

## ON CONE FORMATION ON BURNT ANODE FACE IN ALUMINUM ELECTROLYZERS

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UDC 669.711

*The causes of cone formation on the face of carbon anodes in aluminum electrolyzers are examined. The mechanism of cone formation has not been studied well enough to reduce the coning frequency in practice. In addition, many scientists and experts believe that work on the development and implementation of measures for the prevention of cones is economically inefficient. Data on two fundamental mechanisms of cone formation have now been published: carbon reduction on the anode face and individual sections of the anode falling behind in oxidation. Electrolytic reduction can be secured by bringing carbon to the surface of the anode. As a result of the appearance electrophoresis, carbon particles can move in the direction of one of the electrodes, increasing or decreasing the carbon flux.*

**Keywords:** *electrolysis, production of aluminum, anode, cone, electrophoresis, carbon.*

In the practice of primary aluminum production, various technological disruptions often occur immediately after a new anode is installed in the electrolyzer. Some key disruptions are associated with changes in the profile of the anode face. In [1], these disruptions are conventionally divided into three types:

*typical cone* – a protrusion, cylindrical or conical at its base, on the anode face;

*lagging* – square-shaped protrusions on the working surface of the anode or irregularity occupying 50–60% of the area of the anode; and

*overheating* –irregularly shaped damage (ball, mushroom, etc.) formed directly on any side of the anode block.

A cone is a carbon body with a distinct core (denser central part) and a more porous, soft carbon casing (Fig. 1). As a result of cone formation on an anode face, the operation of the bath becomes unbalanced and the following technical and economic performance indices of the process degrade:

- 1) increase of the horizontal currents as a result of which the magnetohydrodynamic (MHD) balance is lost;
- 2) shorting of the anode and cathode as a result of which the current yield decreases and the specific electricity consumption increases; and
- 3) temperature increase near the cone as a result of which the losses of fluoride salts increase and the current yield decreases, and so on.

The coning mechanism has not been studied well enough to decrease the coning frequency in practice. Many foreign scientists still believe the development and implementation of measures for preventing coning to be economically inefficient and propose the use of anodes on which a cone developed in the course of electrolysis.

Two basic causes of coning stand out:

- 1) high carbon foam (CF) content in the electrolyte;
- 2) defects of the anode.

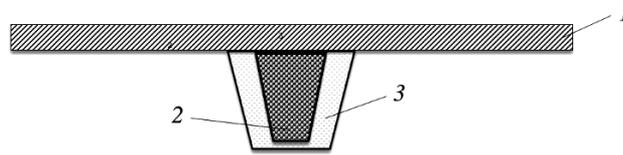


Fig. 1. Structure of a carbon cone on the anode face: 1) surface layer of anode; 2) core of the cone; 3) casing of the cone.

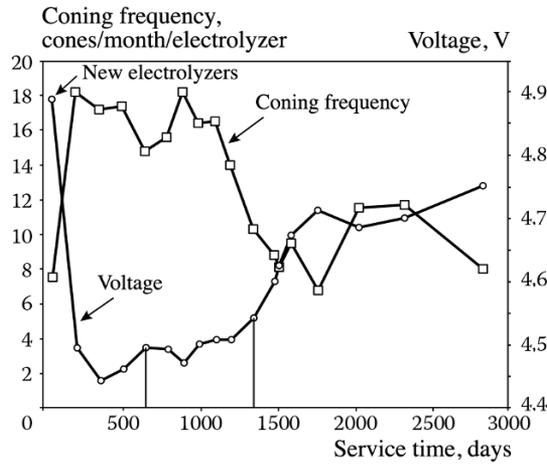


Fig. 2. Correlations between the coning, service time, and voltage on the electrolyzer.

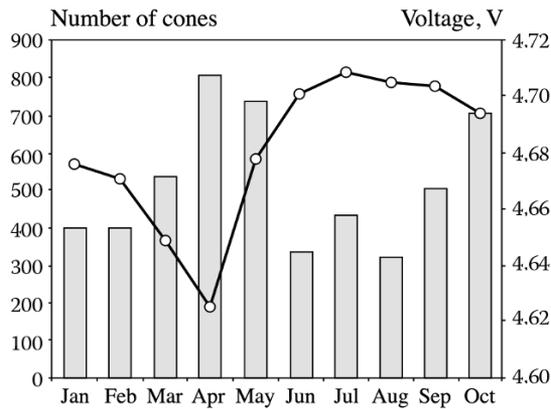


Fig. 3. Coning frequency in a series (one month) versus the voltage on the bath [4].

