APPLICATION OF MECHANICAL FILTERS FOR PURIFICATION OF ELECTROLYTE FROM SOLID PRODUCTS OF THE AIR AND ALUMINUM CHEMICAL CELL REACTION

Nadezhda S. Okorokov
Moscow Aviation Institute (National Research University), Department of Physical Chemistry, Moscow, Russian Federation

Aleksandr V. Perchenok
Moscow Aviation Institute (National Research University), Department of Physical Chemistry, Moscow, Russian Federation

Stanislav D. Sevruk
Moscow Aviation Institute (National Research University), Department of Electric Propulsion, Power and Energy-Physical Plants, Moscow, Russian Federation

Elena V. Suvorova
Moscow Aviation Institute (National Research University), Department of Physical Chemistry, Moscow, Russian Federation

Ariadna A. Farmakovskaya
Moscow Aviation Institute (National Research University), Department of Physical Chemistry, Moscow, Russian Federation

Aung Thu Kyaw
Myanmar Maritime University, Marine Electrical System and Electronics – Myanmar Navy, Defence Services Technological Academy (DSTA), PyinOo Lwin, Myanmar

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APPLICATION OF MECHANICAL FILTERS FOR PURIFICATION OF ELECTROLYTE FROM SOLID PRODUCTS OF THE AIR AND ALUMINUM CHEMICAL CELL REACTION

Nadezhda S. Okorokova*, Aleksandr V. Perchenok, Stanislav D. Sevruk, Elena V. Suvorova, Ariadna A. Farmakovskaya, Aung Thu Kyaw

1Moscow Aviation Institute (National Research University), Department of Physical Chemistry, Moscow, Russian Federation
2Moscow Aviation Institute (National Research University), Department of Electric Propulsion, Power and Energy-Physical Plants, Moscow, Russian Federation
3Myanmar Maritime University, Defence Services Technological Academy (DSTA), Marine Electrical System and Electronics – Myanmar Navy, PyinOo Lwin, Myanmar

This work presents the results of the development and application of a filtration unit – a cartridge filter with a throttle (discharge) hole – for separating the solid phase – crystalline aluminum hydroxide Al(OH)₃, formed during long-term operation of an air and aluminum chemical cell with alkaline electrolyte and power plants based on them. The main theoretical provisions on the filtration mechanism using the discharge hole are formulated, according to which the filtration process consists of two types of filtration – blowout piping and particle coupling. The developed method made it possible to: purify electrolyte with low friction to electrolyte flow at high concentrations of the solid phase; ensure long-term performance of the purification system with large masses of the solid phase formed; be able to quickly regenerate the electrolyte; have a small mass and volume; leave a sufficient amount of solid phase in the electrolyte so that the crystals of aluminum hydroxide passing through the filter are a seed for the crystallization of dissolved aluminum in the circuit. The studies carried out allowed us to conclude that the use of mechanical cartridge filters with an orifice hole is an effective and reliable method for cleaning the electrolyte of a power plant with an air and aluminum chemical cell.

Key words: power plant, reaction products, aluminum hydroxide, throttle hole, crystallization

INTRODUCTION

During the operation of power plants with air and aluminum chemical cells with an alkaline electrolyte in the process of dissolving the aluminum anode in alkali, the composition, and state of the reaction products formed in this process is determined in accordance with the state diagram of the NaOH-H₂O-Al₂O₃ ternary system [1-3], which is shown in Figure 1.

As you can see, the solubility of aluminum depends on the concentration of alkali and has an extreme character [4-6]. Above the left branches of the isotherm, there is an area of supersaturated (metastable) aluminate solutions [7]. The concentration of alumina Аl₂О₃ in them exceeds the equilibrium one. Therefore, solutions in this area are unstable and will undergo decomposition with the release of aluminum hydroxide Al(OH)₃. One of the following equations (Eq. 1) or (Eq. 2) can represent the formation of soluble aluminates:

\[ \text{Al} + 4OH^- - 3e^- \rightarrow 6Al(OH)_4^- \]  \hspace{1cm} (1)

\[ \text{Al} + 4OH^- - 3e^- \rightarrow 6AlO_2^- + 2H_2O \]  \hspace{1cm} (2)

After saturation of the electrolyte with aluminates, crystallization of aluminum hydroxide occurs (left side of the diagram) (Eq. 3):

\[ Al(OH)_4^- \rightarrow Al(OH)_3 + OH^- \]  \hspace{1cm} (3)

or potassium hydroaluminate (right side of the diagram) (Eq. 4):

\[ AlO_2^- + Na^+ + \frac{3}{2}H_2O \rightarrow \frac{1}{2}Na_2OAl_2O_3 \cdot 3H_2O \]  \hspace{1cm} (4)

The presented equations correspond to the anodic dissolution of aluminum in alkali during the operation of the
air and aluminum chemical cell. Associated processes in the cell are:

- the reaction of oxygen reduction at the gas diffusion cathode (GDC) (Eq. 5):
  \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (5) \]
- the reaction of hydrogen reduction from water on the surface of aluminum due to electrochemical corrosion of aluminum in aqueous electrolytes (Eq. 6):
  \[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad (6) \]
The total reactions that take place in the air and aluminum chemical cell are described by the equations:

- total cell reaction (Eq. 7):
  \[ 4\text{Al} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3 \downarrow \quad (7) \]
- corrosion reaction (Eq. 8):
  \[ 2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 \downarrow + 3\text{H}_2 \uparrow \quad (8) \]
and also, reaction (3).

