Method of Defining the Degree of Impregnation of the Dry Aggregate with Pitch in the Process of Anode Production

Victor Buzunov, Sergey Khramenko, Semen Zykov, and John A. Johnson

Abstract

Anode paste is a mixture of coke and pitch. In a continuous mixer, the kneading provides for a uniform distribution of pitch and coke in paste, efficient wetting and maximum pitch impregnation of coke and ultimately, it defines the properties of the mix. The impregnation degree depends on the properties of coke and pitch, and the interaction between them, as well as the kneader design, mixing energy, kneading temperature and time. This paper describes a method for evaluating the degree of impregnation of the dry aggregate with coal tar pitch. The method is based on comparing the porosity of a particular dry aggregate fraction before kneading to the porosity of said fraction after kneading. The porosity before and after kneading is defined by the ratio between the bulk density and the apparent density. The method has proved useful and it helped reveal some characteristics on the process of kneading.

Keywords

Penetration degree • Coke-pitch composition
Open porosity • Coke porosity • Impregnation degree

Introduction

Anode pastes for aluminum production belong to highly concentrated coarse dispersed systems with properties determined by interaction of the coke aggregate with binding pitch in mixing and baking processes. Cokes used to produce the anode paste contain more than 20% of open pores sizing from 10 to 1000 μm. The main purpose of mixing is to produce coke-pitch composition with uniform distribution of coke aggregate components within the body of the anode paste and maximize impregnation of open porosity of coke with binding pitch. Impregnation depends on the size of coke pores and properties of the pitch: viscosity, surface-tension energy and wetting angle when interacting with the coke. In addition to the properties of initial raw materials the efficiency of mixing depends on process variables which can be optimized:

- stability and fineness of the dust fraction (dust particles block large pores and deny pitch access);
- pitch content in the anode paste (pitch should be sufficient to impregnate the porosity and provide for ductility in the interparticle space);
- preheating temperature of the aggregate and pitch (pitch properties strongly depend on the temperature);
- mixing temperature;
- productivity, design and condition of the mixer (kneader) (determine the residence time of the paste in the mixing zone and mixing energy).

Mixing variables can be optimized by «trial and error» method, but this approach results in rejection of considerable amount of product and, accordingly, increases costs. Desired results can be achieved by the method developed by «R&D Carbon Ltd.», called «dynamic process optimization» [1]. This approach involves installation of a modular mobile laboratory in the anode plant; this, however, is fairly long and costly procedure. In any case to optimize mixing requires a prompt and reproducible method of evaluating the impregnation degree of the coke aggregate with coal tar pitch.

To evaluate efficiency of mixing a good method is that of Pechiney—it directly evaluates impregnation degree of porosity before and after mixing the anode paste by mercury porosimetry [2]. The drawback of the method is special costly equipment (mercury porosimeter), long measurement time, and necessity of having a dedicated room meeting labor protection requirements to handle hazard substances.

V. Buzunov (✉) · S. Khramenko · S. Zykov · J. A. Johnson
RUSAL ETC LLC, 37/1 Pogranichnikov Str, Krasnoyarsk, Russian Federation660111
e-mail: viktor.buzunov@rusal.com

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Discussion

The paper presents effective and reproducible method of evaluating the impregnation degree of the coke aggregate with coal tar pitch. The method is to compare total porosity of a certain coke fraction in vibrocompacted state prior to mixing and porosity of ground to the same fraction of anode paste after mixing. The advantage of the method is that it is implemented on the basis of standard techniques available in most plant laboratories: evaluation of vibrobulk density (VBD) according to ISO 10236 [3] and evaluation of density using helium ГОСТ Р ИСО 21687 [4].

The concept of the method is that the bulk density of grain porous material is determined by the density of packing, size and apparent density of grains. This is true both for the coke and for the ground anode paste. During mixing the molten pitch fills the coke pores and increases its density. As 70–85% of the anode paste for an aluminum cell is coke, it is safe to assume that the particles of the fractions of ground anode paste and coke of similar size will be close in size and shape, and coke fraction VBD and VBD of the fraction of ground anode paste will differ by the value determined by the degree of filling the coke pores with coal tar pitch. In [5] VBD of different cokes was shown to correlate with the results of mercury porosimetry evaluation apparent density of coke—this validates the use of VBD as a characteristic of coke porosity. This provision of the method is proved by comparison of the photographs of the coke and anode paste shown in Fig. 1. From the Fig. 1. it can be seen that the particles of the coke (A) and anode paste (B) are of similar size and shape.

