The emission of PAHs from self-baking anodes in aluminum production

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Abstract. The sources of PAH emission from the Soderberg anode surface of aluminum electrolysis cells are analyzed and measures for their minimization due to evaporative cooling of the anode to temperature 100 °C are offered.

1. Introduction

In the aluminum industry, the main source of emission of resinous substances containing various PAHs is coal tar pitch, used as a binder in the production of anode mass, from which the Soderberg anode is formed. Coal pitch used in the production of anodic paste (GOST 10200-83) contains 53-62% of volatile substances that are a complex mixture of organic compounds, a significant proportion of which are PACs.

The US regulatory authorities identified 129 the most dangerous compounds [1], and 16 of them are the most toxic affecting the chromosome apparatus of the cell, as well as their genotoxicity index. There are several ways to determine the toxicity of PAHs, but in most methods the toxicity of a particular type of PAH is compared to the toxicity of benzo(a)pyrene (BaP), the value of which is assumed to be unity [1].

Because of the extremely low concentrations of PAHs in the ambient air, unique analytical equipment is required to determine the content of each PAH, which domestic aluminum plants do not have. Therefore, regular monitoring of these emissions is not carried out, and periodic monitoring is limited to sporadic measurements of the total amount of PAHs in the atmosphere that is performed out by specialized organizations.

A considerable part of the resinous compounds is released through the aeration lanterns of the electrolysis cells bodies and enters the surrounding environment without purification and, despite the low concentration of PAHs in the lantern emission, their contribution to the total emissions is dominant [1]. In this regard, the reduction in PAHs emissions is a prerequisite for improving the environmental safety of electrolytic aluminum production.

2. State of the problem

Reduction of PAHs emission can be ensured only if the reported data on emission, on the basis of which measures are developed to reduce PAHs emissions, adequately reflect the actual state of the matter. The analysis of the current methodology for determining emissions [3] has shown that it needs to be improved, since calculations based on it give underestimated results far from the actual state of the matter.
According to this method, in electrolysis cell with self-baking anodes with an upper current lead during electrolysis, the resinous substances formed during the coking of the anode mass are released into the atmosphere of the electrolysis cell when the anode studs are moved and under the bell gas collector. Thus, the method does not take into account the emissions of tarry substances from the anode surface in the period between rearrangement of the studs, which can not be accepted for the following reasons.

The melting point of at least six of the 16 most toxic PAHs is below the surface temperature of the anode, which is about 150-160 °C, rising in the summer is much higher.

Back in 1959, M.I. Alivoyvodich [4] established that at a temperature of 100 °C the yield of resinous compounds from the BT anode surface reaches 10 g/m²·h, and with an increase in temperature to 190 °C, their amount increases by 12 times.

The laboratory tests carried out by the authors [5] showed that with a binder content approximately 25% at a temperature 100 °C the volatile matter yield is 1.32-2.48 kg/tonne Al, and at a temperature 190 °C the emission rises to 14.7-45.7 kg/tonne Al.

M. Sorle [6], in particular, showed that with an increase in the temperature of the Soderberg anode surface from 140 to 185 °C, the emission rate of common PAHs, including the BaP, increases by 10 times. Thus, the total emission of resinous substances from the anode surface reaches up to 50% of their content in the anode mass, that is, 40-50 kg/tonne Al.

The work targeting the reduction of PAHs emissions into the environment by factories and specialized research institutes is constantly carried out. To date, several methods have been proposed [2] to reduce PAHs emissions: the use of aluminum ribs to increase heat removal from the anode, the use of a dry anode mass, the use of a pitch with a higher softening temperature, an increase in the height of the anode casing, the creation of a colloidal anode, etc. Each of the measures in one way or another can provide a reduction in PAHs emissions, and some of them are applied in production. However, there has been no significant reduction in PAHs emissions and the proposed measures can not ensure that.

Radical reduction in PAHs emission can be ensured only by replacing Soderberg anodes with baked anodes, but the costs of this modernization on the scale of the industry amount to tens of billions of dollars, and therefore such modernization becomes more than problematic.

3. Analysis procedure and results

   The most effective way to reduce PAHs emissions is to reduce the surface temperature of the anode up to 100-110 °C, which will reduce the mass consumption and improve the quality of the anode.

   In a number of branches of non-ferrous metallurgy, the evaporative cooling method is widely used, in which the heat exchange agent is water. Indeed, water has the greatest latent heat of evaporation - at atmospheric pressure and at a temperature of 100 °C it is 2256.25 kJ/kg. For all other substances and chemical elements, the latent heat of evaporation is practically an order of magnitude smaller.

   Therefore, a method of cooling the surface layer of the Soderberg anode by applying fine water droplets (water fog) onto its surface, which, in order to evaporate, will remove heat from the anode and lower the temperature of its surface. To quantify the proposed cooling method, we determine the specific water demand.

