Reducing environmental load of aluminum production by selecting coke-pitch compositions

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Abstract. The problems of the technosphere safety became the key point in the operation of industrial enterprises and are regulated by the law of the Russian Federation on the protection of the environment. The issue of reducing the environmental load of aluminium production by selection of coke-pitch compositions with the use of modified heavy pyrolysis resin (HPR) is considered. The possibility and expediency of using high-temperature coal tar pitch in a mixture of modified heavy pyrolysis resin are shown. That will significantly improve the ecology of aluminum production using Sodeberg's technologies and reduce the content of carcinogenic substances in the air of the work area.

1. Introduction

Modern technologies of aluminium production are associated with the risk of negative impact on the environment: pollution of soils due to mass storage of waste, discharge of insufficiently processed production water into natural water bodies, and technological cycle implies emissions of a whole range of toxic substances including greenhouse gases [1,2].

The main environmental problems of modern production requiring solutions in the shortest possible time should be an assessment of the actual state of the environment, identifying ways to reduce the negative impact on nature, reconstruction of production taking into account the requirements of environmental legislation and public opinion, the introduction of environmental clean technologies.

2. Objects of research

The raw materials for the production of anodic mass and calcined anodes are electrode coal tar pitches and electrode cokes (oil or coke). It should be noted that the right selection of consumables is the most difficult task of production preparation. The basic properties of Cokes and Pitches largely depend on which refined or coke-chemical products they are derived from [3,4].

The main disadvantage of coal tar pitches is the high carcinogenic activity caused by the specific composition and significant content of polycyclic aromatic hydrocarbons (PAH) and phenols that enhance their action.

In the Russian Register of potentially hazardous chemical and biological substances, 3 PAHs are referred to the extremely dangerous class: benzenanthracene, benzapyrene and dibenzanthracene [5,6].
The indicator of carcinogenic danger is benzapyrene, the concentration of which in the air should not exceed 1 ng/m.

It becomes obvious that it is necessary to create sound formulations of composite raw materials taking into account the data of economic and ecological analysis.

One way to improve the properties of the binder for the production of dry anode mass, as well as the production of a more environmentally friendly binder and the reduction of PAH emissions, can be the use of mixtures of high-temperature coal tar pitch and heavy pyrolysis resin.

Representative samples of raw materials that have undergone routine training under industrial conditions were selected for conducting laboratory tests. In order to evaluate the properties of the compounded binder and determine the effect on the quality of the dry anode mass, 4 batches of anode mass were prepared and tested in which the dosage of HPR to coke batch (1-10%) was changed in a fairly wide range, with constant dosing parameters of coke batch and mixing temperature. As the coke-filler, sorted coke materials were used, selected in the shop of the anode mass. To obtain pure coke fractions, all the material was dispersed in classes. The properties of the main fractions of the coke batch are given in Tables 1 and 2. As a binder we used coal tar pitch of grade B, the properties of which are given in Table 3 [7,8].

| Table 1. Properties of coke materials. |
|----------------------------------------|
| Properties | Grit 1 | Grit 2 | Screenings | Dust |
| Ash content, % | 0.11 | 0.14 | 0.19 | 0.34 |
| Actual density, g/sm³ | 2.04 | 2.04 | 2.05 | 2.04 |
| Resistivity, mOm/m | 536 | 539 | 530 | - |
| Sulfur content, % | 1.56 | 1.55 | 1.45 | 1.46 |
| Sodium content, % | | | | |
| Content of impurities in the ashes | | | | |
| Fe | 0.01 | 0.02 | 0.02 | 0.04 |
| Si | 0.07 | 0.01 | 0.004 | 0.02 |
| V | 0.03 | 0.02 | 0.02 | 0.03 |

| Table 2. Sieve composition of coke materials. |
|---------------------------------------------|
| Sieve composition | Grit 1 | Grit 2 | Screenings | Dust |
| + 6 mm | 0.5 | | | |
| - 6 + 4 mm | 85.0 | 0.3 | | |
| - 4 + 2 mm | 14.0 | 87.5 | 1.0 | |
| - 2 + 0.08 mm | 0.5 | 12.2 | 98.5 | |
| - 0.08 mm | | 0.2 | 0.5 | |
| + 0.16 mm | | | 5.0 | |
| - 0.16 + 0.08 mm | | | 20.0 | |
| - 0.08 mm | | | 75.0 | |
| Including − 0.05 mm | | | 53.0 | |

The properties of the heavy pyrolysis resin produced by the OJSC Angarsk plant of polymers are given in Table 4. The relatively high content of aromatic hydrocarbons, especially polycyclic, and a sufficiently high iodine value indicating a significant content of unsaturated hydrocarbons, indicate the propensity of heavy pyrolysis resins to compaction reactions to form products possessing high binding and caking properties [9,10].