The dissolved aluminates formed during the operation of the air and aluminum chemical cell, as well as solid aluminum hydroxide. As they accumulate in the cell, reduce the parameters of the air and aluminum chemical cell, worsen the operation of pumps pumping electrolyte, and significantly reduce their service life. The possible deposition of solid products on the walls of pipelines and units leads, in turn, to a decrease in the reliability of the power plant.

In our previous works [8, 9], the methods of purification of the electrolyte from dissolved aluminates by air and aluminum chemical cell were considered and the dimensions of the electrolyte circuit of the chemical cell and the crystallizer were calculated. It makes it possible to significantly increase the time of continuous operation of the power plant based on the air and aluminum chemical cell. In this work, for the purification of electrolytes from solid products, we investigated the possibility of using special cartridge filters with a throttle hole, which is our know-how, and for which an inventor’s certificate has been obtained [10].

**MATERIALS AND METHODS**

A large number of different filters used in technology are known [11-13]. To be used in power plants with air and aluminum chemical cell, they must meet the following requirements [14]:

- to purify electrolyte with low friction to electrolyte flow at high solid phase concentrations (more than 10-15 mass %);
- to ensure long-term operability of the purification system at large masses of the solid-phase formed;
- to be able to quickly regenerate the electrolyte;
- have a small mass and volume.

At the same time, in some cases, the filters should not completely purify the electrolyte from the solid phase for the aluminum hydroxide crystals passing through the filters to be a seed for the crystallization of dissolved aluminum in the circuit. These requirements are most fully met by cartridge filters with a fabric coating resistant to alkali [15]. Based on the great practical experience gained when working with filters, we have compiled a method for calculating the filtration unit and determined the filtration area and design of the experimental cartridge-type filter. A polypropylene unwoven stitched fabric was used as a filtering material. Due to the high aggressiveness of the alkaline electrolyte, the bulk of the experiments were carried out on a model suspension – distilled water with particles of industrial aluminum hydroxide. The scheme of the cartridge filter used in the experiments is shown in Figure 2.

![Figure 2: The scheme of the cartridge filter](image)

As can be seen from the scheme, the filter consists of a housing (1) and a filter cartridge (2). The housing has an inlet (3) and output (4). The filter cartridge has an inner wire frame covered with polypropylene filter cloth. A special insert (5) with orifice holes is made on the side surface of the filter cartridge.

Two versions of the experimental filter were developed, with an inner diameter of the housing of 60 and 100 mm. In the manufacture of filter housings, both stainless steel grade X18H10T and organic glass were used. The use of organic glass as a housing material allows visual observation of the filtration process. In both cases, a filter cartridge with a length of 200 mm and a diameter of 30 mm was used, the design of which makes it possible to change the diameter and location of the throttle holes. The throttle holes can be positioned along with the filter height in different ways: in the lower part of the filtering partition, in the center of the filter, and near the filter base. Experiments carried out with filters, in which the throttle hole was located at different filter heights showed that the most optimal location for the filtration process is holding near the filter base (Fig. 3).
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**RESULTS AND DISCUSSION**

Initial experiments on the cartridge filter found that within about 17 minutes the concentration of the solid phase decreases from 20 mass % to 2 mass % (Fig. 5). In this case, the thickness of the sediment reached 14 mm. However, despite the good results of the experiment, a low flow rate of filtrate through the filter cartridge was recorded, which dropped to almost zero at the 17th minute of operation, which is unacceptable for practical use in power plants.

As a result of an experimental search, a solution was proposed [10], which made it possible to significantly improve the characteristics of the proposed unit. A throttling (discharge) hole was made in the filter rack, which leads to a sharp increase in flow rate with almost complete retention of filtration characteristics. So, after 20 minutes of the start of work, the concentration of the solid phase in the suspension drops to 1.5 mass % (Fig. 6).

The filtering mechanism using the throttle hole can be represented as follows. During the initial filtration period, most of the solid phase is deposited on the tissue wall. Further, the process consists of two types of filtration – blowout piping and particle coupling. The main flow rate of the suspension goes through a throttling hole in a well-tubulated flow. As a result of which new particles of the solid phase are supplied to the sediment layer, which has deposited on the filter at the initial moment of filtration, and the particle coupling occurs under the action of surface van der Waals forces and electrostatic forces. Simultaneously with the particle coupling, the process of blowout piping occurs – the movement of small particles at a low flow rate of the suspension through relatively large capillaries of the sediment towards the filtering partition. As the thickness of the sediment increases, blow-out piping decreases.
The increase in total filtration resistance with increasing filtrate volume is associated with this resistance by a power-law dependence, which is called the generalized filtration equation (Eq. 9):

$$dR/dV' = k \cdot R^n$$

(9)

where \(k\) is a constant characterizing the intensity of the increase in the total filtration resistance; \(R\) is the total filtration resistance per unit of viscosity; \(V'\) is a specific volume of filtrate (Eq. 10):

$$V' = V/S$$

(10)

where \(S\) is the filtration area; \(V\) is the volume of the filter.

