Formation and emission of sulfur dioxide in aluminum production

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Formation and emission of sulfur dioxide in aluminum production

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Abstract. The sources of formation of sulfur dioxide during the production of anodic mass (baked anodes) and aluminum by electrolysis are analyzed; the method for calculation of the formed sulfur dioxide anhydride depending on the quality of the used raw materials is presented. Total emissions of sulfur dioxide are estimated for different methods of anode mass production, electrolysis cell structures and methods for purifying waste gases.

1. Introduction

In the production of anode mass or baked anodes for aluminum electrolysis cells, electrode (pitch or petroleum) coke and coal tar pitch are used. Fuel oil or natural gas is used for baking or drying coke. This raw material and fuel contains sulfur in its composition, which is the source for sulfur dioxide formation.

Depending on the recipe of the finished product, 1 tonne of electrode production is consumed: baked coke (oil or pitch) – 700-840 kg, coal tar pitch – 180-310 kg. For baking 1 tonne of raw electrode coke 15-50 kg of fuel oil or 20-65 nm^3 of natural gas is consumed, and when coke is dried, the fuel consumption is reduced by 3-4 times. Pitch coke contains from 0.1 to 0.7% sulfur, and petroleum coke – 0.3% -1.6%. The sulfur content in fuel oil, depending on its grade, is from 0.5 to 3.5%, and in natural gas it is usually not great and can be neglected. To determine the amount of sulfur, the reporting indicators for the consumption and quality of raw materials in a particular production should be used. When raw coke is used, it is preliminarily subjected to baking at a temperature of 1100 - 1250 °C; if a pre-baked coke is used, it is dried at a temperature of 250 to 400 °C. As shown by numerous studies, baking of coke at a temperature up to 1250 °C reduces the sulfur content by no more than 5%.

During the coke baking the volatile compounds are combusted, but they practically do not contain sulfur compounds. The composition of the mass also includes pitch, the sulfur content in which, on average, does not exceed 0.2%. The sulfur contained in the pitch passes into the mass or into the burnt anodes. In the process of anodes baking, their desulfurization practically does not occur, and all sulfur contained in the coke and pitch completely passes into the fired block.

Thus, the estimation of sulfur dioxide emissions in the production of aluminum is necessary to find ways to improve its environmental safety.

2. Method for calculation of sulfur dioxide emissions

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In the production of electrode mass, sulfur dioxide is formed due to the oxidation of sulfur contained in the fuel, and its quantity per 1 tonne of electrode mass Q can be determined according to the formula

$$Q = 2 \cdot \left(\frac{q_f \cdot C_f}{100}\right) \cdot \left(\frac{K_c}{1000}\right), \quad (1)$$

where 2 – coefficient of conversion of sulfur content into sulfur dioxide;
q_f – fuel consumption for baking (drying) 1 tonne of coke;
C_f – sulfur content in fuel, %;
K_c – consumption of coke for production 1 tonne of electrode mass, kg.

If the sulfur content in the fuel oil is 0.5 – 3.5%, and its consumption during the baking 1 tonne of coke is in the range 15-50 kg, in this case the amount of the formed sulfur dioxide is 0.15-3.5 kg. When drying the baked coke, the amount of sulfur dioxide will be 3 to 4 times lower. To determine the actual amount of sulfur dioxide produced during the thermal treatment of coke, it is necessary to use the reporting data of the plants on the sulfur content in the coke, the fuel consumption per 1 tonne of coke and the consumption of baked coke for the production of 1 tonne of electrode mass.

During production of baked anodes, the additional amount of sulfur dioxide is produced due to combustion of fuel oil used for kilns, the amount of which, as a rule, is about 150 kg per 1 tonne of ready blocks. Therefore, the amount of sulfur dioxide in this case can increase by 1.5-10.5 kg/tonne.

The amount of sulfur in 1 tonne of electrode mass or baked anode Q_{cm} (kg) can be calculated by the formula

$$Q_{cm} = \left(\frac{q_c \cdot C_c}{100}\right) + \left(\frac{q_p \cdot C_p}{100}\right), \quad (2)$$

where q_k – the content of baked coke per 1 tonne of mass, kg;
q_p – content of pitch per 1 tonne of mass, kg;
C_c – the sulfur content in coke, %;
C_p – the sulfur content in the pitch, %.

In the production of aluminum by electrolysis, sulfur enters the electrolyte with alumina, fluorides (in the form of sulfates) and with anode material (sulphides). Sulphates react with cryolite

$2\ Na_2SO_4 + 2Na_3AlF_6 = Al_2(SO_4)_3 + 12NaF.$

Sulfate dissolved in the electrolyte is reduced by aluminum

$3\ Na_2SO_4 + 8Al = 3Na_2S + 4Al_2O_3,$

and the resulting sulphide is transferred to the anode and oxidized to sulfur, which in turn reacts with carbon dioxide

$S + 2CO_2 = SO_2\uparrow + 2CO.$

The total amount of sulfur involved in the production of 1 tonne of aluminum depends on the consumption of each type of raw material and the sulfur content in them. The overwhelming amount of sulfur contained in all kinds of raw materials is oxidized during electrolysis to sulfur dioxide, the amount of which is equal to doubled sulfur content.