The cokes during grinding are known to increase their VBD [6], due to decrease of the interparticle space and decrease of porosity of the coke particles. In contrast to the coke, uncalcined anode paste is a non-uniform material consisting of calcined coke with actual density 2.04–2.06 g/cm^3 and hard pitch with actual density 1.30–1.33 g/cm^3. Solidified coal tar pitch fills the intergrain space and blocks large coke pores to form closed porosity. When the anode paste is ground the closed porosity opens, less dense pitch partially remains in the coke pores and partially transfers into the oversize fraction to enrich the fraction with light material and reduce VBD. A series of experiments have been carried out to evaluate anode paste VBD depending on the fraction size. Results are shown in Table 1 and Fig. 2. In Fig. 2 we can see that the coke VBD characteristically increases while starting with grinding the anode paste VBD increases due to decreasing intergrain space and then decreases due to increasing number of pitch particles in the oversize product.

To take into account variation of anode paste VBD in grinding and calculate total porosity of coke or anode paste charge including the interparticle space volume and volume of open porosity it is necessary to define apparent density of grain of coke and anode paste, respectively. Then, the total porosity of the charge can be calculated according to a standard formula:

$$\prod_0 = \frac{D_{APP} - D_{VBD}}{D_{APP}} \cdot 100\% \quad (1)$$

where:

Π_0 is the total porosity of fraction charge;
D_{APP} is the apparent density of coke or anode paste grains;
D_{VBD} is the vibrobulk density of coke or anode paste fraction.

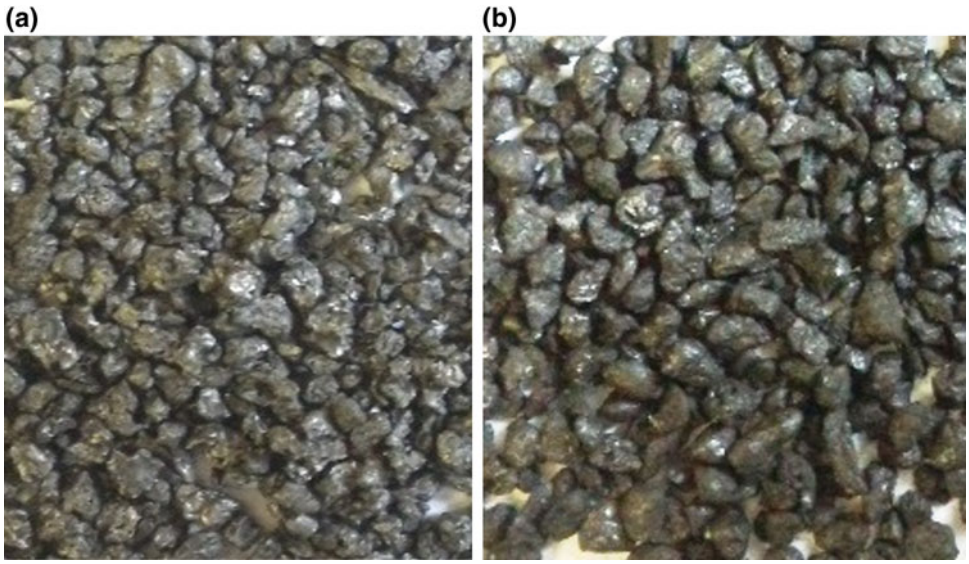

Fig. 1 Coke (**a**) and anode paste (**b**) fractions sizing −2.0 + 1.0 mm

Table 1 Porosity of coke and anode paste charge was calculated by formula (1)

Fraction, mm	VBD, g/cm^3		Apparent density, g/cm^3		Porosity, %	
	Coke	Anode paste	Coke	Anode paste	Coke	Anode paste
−10 + 8	0.64	0.82	1.999	1.709	68.0	52.0
−8 + 4.75	0.71	0.9	1.999	1.723	64.5	47.8
−4.75 + 2.36	0.79	0.95	1.999	1.758	60.5	46.0
−2.36 + 1.18	0.86	0.96	2.001	1.784	57.0	46.2
−1.18 + 0.5	0.9	0.91	2.012	1.834	55.3	50.4
−0.5 + 0.075	0.93	0.87	2.017	1.857	53.9	53.2
−0.075 + 0.063	0.97	0.85	2.03	1.903	52.2	55.3
−0.063	1.01	0.83	2.052	1.918	50.8	56.7

