEORETICAL

Several hypotheses were proposed in [5] concerning the detection of the liquidus point in the electrolytes of commercial electrolysis cells and, hence, their overheating; one of the hypotheses is the influence of the electrolyte velocity.

Let us consider the essence of convective mass transfer and its influence on solidification. Convective mass transfer is described by a set of Navier–Stokes equations, flow continuity, and a convective diffusion equation (Fick's second law) [6]. The mechanism of convective diffusion consists in mass transfer in the form of small amounts of solution, including molecular diffusion inside these small amounts. The rate of convective diffusion increases with the interface surface area, the difference in the concentrations, and the process duration according to the following equation:

$$S = K \cdot F \cdot (C - c) \cdot \tau, \tag{1}$$

where K is the coefficient of convective diffusion, i.e., the mass transferred in 1 s through 1 m^2 at the difference of the concentrations of 1 kg/m^3; S is the mass transferred from the liquid phase into the moving flow, kg; F is the interface area, m^2; $C - c$ is the difference in the concentrations of the substance transferring into the flow near the interface (C) and at the center of the moving flow (c), kg/m^3; and τ is the time, s.

It follows from Eq. (1) that the mass transferring from one phase into another per unit time is proportional to the coefficient of mass transfer, the interface area, the process duration, and the difference of the concentrations. The interrelation between the coefficient of mass transfer and the coefficients of all types of diffusion is as follows:

$$K = \frac{1}{\dfrac{2r}{n \cdot D_{\text{int}}} + \dfrac{\delta}{D} + \dfrac{1}{\beta}}, \tag{2}$$

where $2r$ is the solidification center thickness, n is a coefficient, D_{int} is the coefficient of internal diffusion, D is the coefficient of molecular diffusion, δ is the thickness of the diffusion boundary layer, and β is the coefficient of convective diffusion.

It follows from Eq. (2) that, upon convective diffusion, the size of diffusing substance molecules, the melt viscosity, and the kinetic energy of the molecules

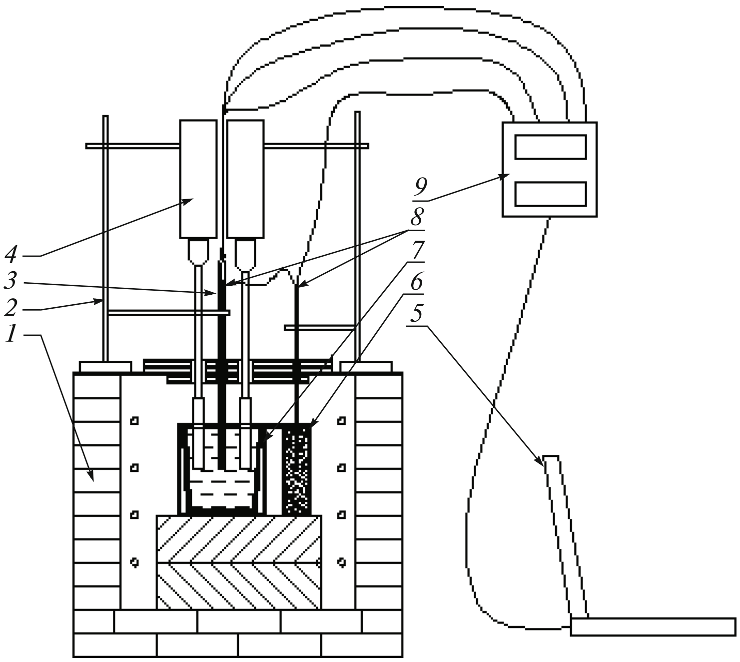

Fig. 1. Experimental facility: (*1*) shaft resistance furnace, (*2*) support with holders, (*3*) chromel–alumel thermocouple, (*4*) overhead stirrer with silicon carbide impeller, (*5*) PC, (*6*) calcined alumina, (*7*) melt, (*8*) differential thermocouple, and (*9*) TRM-200 multichannel thermometer.

are of minor importance. The main factor for the convective mass transfer rate is comprised of hydrodynamic conditions, that is, the velocity and the motion mode of the liquid phase. Therefore, the molecular and convective mass transfers differ from each other not only in mechanism but also in the fact that their rates depend on groups of factors. In general, the rate of convective transfer is higher than that of molecular transfer by many times.

Without convection, the coefficient of convective diffusion is zero and the thickness of diffusion layer equals to the surface area of all solidification centers. Herewith, the coefficient of mass transfer is only identified by internal diffusion and free molecular diffusion in stationary liquid. Such a phenomenon is observed upon electrolyte solidification without mixing, and the phase transition in this case occurs at the minimum rate.

When a center of solidification moves even at an insignificant velocity, the coefficient of mass transfer is determined by qualitative characteristics of all three stages of a diffusion path. The electrolyte overheating in this case is lower, since the layer of stationary liquid decreases and convective currents promoting mass transfer appear. In this case, the coefficient of convective diffusion increases to infinity, and the thickness of diffusion layer becomes zero.

