Dimensions for reducing the consumption of fluoride salts in the production of aluminum

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Abstract. This article is devoted to the dimensions for reducing the consumption of fluoride salts in the production of aluminum. The main dimensions are: production and use of alumina with a lower sodium content; processing of a part of the excess electrolyte using a new technology to produce aluminum fluoride; processing of the heat insulating part of the spent lining with the production of regenerative cryolite, which is processed into a low-modulus cryolite with the help of a new technology. With the use of new technologies, secondary wastes are used in the production of cement, and aluminum smelters can become completely non-waste ones.

1. Introduction
The current consumption of aluminum fluoride in the use of electrolyzers with baked anodes and “dry” gas scrubbing is in the range of 16-22 kg per ton of aluminum, which, in terms of fluorine, is about 10-14 kg [1,2]. The balance of the distribution of fluorine losses in electrolytic aluminum production is given in table 1.

Table 1. Balance of the distribution of fluorine flowrate.

| S No | Reason of losses                                      | Kg/tn Al | %   |
|------|-------------------------------------------------------|----------|-----|
| 1    | Losses with gases                                     | 1.0      | 8.3 |
|      | With excess electrolyte introduced to maintain the cryolite |          |     |
| 2    | ratio (with Na2O content in alumina 0.35-0.45%)       | 5.0      | 41.7|
|      | With spent lining including:                         | 5.5      | 45.8|
| 3    | Carbon part                                           | 3.0      | 25  |
|      | Heat insulating part                                   | 2.5      | 20.8|
| 4    | Coal foam and mechanical losses                       | 0.5      | 4.2 |
| 5    | Losses of everything                                  | 12       | 100 |
Losses with gases do not exceed 1 kg/t of aluminum, further reduction of fluorine losses is constrained by existing designs of sealing shelters. The formation of excess electrolyte is associated with the need to maintain the cryolite ratio specified by the technology in the electrolysis process. Cryolite ratio is the molar ratio of the content of sodium fluoride to the content of aluminum fluoride. Cryolite ratio, with modern technologies of aluminum production, is maintained at 2.4-2.6. The main raw material for the production of aluminum - alumina - contains tenths of a percent of sodium oxide, which leads to a shift of the cryolite ratio to the alkaline side. To maintain the cryolite ratio at a given level, aluminum fluoride is introduced into the electrolysis cell, and excess electrolyte is removed from it.

2. Calculation of excess electrolyte formation is given below

Average content of Na$_2$O in alumina is ~ 0.35% wt. With a specific consumption of alumina of 1920 kg/t of produced aluminum, the sodium entrance into the electrolysis cell is:

$$1920 \times \frac{0.35}{100} \times \frac{46}{62} = 4.986 \text{ kg Na/t Al}$$

To impregnate the lining materials of the cathode shell, ~ 30% is spent:

$$4.986 \times 0.3 = 1.496 \text{ kg Na/t Al}$$

The loss of electrolyte during the processing of turnover is ~ 5%:

$$4.986 \times 0.05 = 0.249 \text{ kg Na/t Al}$$

Thus, the accumulation of sodium in the electrolyte is:

$$4.986 - 1.496 - 0.249 = 3.241 \text{ kg /t Al}$$

With a sodium content in the electrolyte of ~ 22% wt. The accumulation of electrolyte is:

$$3.241/0.22 = 14.73 \text{ kg /t Al}$$

This correlates with the data obtained during the operation of the pilot section “Electrolysis 300” of the Ural Aluminum Plant, where the accumulation of electrolyte was 10-15 kg/t of produced metal [3].

Abroad, heat insulating part of the spent lining is neutralized and stored in dumps, or used in the production of cement and construction materials [4]. In Russia, the heat insulating part without neutralization is stored in specially equipped storage tanks. We carried out research to study the composition of the heat insulating part of the spent lining and the methods of its processing [5, 6]. The average chemical composition by the results of the analysis of samples from five electrolyzers of the C8BM type wt. %: C – 1-5; F – 7-10; Al – 12-16; Na – 7-10; Ca – 0.5-1.0; Si – 16-20; Mg – 0.5-1.0; Fe – 1.0-2.0; others – 35-45 (oxygen in the form of aluminum oxides and silicon).