The exponent \(n\) in the generalized equation can take any value from 2 to \(-\infty\). However, only for fixed values of this indicator, equal to 2; 1.5; 1; 0.5; 0 and \(-\infty\), (Eq. 9) describes the processes that, respectively, can be identified with the following types of filtration:

- with complete clogging of the filter pores \((n = 2)\);
- with gradual clogging of the filter pores \((n = 1.5)\);
- intermediate type \((n = 1)\);
- with clogging of the pores of the precipitate formed \((n = 0.5)\);
- with the formation of sediment \((n = 0)\);
- at constant resistance \((n = -\infty)\).

In practical terms, the actual process very rarely fully corresponds to any particular type of filtration. The most significant deviations are observed during the initial filtration period. This period is difficult to describe mathematically. The exponent in the generalized equation gradually decreases. The type of filtration changes, filtration with clogging of pores turns into filtration with the formation of a precipitate.

According to Darcy’s equation, the flow rate through the filter is directly proportional to the applied pressure and filtration area, and inversely proportional to the viscosity and total flow resistance, taking into account the resistance of the sediment layer and filter material [16-18] (Eq. 11):

$$dV'/dt = P/(\mu(\alpha \cdot \delta + \beta))$$

(11)

where \(P\) is the pressure drop; \(\mu\) is the viscosity of the suspension; \(\alpha\) is specific resistivity of the sediment; \(\delta\)– sediment thickness; \(\beta\) – material resistance.

When integrating equation (11), some assumptions are made [19, 20]:

- the sediment and the filtering partition are incompressible;
- the solid phase does not precipitate during filtration;
- the volume of the precipitate formed is proportional to the volume of the filtrate obtained (Eq. 12):

$$U = \delta \cdot S/V = d/V' = \text{const}$$

(12)

Substituting expression (12) into (11) and integrating the resulting equation with \(P = \text{const}\) from 0 to \(t\) and from 0 to \(V'\), as well as after some transformations, we obtain (Eq. 13):

$$\tau = \mu \cdot \alpha \cdot U \cdot (V'/2P + \beta \cdot \mu \cdot V'/P)$$

(13)

or, taking into account that \(V' = V/S\) (Eq. 14):

$$\tau \cdot S/V = \mu \cdot \alpha \cdot U \cdot V/(2 \cdot P \cdot S) + \mu \cdot \beta/P$$

(14)

This equation can be represented in the form (Eq. 15):

$$\tau \cdot S/V = (Y'/X') \cdot V'/S + Y'$$

(15)

where (Eqs. 16-17):

$$X'/Y' = \mu \cdot \alpha \cdot U/(2 \cdot P),$$

(16)

$$Y' = \alpha \cdot \beta/P$$

(17)

This dependence is shown in Fig. 7. The deviation of curve 1 from straightness indicates a progressive increase in the specific resistivity of the layer during filtration, which is caused by blockage of the initially open channels of the filter cake layer. Line 2 has a very small slope, which indicates small flow friction of the sediment layer.

Figure 7: Change in the filtration process depending on the thickness of the sediment:
1 – without the throttle hole; 2 – with the throttle hole
Equations (14) and (15) are commonly used to experimentally determine the average resistivity of the sediment and filter partition (Eqs. 18-19):

$$\alpha = 2 \cdot \left( Y' \cdot x' \right) \cdot P \cdot \left( \mu \cdot U \right)$$  \hspace{1cm} (18)$$

$$\beta = y \cdot P / \mu$$  \hspace{1cm} (19)

Experiments have shown that in instances where the introduction of a new portion of the solid phase to the filtration system by a power plant with an air and aluminum chemical cell has practically no effect on the filtration efficiency [21-23]. The studies carried out allow us to conclude that the use of mechanical cartridge filters with a throttling hole is an effective and reliable method for purifying an electrolyte by a power plant with an air and aluminum chemical cell. It is also of great interest to study the possibility of joint use of a cartridge filter with other purification units. For example, a combination of a cartridge-filter-hydrocyclone, which, in our opinion, can significantly improve the purification process.

CONCLUSIONS

The parameters of the unit for cleaning the electrolyte from solid reaction products by an air and aluminum chemical cell – a cartridge filter with a throttling hole – have been calculated. The method allowed to purify electrolyte with low friction to electrolyte flow at high solid-phase concentrations (more than 10-15 mass %); to ensure long-term operability of the purification system at large masses of the solid phase formed; to be able to quickly regenerate the electrolyte; to leave a sufficient amount of solid phase in the electrolyte so that the crystals of aluminum hydroxide passing through the filter are seeds for the crystallization of dissolved aluminum in the circuit.

The experiments carried out on the prototype suspension samples confirmed the set parameters. Which makes it possible to recommend its use as a part of the purification system by a power plant with an air and aluminum chemical cell.

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