A similar phenomenon can be attributed to the nature of solidification and mass transfer. Solidification is comprised of two elementary stages: (1) nucleation of solidification centers (NS); (2) crystal growth from these centers (GS). The energy state of a system with a large amount of particles involved in thermal motion is characterized by free energy (F). The higher the free energy of the system, the less stable the system; if possible, system transforms into a state with the minimum free energy. When temperature changes, the free energy of the system changes according to different laws for the liquid and solid states.

With increase in ΔT, the difference in the free energies $\Delta F = F_l - F_s$ increases; at a high activity, NS and GS increase and reach maximum. The subsequent decrease in NS and GS is attributed to a decrease in the mobility of molecules when temperature decreases. At a strong overcooling, NS and GS are zero, the liquid is not solidified and an amorphous substance forms.

Therefore, upon an increase in the mixing rate (convective mass transfer) of the cryolite–alumina melt GS increases and the electrolyte overheating decreases.

EXPERIMENTAL

The influence of the cryolite–alumina melt (2.28 cryolite, 5.5% CaF_2, 1.5% MgF, 2% Al_2O_3) velocity on the solidification kinetics was studied by means of differential thermal analysis (DTA) [7].

The facility for studying the liquidus point (Fig. 1) is comprised of shaft resistance furnace *1*, where carbon crucible *7* with a considered melt (2 kg) and corundum crucible *6* with reference calcined alumina are placed. Both crucibles are covered with a common

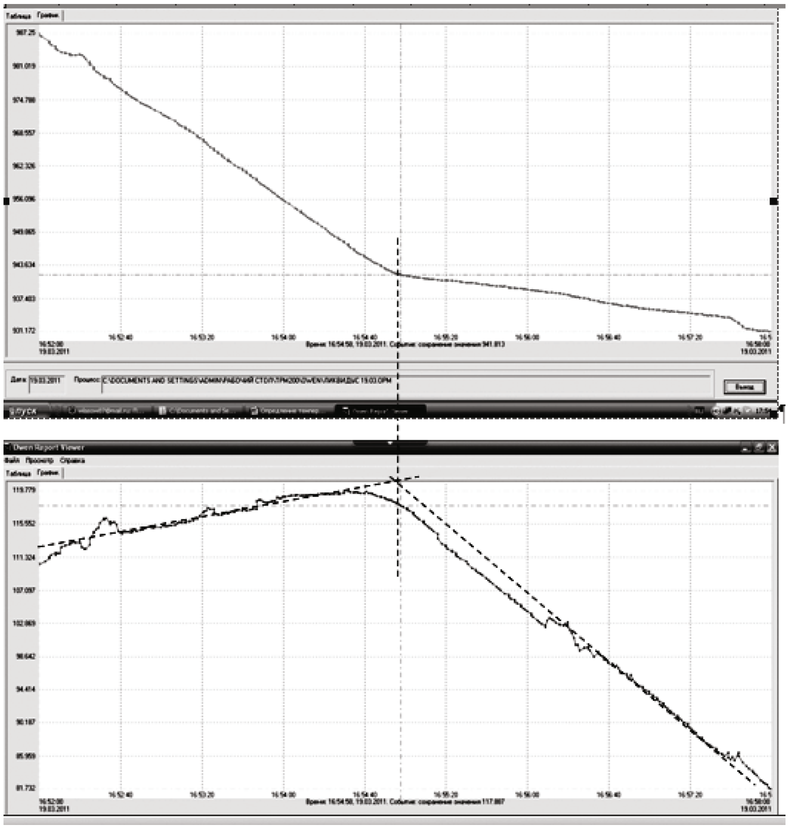

Fig. 2. Thermogram of the cryolite alumina melt at velocity of 58 cm/s.

carbon cap. The melt dynamics is simulated by two overhead stirrers *4* with silicon carbide impellers. The melt temperature was measured using a chromel–alumel thermocouple *3* located in a stainless steel casing and immersed into the melt. Differential thermocouple junctions *8* were positioned at equal depth in the considered sample and in reference alumina preliminary calcined at 1250°C. The thermocouples and stirrers were fixed to stands *2*. Thermocouples *3* and *8* were connected to a TRM-200 multichannel thermometer, which communicates with PC *5* for data recording.

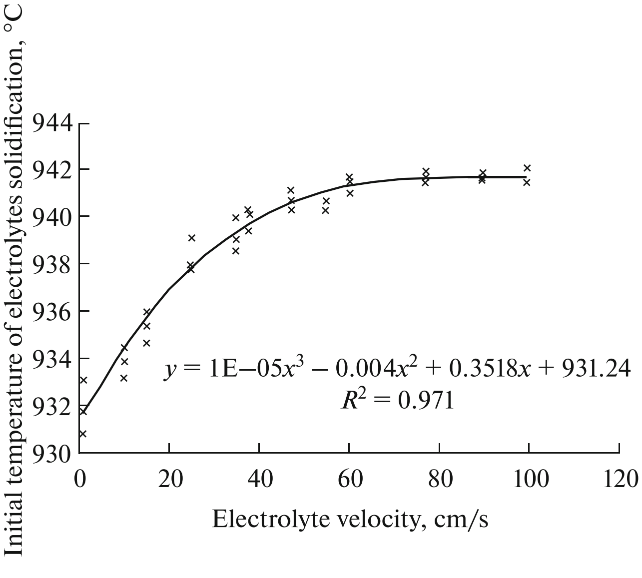

Fig. 3. Initial temperature of electrolyte solidification vs. the electrolyte velocity.