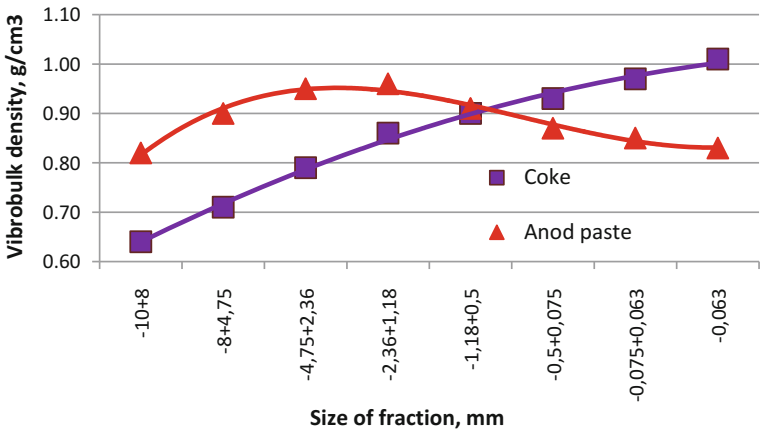

Fig. 2 Vibrobulk density of coke fraction and anode paste depending on the fraction size

Apparent density of ground coke and anode paste fractions was evaluated with helium density meter AccuPyc 1340. Results are presented in Table 1 and Fig. 3.

From Fig. 3 it can be seen that the apparent density of coke grains for the particles' size ranging 1.18–10.0 mm varies insignificantly, when ground below 0.5 mm the apparent density starts growing due to destruction of closed porosity and goes to the density value of nonporous material (so called, actual). In contrast to coke the apparent density of anode paste grains grow linearly in grinding remaining always below the density of coke due to the presence of less dense particles of coal tar pitch.

Porosity of coke and anode paste charge was calculated by formula (1); results are shown in Fig. 4 and presented in Table 1.

From Fig. 4 we see that −4.75 + 2.36 mm and −2.36 + 1.18 mm fractions exhibit the smallest porosity. I.e. these fractions contain maximum number of pores blocked

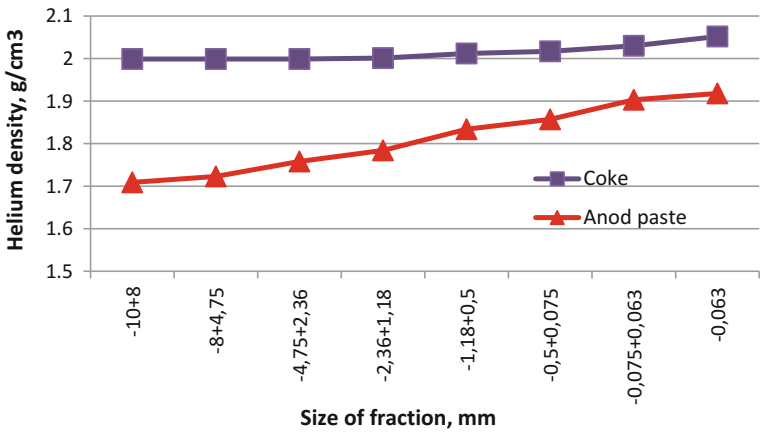

Fig. 3 Apparent density of coke and anode paste grains depending on the fraction size

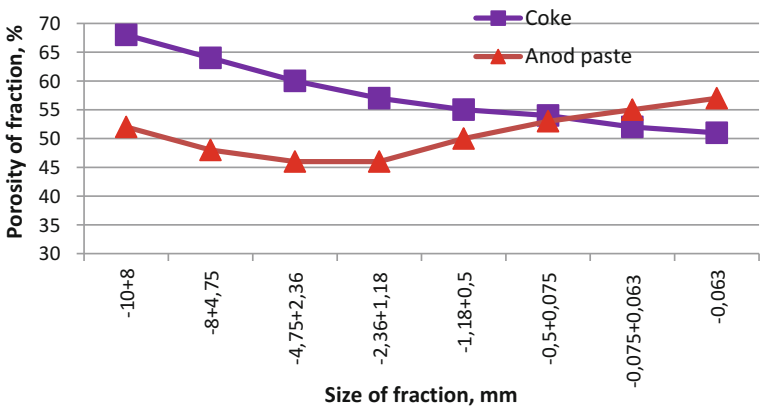

Fig. 4 Total porosity of coke and anode paste grains depending on the fraction size