An important advantage for the wide use of HPR is the low sulfur content. This makes it possible to obtain low-sulfur composite carbonaceous materials from pyrolysis resins, which is very important from the technological point of view (increasing the plant's running time) and the ecological situation in the electrolytic aluminum production shop.
### Table 3. Physicochemical properties of pitch B grade.

| Properties                             | Pitch of grade B |
|----------------------------------------|------------------|
| Softening temperature, °C              | 90.5             |
| Volatile matter yield, %               | 51.56            |
| Ash content, %                         | 0.15             |
| Group composition, %                   |                  |
| a - fraction                           | 36.6             |
| a.j - fraction                         | 11.5             |
| P - fraction                           | 31.0             |
| y - fraction                           | 32.4             |
| Coke residue, %                        | 59.1             |
| Actual density, g/sm³                  | 1.3304           |
| Sodium content, %                      | 0.0041           |
| Sulfur content, %                      | 0.58             |
| Viscosity                              |                  |
| 140 °C                                 | 41017.0          |
| 160 °C                                 | 5178.0           |
| 180 °C                                 | 967.0            |
| 200 °C                                 | 276.0            |
| 220 °C                                 | 74.0             |

### Table 4. Specification of heavy pyrolysis resin (HPR).

| Properties                                                                 | Grade A |
|---------------------------------------------------------------------------|---------|
| Density at 20 °C, g/cm, not less than                                     | 1.04    |
| Kinematic viscosity at 100 °C, mm²/s, not more than                        | 25      |
| Temperature of distillation of 3%-volume, °C, not less than               | 180     |
| Coking capacity, %, not more than                                         | 12      |
| Mass fraction of sulfur, %, not more than                                 | 0.3     |
| Mass fraction of water, %, not more than                                  | 0.3     |
| Mass fraction of mechanical impurities, %, not more than                  | 0.01    |
| Correlation index, not less than                                          | 125     |
| Mass fraction of sodium ions, %, not more than                            | 0.005   |
| Mass fraction of potassium ions, %                                       | 0.0005  |

3. **Experimental part**

The anode mass is produced according to TR 1914-004-4469951-99 in the anode mass workshop and consumed by the electrolysis shop. The evaluation of the quality of the mass is carried out according to the physicochemical, mechanical properties and the plasticity index.

All blends were prepared in a laboratory heated mixer with Z-shaped blades (mixing temperature of the mass was assumed to be 180 degrees Celsius). The dosage of the binder was selected from the calculation of the dry anode mass with a flow rate of 1.2 to 1.3 relative units. In mixtures with the addition of pyrolysis resin, the binder content was reduced in proportion to the dosage of the pyrolysis resin. The work was carried out in such a way as to minimize the influence of the physicochemical properties of the coke filler, the granular composition of the coke batch, and the technology of preparing the anode mass for the results of the studies. Thus, conditions were created to maximize the effect of the pyrolysis resin on the quality of the anode mass [11,12].

4. **The discussion of the results**

The results of technological testing of the anode mass are presented in Table 5.
The data show that the properties of coal tar pitch change significantly when adding HPR to it. The established patterns of changes in the properties of the compounded binder show that when the amount of pyrolysis resin is increased in the mixture, the rheological properties are substantially improved, which indicates the plasticizing ability of HPR. The addition of 1-10% TSP does not significantly affect the porosity and the specific electrical resistance of the mass [13,14].

