Ecological Aspects of the Interaction of Moisture and Hydrogen Fluoride Contained in Alumina in the Electrolytic Production of Aluminum

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Abstract. The present article deals with the problems of drying kinetics with regard to ill-conditioned alumina. Relations of removed moisture quantity and alumina trial retention interval are determined as well as moisture residual quantity in the alumina on the retention interval. The paper materials prove the possibility of alumina acquisition taking into consideration its prolonged transportation to the Russian intracontinental plants and a considerable amount of crystallized moisture, up to 1% or more, and the corresponding growth of the fluorhydric acid quantity being released into the atmosphere. The investigations of fluorhydric acid releasing into the atmosphere were carried out.

1. Introduction
A lower total emission of fluorhydric acid is the most important problem of the surrounding protection, economy and technology of modern electrolysis in the aluminium metallurgy. With regard for B.A. cells (AP-18 Canada) more than a half of fluorine losses conditioned by the formation of hydrogen fluoride. This item of losses exceeds the evaporation losses by a factor of 1.5. As an experiment, at a plant using self-baking anodes in an Ardal (Norway) it is registered that in the condition of automated alumina feeder (AAF) passing to alumina point feeder technological elements and changes of raw materials are the most important causes of periodical increase of fluoridic acid emission [2].

2. Research part
It is known that fluorhydric acid is a result of aluminium fluoride hydrolysis at high temperatures, aluminium fluoride being a component of electrolytic conductor:

$$2\text{AlF}_3 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 6\text{HF}$$ (1)

Moisture enabling the reaction to pass delivers itself from all raw materials, but its inflow with fluorides is smaller by the order of 2 in comparison with alumina. The delivery of moisture and hydrogen with anode mass that can also form water corresponds to the following:
H₂O + CO₂ = H₂O + CO  \hspace{1cm} (2)

But evidently this moisture can contact with an electrolyte in a small degree. In this case alumina is the main deliverer of moisture into the electrolyte and fluorhydric acid into the atmosphere. The moisture contained by alumina is in a hygroscopic form and is removed while drying, and also in a bound form as hydrates [3]. The hydrate moisture is held in the alumina very firmly and is removed completely only at the temperature of above 1000°C. In correspondence with these ideas the State Standard of RF affects the method of evaluating moisture in alumina by drying at the temperature of 300°C [4] and the inter-country standard affects the method of mass loss identification in alumina by baking at 1100°C [5].

Technical alumina in different periods, and in accordance with the data received from different sources, contains 0.1 – 1 % moisture. In the secondary alumina used in the systems of dry gas purification the moisture content reaches 2.4 %. In the 30th years of the last century, it was indicated by V.P. Mashovets, that in the condition of alumina being stored for a long time, its water content can reach 1.5 % or more.

The last years saw a drive to using underbaked though quick-dissolving alumina in view of a mass introduction of point feeding systems (PFS) at the world’s plants operating with baked anodes. In domestic publications it was a common practice to indicate the required content of α-modification in alumina to be 15-20 %, whereas in underbaked alumina from “a far abroad” the content of α-modification drops to 2 % (!).

Thus, in the conditions of Kraz OJSC the providers are divided in two distinct groups (Table 1).

**Table 1.** The degree of baking (the content of α-modification) in the alumina of different providers for KrAZ.

| Group of providers                      | Content of α–Al₂O₃ % mass. |
|----------------------------------------|-----------------------------|
| Ireland, India, Jamaica, Greece, Finland, Holland | 2-5                         |
| Jamaica, Turkey, Germany, Achinsk, Klimki, UAZ, Nikolayev | 25-30                      |

In fact, one and the same firms or countries, for example, Jamaica, deliver both lightly and deeply baked alumina.

Lightly baked alumina is characterized for a 2-3 times shorter period of dissolving in an electrolyte which is, of course, its advantage when used in the systems of point feeding, APF. Nevertheless, alumina of this kind must have inevitably been adsorbing greater amounts of moisture during transportation, whereas its use is accompanied with an increased emission of fluorhydric acid, a greater discharge of fluoride aluminium and a lower metallic yield on current. The most part of the water adsorbed by alumina is considered to be crystallized moisture which is easily removed while being dried, not hydration one.

