The Use of Petroleum Components for Preparing a Pitch Binder for Anode Pastes

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Abstract

Aluminum production is associated with a high consumption of carbon materials, which are used as electrodes. Pitch is a binder for green anode paste that releases harmful substances into the environment during the baking process. The goal is to reduce emissions while maintaining the technical characteristics and anode consumption at the existing level. Various petrochemical products are considered as alternatives of the typical coal tar pitch and coking coal products. Two methods are described for producing the mixed petro/coal tar pitch. The requirements for two petroleum products used as raw material for non-carbon-coal pitch are detailed. The requirements for two petroleum products are detailed that can be used as raw materials for the mixed petro/coal tar pitch.

Keywords: coal tar pitch, anode paste, petroleum pitch, heavy gas oil from catalytic cracking, heavy resin from pyrolysis.

1. Introduction

The technology of aluminium smelting by the Soederberg method today is the main consumer of coal tar pitch, which is used as a binder in the anode paste. Technological operations related to the pitch melting, the anode paste mixing and its carbonization in the Soederberg anode produce harmful emissions [add references]. Therefore, there is a serious reason to look for a coal tar pitch substitute to ensure compliance with emissions standards in the production of aluminium. The most obvious substitute for coal tar pitch is a petroleum pitch [– 1, 2]. The similarity of the physical properties and chemical composition between coal tar pitch and petroleum pitch have prompted aluminium producers in the 70–80s to use petroleum pitch. But the quality of the anodes was worse than in case of a standard pitch.
In the 90s, the Venezuelan state-owned oil and natural gas company began to produce a petroleum pitch. This pitch was used by Alcoa aluminium company to produce a large batch of prebaked anodes. Anodes were installed in pots at one of the North American smelters. The quality of this pitch was comparable to the that of the standard anodes and specific consumption of the pots was not adversely affected when operating with those anodes. Unfortunately, reports about the production of such a pitch later than 2000 and its use as a pitch binder were not found [3, 4]. In the 90s, the Novo-Ufa refinery produced and supplied the petroleum pitch to the Bratsk aluminium smelter [5]. It was recognized that it is advisable to use such a pitch in a mixture with coal, since the use in pure form resulted in several process violations and an increase in specific consumption [5].

Petroleum coal tar pitch is a mixture of petroleum and coal origin products. To date, several Western smelters use the mixture of petroleum and coal tar pitch, which is dictated by environmental requirements. Manufacturers of such pitch mix (15–40) % of petroleum pitch with a coal tar pitch [6, 7]. In Russia, the petroleum pitch binder is not produced. Analysis of the specifications of Western smelters shows that petroleum pitches have a lower density, which indicates their less aromatic structure than that of coal tar pitch. They have lower alpha and alpha-1 fractions and give a low coke residue during carbonization. At the same time, the viscosity and the softening point of commercial petroleum pitches are higher than that of coal tar pitches. Petroleum pitches, as a rule, contain more light substances, distilled at a temperature of up to 360 °C, in some cases, an increased proportion of sulphur [6].

There are two approaches to produce petroleum coal tar pitches [8, 9]. The first method is the mechanical mixing of petroleum and coal tar pitches. The second method is the joint distillation of the initial resins, in which case the share of the petroleum component in the mixture of resins reaches 50 %. The resulting petroleum coal tar pitches have the same chemical composition, softening point, coking value etc. Tests of anode paste with the use of petroleum coal tar pitches demonstrate the key performance indicators of pots at the reference level. At the same time, reduction of benz[a]pyrene emissions by 20–40 % in comparison with pots operating with a standard anode paste was recorded instrumentally [6, 7].

2. Test Methods

Binder pitches for anode paste are characterised by certain parameters, some are determined dy standart methods as shown in Table 1.
Pitch density was measured at 25 °C using the picnometer method for water, after a pitch sample with particle sizes ranging from 1 to 2 mm had been degassed. The pitch softening point was determined using a standard Mettler apparatus as per ASTM D 3104. Dynamic viscosity was determined using Brookfield rotational viscometer. Coke residue was determined, after a pitch sample of 1 g had been kept in a closed cup at 550 °C for 2.5 hours. Toluene-insoluble material was determined as a residue following the extraction of a sample of 1 g after boiling in toluene and filtration. Quinoline-insoluble material was determined as a residue following the extraction of a sample of 0.25 g, after it had been kept in quinoline at 100 °C; the insoluble part was then separated at the centrifuge. Distillation at a temperature of 360 °C was determined using a pitch sample of 100 g, which was heated at such rate that would result in 0.03–0.05 grams of distillate per minute. Moisture was determined by azeotropic distillation of a pitch and toluene sample of 100 g using a special glass trap for water (Dean and Stark method). Sulphur content was determined based on the amount of sulphur oxides released when burning a weighed pitch quantity of 0.5 g in oxygen.

To determine wettability, a pitch sample of 5 g is placed above calcined petroleum coke and is kept at 200 °C for 2 hours. Following the test, the amount of coke that is adhered to the pitch is determined by weighing. Wettability is a proportion between the coke and pitch mass.

To determine benz[a]pyrene, 0.1 g of pitch is extracted with toluene, and is then converted to acetonitrile solution; a high-performance liquid chromatography method is further used. A chromatography column with bonded reversed phase C18 Supelcosil LC-PAH 150 x 4.6 mm, grain size of 5 µm, was used. A diode bar was used as a detector, with the detection wave being preset to 250 nm. The calibration curve was built based on standard benz[a]pyrene solutions in acetonitrile.

3. Characteristics of Pitch Binders

Differences in the chemical composition of the coal tar and petroleum pitches with similar softening points account for different properties, which are presented in Table 1. Aromatic compounds that are part of the petroleum pitches have a lower degree of condensation and a

The advantage of the oil products concerned is a low content of ash and sulphur. This makes it possible to minimise mineral admixtures and sulphur content in the resulting petroleum coal tar pitch.

Table 2. Minimum requirements for oil raw materials.

Indicators	Heavy gas oil from catalytic cracking	Heavy resin from pyrolysis
1. Kinematic viscosity, at 50 °C, mm^2/s, max	25	40
2. Correlation index, min	102	120
3. Coking capacity, % by weight, max	5	16
4. Mass fraction of water, %, max	0.2	0.5
5. Content of mechanical impurities, % by weight, max	no limitation	0.01
6. Ash content, %, max	0.08	0.1
7. Density at 20 °C, kg/m^3, min	1 045	1 030

5. Conclusions

We have investigated the possibility of using low-carcinogenic petroleum components in the production of pitch binder for anode paste. During the laboratory experiments we have identified that heavy gas oil from catalytic cracking with a minimum density of 1045 kg/m3 or heavy resin from pyrolysis with a minimum density of 1030 kg/m3, with low ash content and low sulphur content can be used to obtain petroleum coal tar pitch, applying the method of joint distillation together with coal tar.

6. References

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