The sulfur content in alumina does not exceed 0.02% according to the data in [1], and in fluoride salts (in terms of sulfur) it is about 0.3%, but for calculations the actual sulfur content should be clarified according to the reporting data of the specific production.

3. Results of calculations of sulfur dioxide emissions and their discussion

Thus, to calculate the amount of sulfur dioxide produced during electrolysis, it is necessary to know the consumption factors for 1 tonne of aluminum of all types of raw materials and the sulfur content in them. Table 1 gives data on the consumption coefficients of the main types of raw materials for the production of 1 tonne of aluminum, the maximum permissible sulfur content in them and the amount of sulfur dioxide produced during electrolysis from each type of raw material. These data represent the maximum possible amount of the produced sulfur dioxide. If foam is removed from the electrolyte surface during the process, the amount of anode mass consumed for electrolysis should be reduced by the amount of carbon in the foam, which usually does not exceed 30% [2].

Table 1. The main types of raw materials for aluminum electrolysis and sulfur content in them.

Type of raw material	Consumption, kg	Sulfur content,%	Amount of SO_2, kg
Anode material	560	1.5	16.8
Alumina	1890	0.02	0.76
Fluorides	70	0.3	0.42
Total			18.0

From the data given in table 1 it can be seen that the main source for sulfur dioxide formation is the anode material, which accounts for more than 93% of the sulfur content in the raw material.

Therefore, in order to determine the amount of sulfur dioxide produced during electrolysis Q_{ce} (kg), the following expression can be used

$$Q_{ce} = 2 \cdot \frac{\left[\left(q_a - q_{cp}\right) \cdot C_a\right]}{100} + \left(\frac{q_{al} \cdot C_{al}}{100}\right) + \left(\frac{q_{fl} \cdot C_{fl}}{100}\right), \quad (3)$$

where q_a, q_{al}, q_{fl} – consumption, respectively, of anode material, alumina and fluorides per 1 tonne of aluminum, kg;

q_{cp} – carbon content in the removed pitch, calculated per 1 tonne of Al;

C_a, C_{al}, C_f – sulfur content, respectively, in the anode material, alumina and fluorides, %.

Thus, the maximum amount of sulfur dioxide produced during electrolysis does not exceed 18 kg/tonne of aluminum, and the amount of sulfur dioxide released into the environment depends on the availability and type of gas cleaning systems.

The maximum amount of sulfur dioxide emissions will be in the facilities that are not equipped with gas purification system, which, unfortunately, can be found at domestic aluminum plants (NkAZ, BAZ, KAZ, UAZ).

If there is a system for wet cleaning of waste gases, sulfur dioxide reacts with soda solution

$$Na_2CO_3 + SO_2 + 0.5O_2 = Na_2SO_4 + CO_2,$$

and the resulting sulphate is excreted in the process of production of the regenerated cryolite. The efficiency of wet gas cleaning for sulfur dioxide does not exceed 85%. Therefore, all gas which is not caught by the gas gathering system get into the surrounding atmosphere. The efficiency coefficient of gas gathering devices (curtains, gas gathering bells, shelters) is 60-85% and therefore from 30 to 50% of the formed sulfur dioxide gets into the environment.

The situation is further exacerbated by the use of a dry flue gas cleaning system, which is not capable of capturing sulfur dioxide, and therefore all the sulfuric anhydride formed gets into the

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surrounding atmosphere. This type of gas cleaning is widely used in cells with baked anodes, and for reduction of emissions of sulfur dioxide wet-gas purification system can be installed after dry cleaning, but this should be justified for each particular production.

Analyzing the statistical reports, the data on emissions of sulfur dioxide at aluminum plants of Russia seem to be not well grounded. So, emissions of sulfur dioxide for 1994 at different plants are in the range from 1.51 (IrkAZ) to 28.64 (KAZ) kg/tonne A1. At Kandalaksha (KAZ) and Nadvoytsky (NAZ) plants they are about 25-29 kg/tonne, while at Bogoslovsk (BAZ) plant they do not exceed 6.5 kg/tonne. At the same time, KAZ and NAZ use the anode mass produced at BAZ. The reporting data on emissions of sulfur dioxide at IrkAZ, which are 4 to 5 times lower than at Bratsk and Krasnoyarsk plants, hardly correspond to reality. The production of anode mass, electrolysis and gas cleaning technology, and the quality of the raw materials used are practically the same in all three plants.

Such contradictory and inexplicable data on emissions of sulfur dioxide are, in our opinion, a consequence of the lack of calculation method, which would not be based on single measurements (as it is at present), but on actual data characterizing the quality of the used raw materials for the production of electrode mass and aluminum.

The proposed method, in our opinion, will allow the amount of sulfur dioxide formed and emitted at aluminum and electrode plants to be significantly clarified.

4. Conclusion

The calculation method is proposed for determining the amount of sulfur dioxide formed in the electrolysis process, taking into account the sulfur content in the anode, alumina, fluorides, carbon content in the coal foam, consumption and formation of these materials. It is shown that the maximum amount of sulfur dioxide formed in the process of electrolysis does not exceed 18 kg/tonne of aluminum, the amount of sulfur dioxide released into the environment depends on the availability and type of gas cleaning system of the pot line.

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