The presence of cracks, air cavities, foreign inclusions, and other defects altering the electrical resistance of the anode disrupts the current distribution. As a result, higher-resistance sections of the anode are less actively consumed, which results in the appearance of a cone.

The impact of CF on the coning frequency was observed in industrial baths (Fig. 2). The influence of different factors on the coning frequency was analyzed in [2, 3], from which it follows that this index increases significantly after a series of

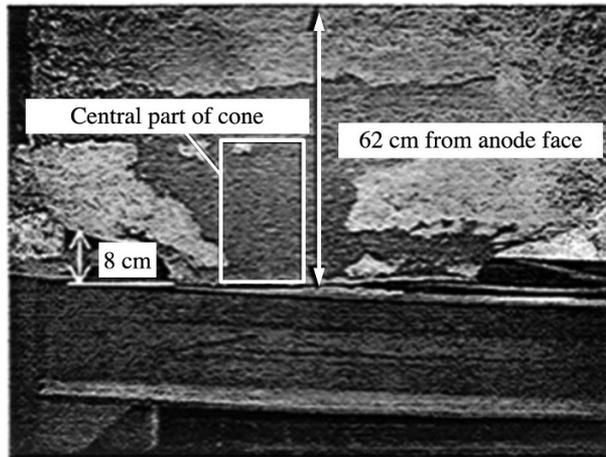


Fig. 4. Frustum of a cone formed on the anode face after four days of operation [4].

electrolyzers were switched from wet to dry gas purification (which increases the amount of CF). The increase in the number of cones resulted in a reduction of the current output on average by 1.6%.

After the old anode is removed, CF starts to form on the surface of the electrolyte [4], forming a layer up to 50 mm thick, which can form a crust even before a new anode is installed, since 20% more heat is lost with radiation than from a clean surface of the electrolyte. The installation of a cold anode leads to the formation of a solid layer of electrolyte up to 40–55 mm thick on part of the surface of the anode face.

Rolofs and Wai-Poi [2] give a relation between the amount of CF in the electrolyte, the service time of the electrolyzer, the interpole distance (IPD), and the coning frequency in industrial electrolyzers (Figs. 3 and 4): cones appear more frequently in baths with short service time (startup) operating with approximately 200 mV lower voltage.

In [4], the foaming of the electrolyte was evaluated visually on the basis of observations of the condition of the surface (pockets). Three categories of foam formation were identified:

- 1) no visible foam in the opening – foam index 1;
- 2) some visible foam, which can be removed in one pass – foam index 2;
- 3) foam amount greater than can be removed in one pass – foam index 3.

The coning frequency increases with the amount of CF, and more noticeably if the amount of foam corresponds to the indices 2 and 3. To prevent sharp growth of the coning frequency, the process parameters must be adjusted: increase IPD, decrease the anode installation time, and in especially extreme cases reduce the current strength.

These results indirectly attest an appreciable effect from the carbon present in the electrolyte on the cone formation and growth. The mechanism responsible for the motion of carbon particles can be of hydrodynamic and/or electrophysical in nature. Carbon transport under the expelling force of the melt occurs, but it does not secure the particles on the anode face. Probably, the transport of matter by the electrophysical phenomenon of electrophoresis is of great significance in the process leading to the formation and growth of cones on anodes.

*Electrophoresis* is an electrostatic phenomenon where particles of matter move in liquid or gaseous media under the action of an electric field (Fig. 5) [5]. Electrophoresis arises under the action of an electric field on an electric double layer (EDL): a solid particle is set in motion relative to the electrolyte. A planar EDL is the condition for the analysis of electrophoresis by Smoluchowski [6], where the speed of electrophoresis is defined as

$$U_{ef} = -\frac{\varepsilon\varphi}{4\pi\eta}E, \quad (1)$$

where  $U_{ef}$  is the speed of electrophoresis,  $\mu\text{m}/\text{sec}$ ;  $\varepsilon$  is the permittivity;  $\varphi$  is the potential of the glide plane, V;  $\eta$  is the coefficient of dynamic viscosity of the electrolyte; and  $E$  is the electric field strength, V/m.