DTA curves were recorded upon heating and cooling at a temperature variation rate of 3–5 K/min. The frequency of thermocouple data recording on PC memory was 60 measurements per minute. The obtained data were used for plotting heating and cooling curves for normal and differential thermocouples and subsequent determination of the liquidus point (Fig. 2).

The electrolyte liquidus points upon variation of the electrolyte velocity are illustrated in Fig. 3. In fact, this is not about the variation of liquidus point but the variation of phase transition rate, which leads to a change in the measured electrolyte overheating.

It can be seen in Fig. 3 that the phase transition rate of cryolite alumina melt increases linearly up to 30–40 cm/s with its velocity. The subsequent increase in the electrolyte velocity does not lead to such a sharp increase in the solidification rate and does not influence it at velocities higher than 75–85 cm/s.

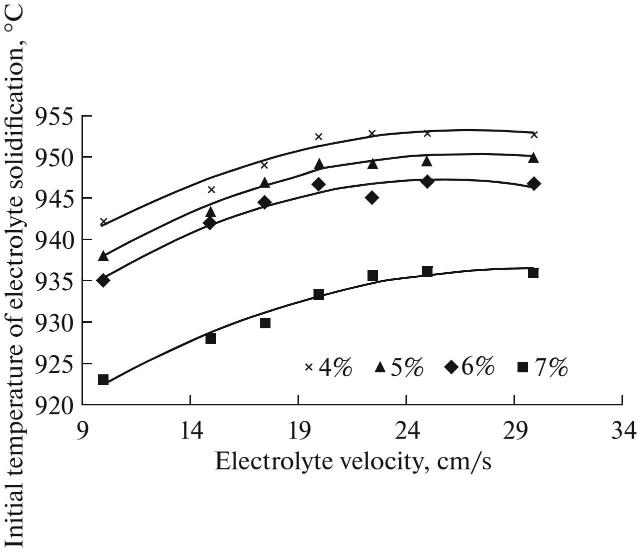

Fig. 4. Initial temperature of electrolyte solidification vs. the electroyte velocity when the CaF_2 content changes from 4 to 7 wt %.

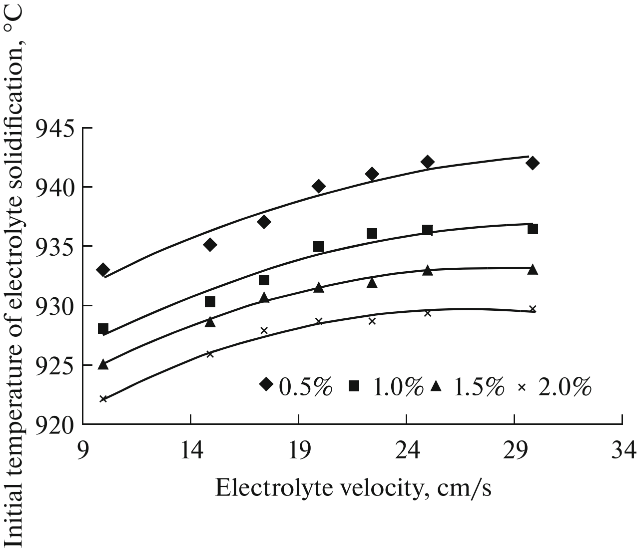

Fig. 5. Initial temperature of electrolyte solidification vs. the electrolyte velocity when the LiF content changes from 0.5 to 2 wt %.

The inflection point in the curve in the vicinity of 40–60 cm/s is attributed to mutual collisions of growing electrolyte crystals, which prevents their growth (Fig. 3). Crystal growth is also hindered by the fact that the amount of liquid where new nuclei form decreases due to the impingement and coalescence of crystals.

Figures 4 and 5 illustrate the experimental curves of liquidus point as a function of the electrolyte velocity at various contents of fluoride additives (Fig. 4, CaF_2; Fig. 5, LiF). These dependences agree with Fig. 3 and the data on the influence of the concentrations of various fluorides on the electrolyte liquidus point [8].

CONCLUSIONS

It follows from the experimental data that the electrolyte phase transition rate increases by 9–11°C when the melt velocity increases from 0 to 100 cm/s. Under high-power electrolysis, at the maximum electrolyte velocity of 24 cm/s [7], the melt overheating decreases by 5–6°C. Thus, when the electrolyte velocity increases, the conditions of alumina dissolution become more critical and promote a change in the optimum profile of the working space and the formation of cryolite–alumina cakes on the bottom.

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