Table 5. Physicochemical properties of dry anode mass with different dosage of HPR.

| #  | HPR content, % | Carboniferous pitch content, % | Resistance, mOhm-m | Apparent density kg/m | Reactivity in a current, mg/cm-h | Porosity, % |
|----|----------------|-------------------------------|--------------------|-----------------------|-------------------------------|-------------|
| 0  | -              | 26                            | 71.0               | 1520                  | 43.6                          | 24.49       |
| 1  | 1              | 25.74                         | 74.52              | 1480                  | 43.3                          | 26.65       |
| 2  | 5              | 24.7                          | 76.61              | 1480                  | 39.5                          | 26.85       |
| 3  | 10             | 26                            | 70.31              | 1480                  | 37.0                          | 26.68       |

The results of the anode mass studies indicate that in order to achieve similar yield values, the anode mass based on the pitch mixture and the pyrolysis resin requires a smaller (1.0-1.5%) binder dosage. This is due to the lower viscosity of a mixture of coal tar pitch and pyrolysis resin, which entails a natural increase in the yield coefficient. The dosage of the binder to the anode mass on the pitch mixture and the pyrolysis resin was higher by 1.0-1.5% compared to the weight on the coal tar pitch, so the proportion of coke from the binder is larger and the pore volume of the carbonizing binder is larger in the mass prepared in the mixture. On the basis of this, it can be said that the two components of the porosity of the three above should increase. Therefore, an increase in the porosity of the anode mass should be expected with an increase in the addition of the pyrolysis resin to the coal tar pitch. This is confirmed by the results of these studies. To this we can add that the porosity of coke from the binder depends on the process of pitch structuring in the near-surface layers of the coke-filler, which in turn depends on the group composition of the pitch [6].

The chemical composition and structure of coal tar pitch, as already mentioned, determine the complex physicochemical processes of its carbonization and its technological properties as a binder in the production of anode materials. The electrical conductivity, as well as the mechanical strength of the anode mass, is directly dependent on the coke-forming and sintering capacity of the pitch. The resistivity increases with increasing fraction of pyrolysis resin in the binder, and then sharply decreases. This means that the more the content of light-boiling fractions in the pitch, the better the wettability of the pitch, the more intensive the impregnation of coke with pitch and, accordingly, the electrical conductivity of the burned anode mass improves. This is explained by the growth of the OH⁻ fraction in the pitch with an increase in the content of the pyrolysis resin, which at certain amounts in the pits adversely affects the ordering of the coke structure from the pitch and, accordingly, worsens its electrical properties [15-17].

The chemical activity of the anode mass, estimated by the destructibility index in CO₂, which largely determines the electrolysis technology and anode consumption, is the main criterion for estimating the quality of the anode mass. In world practice, when choosing the electrode raw materials, the technological parameters of its preparation, and the composition of the anode mass, first of all they are guided by the need to ensure the destructible™ of the anode mass in CO₂ [18].

According to the study, when the content of the pyrolysis resin is increased, a regular decrease in the destructible™ of the anode mass in CO₂ is observed.

As a result of the conducted laboratory studies, the following conclusions can be drawn:

- established patterns of changes in the properties of the compounded binder show that when the amount of pyrolysis resin is increased in the mixture, rheological properties are significantly improved;
- the requirement of anode mass in the compounded binder is 1.5% less compared to the coal tar pitch of B grade for the same plastic properties;
the addition of a pyrolysis resin in the amount of 1-10% to high-temperature coal tar pitch (HTP) does not significantly affect the parameters: porosity and specific resistance of the mass. Their values are completely within the requirements for the brand AM-0. At the same time, the strength of the baked mass adversely affects the addition of pyrolysis resin at the level of 10%;

- heavy pyrolysis resin mixed with coal tar pitch acts as an inhibiting additive, which is confirmed by experimental data on the reactivity of anode mass samples;
- the use of a compounded binder in the form of a mixture will reduce the binder's dosage to the anode mass as compared to that of a coal-bearing HTP, improve the performance of the dry anode mass [19].

Taking into account the obtained test data, the expected technical and environmental effect was estimated.

Based on the results of calculating the expected consumption of anode mass per ton of aluminum and the amount of carcinogenic substances using coal tar high-temperature pitch and heavy pyrolysis resin, the following parameters were obtained as binder:

- reduction in the consumption of coal tar pitch by 6.7 kg/t aluminum;
- reduction of the content of benzapyrene in the anode mass by 12.4% [20-22].

5. Conclusion

Thus, the results of the tests demonstrated the possibility and feasibility of using high-temperature coal tar pitch in a mixture with modified heavy pyrolysis resin, which will significantly improve the ecology of aluminum production using Sodeberg's technology, in particular to reduce the content of carcinogenic substances in the air of the working area, and rationally use the non-target product of oil refinery - modified heavy pyrolysis resin.

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