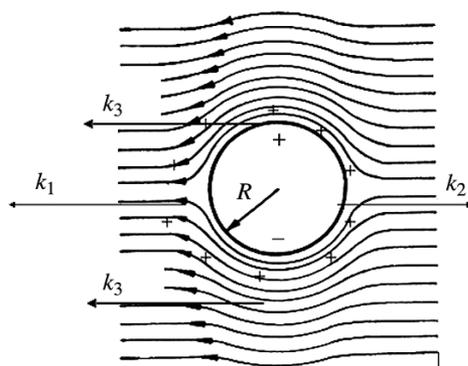


Fig. 5. Motion of a spherical particle in an electric field ( $k_1, k_2, k_3$  are the vectors of the forces action on the particle) [7].

To a first approximation, the speed of electrophoretic motion  $U_{ef}$  is independent of the particle size in a wide range and for spherical particles [7]

$$U_{ef} = 2/3 \frac{eER}{3\eta}, \quad (2)$$

where  $e$  is the surface density of the charge,  $C/m^2$ , and  $R$  is the radius of the particle,  $\mu m$ .

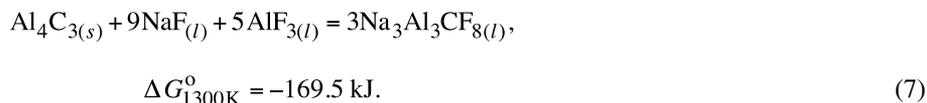
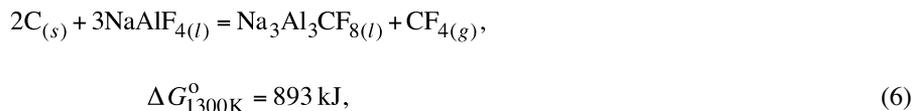
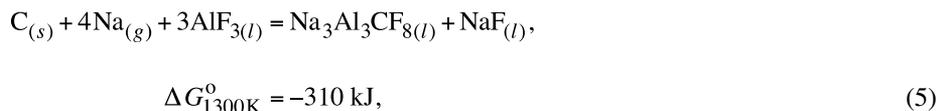
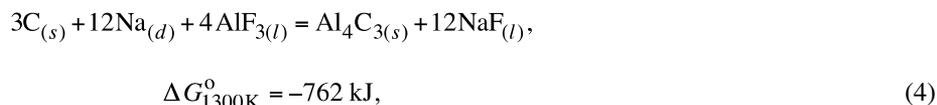
For particles that are large compared with the thickness of the diffusion part of the EDL, the basic hydrodynamic equation can be written assuming, as in the classical theory, that electrophoresis is the inverse of electroosmosis [7]. Therefore, the rate of electrophoresis can be determined from the relation

$$U_{ef} = eE\delta / \eta. \quad (3)$$

*Behavior of the components of the electrolyte in aluminum production.* The anodic process is interactive [8], i.e., multiphase (more than two phases). The influence of carbon and aluminum carbide, present in the electrolyte, on the electrolyzer indices is discussed in [9, 10].

It is established in [10] that the content range of disperse carbon in the electrolyte of the RA-300 bath is 0.1–12.5 wt.%, and ~90% of these values fall into the range 0–5 wt.%. The aluminum carbide content in RA-300 electrolyzers fluctuates from 0.01 to 0.79 wt.%, of which more than 90% are in the range 0.01–0.25 wt.% (Fig. 6 and 7).

It is shown in [11] that at temperatures close to that of electrolysis, carbon and aluminum carbide dissolve in cryolite and cryolite-alumina melts to content 0.7–2.2 wt.% via the reactions ( $\Delta G_{1300K}^0$  is the change in the Gibbs energy)