The following substances were detected as the main phases in the heat insulating part of spent lining by X-ray diffraction analysis: mullite 3Al$_2$O$_3$·2SiO$_2$, sodium fluoride NaF, cryolite Na$_3$AlF$_6$, kyanite Na$_3$Al$_2$F$_14$, silicon oxide SiO$_2$ (in the form of cristobalite, quartz, tridymite), calcium fluoride CaF$_2$, aluminum oxide Al$_2$O$_3$, nepheline NaAlSiO$_4$, albite NaAlSi$_3$O$_8$.

3. Water leaching

As a result of water leaching of the heat insulating part of the spent lining, a solution of the following composition is formed: g/dm$^3$: NaF-15-25; Al$_2$O$_3$ - 0-0.1; Na$_2$SO$_4$ - 1-3; SiO$_2$ - 0.05-0.7. From the solutions, obtained after leaching of the heat insulating part of the spent lining, cryolite can be
precipitated with the help of one of the known methods [7,8]. This solution is similar to solutions of wet gas purification of aluminum electrolyzers and can be processed with the production of cryolite according to a conventional sodium bicarbonate scheme [7,8]. For the precipitation of cryolite, additional addition of reagents in the form of an aluminate solution and sodium bicarbonate is necessary.

Aluminate solution is prepared from aluminum hydroxide and caustic alkali. The process of cryolite formation is carried out according to the reaction:

$$6\text{NaF} + 4 \text{NaHCO}_3 + \text{NaAlO}_2 = \text{Na}_3\text{AlF}_6 + 4 \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} \quad (1)$$

Reduction of the silicon content in solutions from the leaching of spent lining can be achieved using various ways as described below.

In the technology of hydrochemical processing of the carbon part of the spent lining, desiliconization is achieved by contacting the solution after leaching with its own slime for 6-8 hours due to the formation of sodium aluminosilicates [9]. In case of the heat insulating part of the spent lining, this process is accompanied by difficulties associated with a low content of aluminum compounds in the slime.

It is also possible to regulate the leaching process at a level of pH 6-9 by introducing of acidic additives (acid salts of aluminum, acids), however this complicates and increases the cost of the process.

In addition, the use of the cryolite produced with the help of this technology is currently limited in the production of aluminum due to the transition to acid electrolytes in the production of aluminum. A radical solution to the problem is the process of obtaining a low-modulus cryolite (a mixture of cryolite and chiolite), which will be considered below. The low-modulus cryolite obtained by us contains 0.2-0.3% of silicon.

An increase in the consumer properties of cryolite can be achieved by processing cryolite with a high sodium content of 30-32% per chiolite (Na$_5$Al$_3$F$_{14}$). The technology of processing cryolite with aluminum sulfate solution was carried out at the Irkutsk Aluminum Smelter on a pilot scale [10]. The composition of the initial regeneration cryolite, cryolite treated with aluminum sulfate solution and the precipitate after leaching is given in table 2.

| Name of product                 | F   | Na  | Al  | SO$_4$ | C   | Ca  | Fe  | Si  |
|--------------------------------|-----|-----|-----|--------|-----|-----|-----|-----|
| Initial regenerative cryolite  | 45.47 | 30.27 | 12.34 | 6.18 | 0.74 | 0.61 | 0.11 | 0.60 |
| Cryolite treated with          | 47.74 | 22.56 | 17.32 | 1.35 | 0.62 | 0.72 | 0.23 | 0.3  |
| aluminum sulfate               |     |     |     |        |     |     |     |     |

The main phases of the initial regeneration cryolite are cryolite and sodium sulfate, cryolite treated with sulfate aluminum - cryolite and chiolite.

4. Conclusion
The main directions of reducing the consumption of aluminum fluoride are:
- production and use of alumina with a lower sodium content;
- processing of a part of the excess electrolyte using the new technology to produce aluminum fluoride;
- processing of the heat insulating part of the spent lining with the production of regenerative cryolite processed with the help of a new technology into a low-modulus cryolite.
With the use of new technologies, secondary wastes are used in the production of cement, and aluminum plants are approaching to become completely non-waste ones.

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