with pitch. Therefore, the porosity of these fractions can be used to evaluate impregnation of coke with coal tar pitch when mixing the anode paste. To exclude effect of internal distribution of particles in the fraction on evaluation of the impregnation degree we have chosen a more narrow fraction −2.36 + 1.18 mm. Then the impregnation degree (*Id*) can be evaluated by formula:

$$Id = \frac{P_{coke} - P_{anod\ paste}}{P_{coke}} \cdot 100\% \qquad (2)$$

where:

P_{coke} and $P_{anod\ paste}$ are the porosity of coke and anode paste calculated by formula (1)

Impregnation of the coke aggregate porosity depends on numerous factors, among them basic factors are: properties of cokes and pitches, their interaction, surface tension, wetting angle, mixing temperature, mixing time, mixer design equipment wear.

The method developed was used to evaluate effect of the above mentioned factors on impregnation of the anode paste. Examples of such studies are given below in Figs. 5 and 6.

Figure 5 shows time variations in the nature of mixing the anode paste in terms of impregnation degree.

From Fig. 5 we see that at the outlet of the mixer the anode paste is non-uniform in terms of impregnation. This can be assumed to be due to cyclic operation of pitch

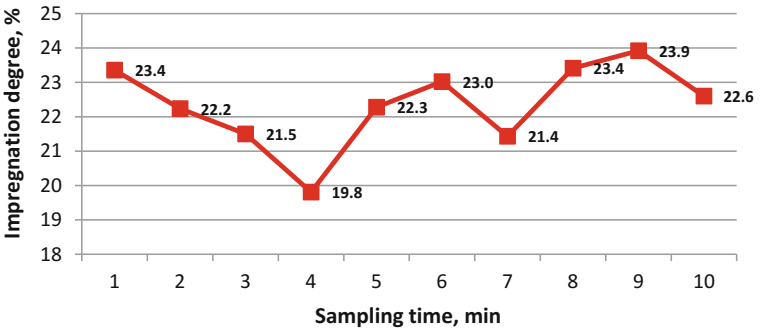

Fig. 5 Variation of anode paste impregnation in mixing process

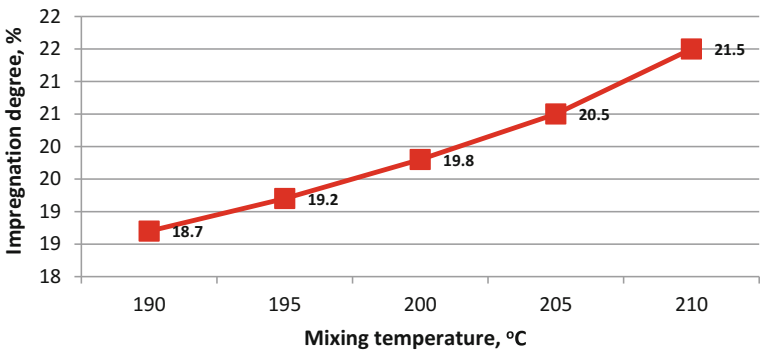

Fig. 6 Effect of mixing temperature on impregnation degree of coke aggregate

dispenser: loading—dispensing. When the weight feeder is loaded pitch dosing is suspended.

Temperature is among the factors that can be easily varied under process conditions and facilitate deeper penetration of pitch into the coke pores. Figure 6 shows the effect of temperature on impregnation of the coke aggregate.

Figure 6 shows that coke impregnation with coal tar pitch improves with increase of mixing temperature. This is associated with variation of thermodynamic characteristics of the pitch. Viscosity, surface tension and the angle of wetting the coke with coal tar pitch decrease with increasing temperature; this improves the impregnation conditions.

Conclusion

A method to control quality of mixing in terms of impregnation degree of the coke aggregate with coal tar pitch has been developed. The method is based on standard techniques and can be implemented in plant laboratories of aluminum smelters. The method is to compare porosity of a coke fraction with the porosity of anode paste after mixing. Porosity of coke and anode paste after mixing are determined by the ration between the vibrobulk and apparent density of a certain fraction.

Industrial tests proved the efficiency of the method to evaluate factors influencing the quality of mixing the anode paste.

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