The total supplies of hygroscopic (crystallized or “free”) moisture in the conditions of modern metallurgic works make up enormous values reaching ten thousand tons a year (Table 2). For example, with regard to Bratsk Works average supplies of water make up about 12.5 kg per 1 ton aluminium. The greatest part of the moisture is removed while being heated on the crust to the temperature of the order of 300-400°C.
Table 2. Product flows observed moving down the alumina, hygroscopic moisture and aluminium.

| №  | Group of providers | Supplied Al₂O₃, ton | Hygroscop. moisture tons | H₂O/t. Al |
|----|--------------------|---------------------|-------------------------|-----------|
| 1  | RF and CIS         | 519376              | 2361                    | 8.7       |
| 2  | Far abroad         | 885305              | 6742                    | 14.6      |
| 3  | TOTAL              | 1404681             | 9103                    | 12.44     |

With regard to traditional schemes of maintaining cells, its crust being ruined, it was accepted that 65-75 % moisture is removed when alumina (and fluorine salts) is heated on the crust, whereas 25-35 % enter into a reaction of hydrolysis. As for the punctuated systems of APF without alumina being heated an invert correlation seems to be real, i.e. about 70 % moisture is consumed by the reaction of hydrolysis while 30 % of it has time enough to evaporate without any chemical interaction. In this case, the expected amount of fluorhydric acid formed makes up 8.3 kg per ton of the metal for the schemes of cell treatment exposed to systematic crump failure and 19.4 kg/t Al for the schemes of APF (Table 3).

Table 3. Assessment of HF quantity formed on the basis of moisture in alumina.

| Schemes of cell servicing         | Expenditure of moisture per reaction (2) kg/t. Al | Formation HF kg/t Al |
|----------------------------------|-----------------------------------------------|---------------------|
| Systematic crust failure         | 3.75                                          | 8.3                 |
| PF                               | 8.75                                          | 19.4                |

In view of the above, it is evident that the use of underignited alumina following its prolonged transportation to intracontinental works is accompanied with substantially greater amounts of crystallized moisture in it and an increased amount of fluorhydric acid emitting into the atmosphere. For the APF systems a preliminary warming of alumina being delivered to the cell is necessary in order to eliminate additional emissions of fluorhydric acid into the atmosphere.

3. Kinetics of substandard alumina drying
The initial mass of moisture substandard alumina samples made up about 5 t. The samples after weighing with an analytical balance were placed into crucibles of corundum and after that were being kept in a drying oven for 2 hours at different temperatures. 5 replicate observation were performed at each of the temperatures. The level of reliability observed for average experimental values was 95 %. The discrepancy with regard to the replicate observation results does not exceed 0.5 % which meets the requirements of the State Standard of P 59332. When the temperature increases from 323 K to 523 K, the mass of moisture removed from alumina grows exponentially in accordance with the ratio of

$$\Delta m = 2.8 \times 10^{-3} \, e^{0.00677 T} \quad (3)$$

its correlation coefficient being 0.98. The data obtained can be used in calculating the pressure of saturated vapour over alumina P in accordance with the relation of Mendeleev – Clapeyron and the heat of moisture evaporation (\(\Delta H_{eva}\)), the relation of Clasius-Clapeyron being used. The temperature dependence of moisture evaporation heat from alumina is expressed by the following ratio:

$$\Delta H_{eva} = 989.7 \, e^{0.006 T} \quad (4)$$
The kinetics of drying substandard alumina has been studied, its \( \alpha \)-modification being 12 ± 3 % and initial moisture content being 3.2 %. The calculated dependence of the moisture quantity removed on the time of its exposure at 300\(^{0}\) C is indicative of the fact that 65 % of moisture is removed for the first 15 minutes period (Fig. 1).

\[\text{Figure 1. Dependence of a removed moisture amount on curing period of an alumina sample.}\]

\[\text{Figure 2. Dependence of the moisture residual quantity and alumina on the curing time.}\]

At the same time it should be marked that the calculated kinetic dependences are connected with the conditions of experiments with alumina placed in crucibles as a layer which is 2.5 cm. thick. Such conditions are certainly not optimum and cannot make the delay of the process minimum.

Evaluations of moisture evaporation heat from alumina grow with increasing drying temperature from 350 to 550 K in the interval of 8-30 k J/mole. It is evident that in the alumina containing moisture up to 3 % practically all of it is adsorptive water and is physically adsorbed from the air while the alumina is being transported and stored. An exposure at the temperature of 300\(^{0}\) C for 2 hours of curing period is enough to remove a greater part of the moisture adsorbed.

4. Conclusions
The use of underignitive alumina during its prolonged transportation to Russian intracontinental works is accompanied by a considerable, up to 1 % or more, increase of crystallized moisture content in it and a corresponding growing content of fluorhydric acid releasing into the atmosphere, the increase in concentrations of which is one of the reasons for exceeding the standards of atmospheric air quality [1].
With regard to APF systems, drying of the alumina delivered into a cell is necessary along with warming in order to remove additional emissions of fluorhydric acid released into the atmosphere and to increase the metallic yield.

5. References
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