   The density of the anode mass at a temperature of 200 °C is equal to $d_{am} = 1.5 \text{ g/cm}^3 (1.5 \text{ t/m}^3)$ [7]. The volume ($V, \text{ m}^3$) of the mass layer of 1 m² and the thickness of 5 cm (0.05 m) is 0.05 m³, and its mass (weight) ($P_{am}$) is equal to:

   $$P_{am} = 1.5 \cdot 0.05 = 0.075 \text{ tonne} = 75 \text{ kg}.$$  

   At the temperature of the mass surface $T = 150$ °C and the specific heat capacity $C_{am} = 1.8$ kJ/kg·°C, the heat content of this quantity of mass $Q_{am}$ (kJ) is:

   $$Q_{am} = 75 \cdot 1.8 \cdot 150 = 20250 \text{ kJ}.$$
To reduce the temperature of this anode layer to 100 °C, one third of the accumulated heat, i.e., 6750 kJ, must be subtracted from this volume. For heating to 100 °C and evaporation of 1 kg of water, it is necessary to spend about 2672 kJ. Therefore, to reduce the temperature of 75 kg of the anode surface by 50 °C, it is sufficient to evaporate only 6750/2672 = 2.53 kg of water. This amount of water is sufficient to reduce the temperature of 1 m² of the anode surface to 100 °C. However, when heat is removed, heat from the lower layers of the anode will flow to the top layer of the anode.

Due to the low value of the coefficient of thermal conductivity $\lambda$ (1.5 W/m·°C = 5.4 kJ/m·h·°C) and the temperature difference between the cooled and adjacent lower layer $t$, which is assumed to be 50 °C, each hour the cooled layer of the mass receives about 3600 kJ of heat, for the removal of which it will be necessary to use water in the amount 3600/2672 = 1.34 l/m². With an anode area of a C8BM cell being equal to 24 m², the water flow will be approximately $24 \cdot 1.34 = 32.3$ l/h.

The given considerations are approximate, since they do not take into account the presence of heat-conducting studs in the anode, and also the fact that the heat capacity and thermal conductivity of the mass can vary within fairly wide limits. Of course, more accurate data can only be obtained after industrial tests.

If 90 electrolysis cells are installed in the pot room, which provide the total aluminum output of about 4750 kg/h, 32.3·90 = 2907 l (2.9 m³) of water will have to be evaporated hourly, or about 612 l/tonne of aluminum. Evaporation, this amount of water forms about 3000 nm³/h of steam. According to [8] the amount of ventilation air supplied to the pot room equipped with Soderbergh VT cells is $(1.8-2.0) \cdot 10^6$ nm³/ton of aluminum.

Consequently, within an hour the volume of ventilation air will be about $9 \cdot 10^6$ nm³. In this case the volume of water vapor formed during the anode cooling will amount to $(3000/9 \cdot 10^6) \cdot 100 = 0.03\%$ of the total volume of ventilation air, which, apparently, can not have a noticeable effect on the freezing of water vapor in winter season.

The development of the device and its control circuit can be started only after carrying out the industrial tests of the proposed method. However, the efficiency of this method gives grounds to hope that the considerable difficulties that will inevitably arise when an industrial plant for anode cooling by vaporization is created will be successfully overcome.

4. Conclusion
The feasibility of reducing PAHs emissions by reducing the anode surface temperature by 100 °C through evaporative cooling is substantiated. With the area of electrolytic cell anode 24 m², the water flow rate is 32.3 l/h. The volume of water vapor is 0.03% of the total volume of the ventilation air of the pot room. The implementation of technological measures allows us to predict a 10-fold reduction in PAHs emissions.

References
[1] Kulikov B P and Istomin S P 2004 Processing of Aluminum Waste Products (Krasnoyarsk: Classic-Center) p 477
[2] News bulletin 2001 (8)14 29–43
[3] 2005 Settlement instruction (methodology) for determining the composition and amount of harmful (polluting) substances emitted into the air during electrolytic aluminum production. Approved by the Order of the Federal Service for Environmental, Technological and Nuclear Supervision of March 31, 2005 No. 182
[4] Alivoyvodich M I 1959 Non-ferrous metals 12 42–47
[5] Mintsis M Ya 2006 RUSAL Technical and Economic Bulletin 16 3–5
[6] Sorle M 2005 RUSAL Technical and Economic Bulletin 11 33–37
[7] Korobov M A and Dmitriev A A 1972 Self-baking Anodes of Aluminum Electrolysers (Moscow: Metallurgy) p 207
[8] 2007 Aluminum of Siberia-2007 (Krasnoyarsk) p 29