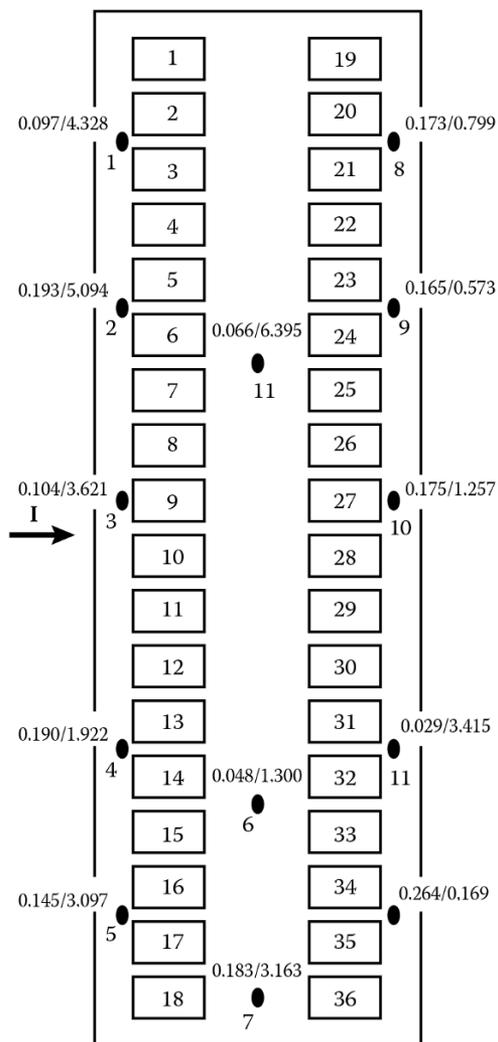


Fig. 6. Typical aluminum carbide concentration distribution in wt.% / carbon concentration in wt.% in the electrolyzer with current strength 300 kA.

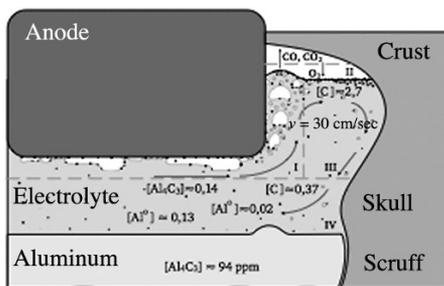


Fig. 7. Carbon and aluminum carbide distribution (wt.%) in the electrolyte.

The aluminum carbide formed in the reaction (4) can enter into reaction with the components of the electrolyte with formation of the compound  $\text{Na}_3\text{Al}_3\text{CF}_8$ , which can be regarded as the final product of the dissolution of carbon and aluminum

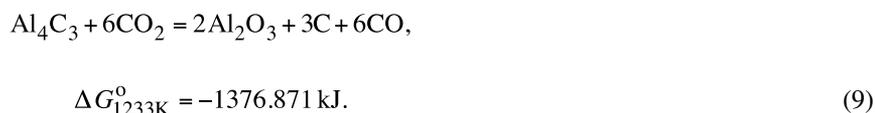
carbide in the electrolyte. The compound  $\text{Na}_3\text{Al}_3\text{CF}_8$  can dissociate in the melt into the ions  $\text{Na}^+$  and  $\text{Al}_3\text{CF}_8^{3-}$ . The degree of oxidation of the carbon in the anion equals 4, so that it can oxidize on the anode with elemental carbon being formed. According to [12], the oxidation reaction has the form



and the carbon obtained forms a solid precipitate on the anode.

The experimental results on the precipitation of carbon suggested that in industrial electrolysis this process can be responsible for the formation of cones, but provided that the maximum current density for the precipitation of carbon is greater than the partial current density for the release of  $\text{CO}_2$  (otherwise the carbon released will burn up, just like an anode block). This situation can occur if a very small current passes through a portion of the anode face as a result of its being screened by the carbon foam, or a low concentration of alumina is present at this location – then the carbon precipitate can grow in a pure form and a cone can form. Since the maximum current density (reaction 8) is all the higher, the higher the concentration of the dissolved carbon, on the basis of the solubility data for aluminum carbide [12], the number of cones can be expected to increase with decreasing cryolite ratio (CR), temperature, and  $\text{Al}_2\text{O}_3$  and  $\text{CaF}_2$  concentrations.

The concentration of aluminum carbide in the electrolyte near the anode decreases as a result of its oxidation by the released gas via the reaction [13]



Analysis of the carbon distribution in the electrolyte showed that the hydrodynamic characteristics of the bath have a significant effect on it, while the composition and temperature of the electrolyte have no appreciable effect. The average content of the foam in the current entry side of the RA-300 electrolyzers is higher than on the exit side. Aluminum carbide is distributed uniformly in the electrolyte. The bulk of the aluminum carbide is in dissolved form.

**Conclusions.** The electrophoretic nature of the motion of the dispersed particles in an aluminum electrolyzer has been little studied. However, considering the high electric currents and the electromagnetic fields formed it is evident that electrophoresis plays an important role in the formation of material fluxed in the bath and it can also lead to the formation of nonuniformities on the anode face and the growth of cones.

This article is based on work performed in the course of the project 02.G25.31.0181 “Development of superpowered, energy-efficient technology for producing aluminum RA-550” as part of the program of complex projects on the development of high-tech production, approved by Decree No. 218 of the Russian Government, April 9, 2010.

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