Production of graphene concentrates based on synthetic oils in rod drum mills

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Abstract. The article presents the results of the refinement of the mathematical model of the process of liquid-phase shear exfoliation of graphite and experiments on the production of graphene concentrates based on synthetic oils in a rod drum mill. The model parameters were identified and its adequacy to the real process was experimentally confirmed. It is given the dependence of the coefficient of light absorption, which characterizes the average integral value of graphene layers in suspension particles and their concentration on the processing time.

1. Introduction
Beginning in the second half of the nineteenth century, grinding in ball drum mills has been widely used in various industries, and now grinding by balls is one of the largest industries in the world [1]. A little later, planetary mills were invented, but the rotating drum and spherical grinding bodies play the main roles in the grinding process. The intensity of grinding and the quality of the finished product depend on the mode of movement of the grinding balls and the material in the cross section of the rotating drum. Modes of movement of the material in the cross section of the drum are well defined [2]: avalanching, slumping, rolling, cascading, cataracting, and centrifuging. In practice, most often use two modes cascading [3, 4] and cataracting [5, 6] and these two modes are the most well studied, both theoretically and experimentally [7].

In recent decades, a number of methods have been developed for producing graphene plates containing several layers using ball mills. For example, in the work [8] a top-down method was developed for producing colloidal dispersions of graphene sheets. After 30 hours of the shear-force-dominated grinding and centrifugation, single- and few-layer graphene sheets were readily prepared and homogeneously and stably suspended in the solvent medium N,N-dimethylformamide, at a concentration up to 0.08 mg/ml, achieving a yield higher than 32.0wt %. The graphene materials in the colloidal suspension were characterized using scanning and transmission electron microscopy and atomic force microscopy.
Graphene nanoplatelets (GNPs), one of the most widely used forms of graphene, consist of stacks of several graphene monolayers and may be of different thicknesses. Graphene plates, which consist of 7-10 monoatomic layers, are called multilayer graphene [9].

In-Yup Jeon et al [10] reported that graphene nanofilters selectively functionalized at the edges (EFGnP) with various functional groups were efficiently prepared simply by using ball-grinding of graphite in the presence of hydrogen, carbon, a mixture of dioxide, sulfur trioxide or carbon dioxide. The authors believe that due to the universality of mechanochemical reactions that occur during the processing of graphite in a ball mill, various functional groups can be introduced into the broken edges of graphite with the presence of appropriate chemical vapors, liquids or solids in a ball crusher.

As it is known, grinding is the process of repeated destruction of the body under the action of external loads [11]. As a result of this process, the specific surface area of the material to be ground increases. The main grinding mechanisms: blow; abrasion; cutting; cracking. Since abrasion occurs mainly from shear stresses, this grinding mechanism is closest to the delamination of graphite. It should be noted that the destruction of particles by shear is considered the most economical method of grinding [12]. The ratio of average particle diameters before and after grinding is called the degree of grinding (1):

$$i = d / d_0,$$

where $d$ is the average particle diameter after grinding, $d_0$ is the average diameter before grinding.

By analogy, you can enter the parameter degree or degree of exfoliation $i_E$ and given that the specific surface depends on the number of layers, define it as follows:

$$i_E = n / n_0,$$

where $n$ is the average number of layers after exfoliation, $n_0$ is the average number of layers in the particles of the original graphite.

In [13, 14], we reported that graphene plates produced in a rod drum mill increase the tribological characteristics of lubricants, including frost-resistant ones. To increase the quantity and quality of graphene plates that are produced in a rod mill, it is necessary to optimize the process parameters and this can be done with the help of mathematical modeling.

To describe this process, a mathematical approach of random Markov processes, discrete in space and time, was implemented [13]. In the present work, we continue to improve this model and conduct experiments on the production of graphene concentrates in a rod drum mill.

2. Mathematical model

Earlier, we used the mathematical apparatus of random Markov processes in simulating the process of liquid-phase shear exfoliation of graphite in a rotary-type apparatus [15]. In fact, the separation of graphite occurred as a result of the simultaneous hard contact of the particle with the fixed and moving surfaces. In our case, the same exfoliation mechanism takes place and in [16] we proposed a mathematical model of the process, but did not consider the issues of identifying model parameters and checking its adequacy.

The object of modeling is the system, which is a suspension of graphite particles of a specific particle size distribution in oil with a specific concentration of graphite.

The state of the system can be characterized by the vector $S(k)$:

$$S(k) = [c(1, k), c(2, k), \cdots, c(i, k), \cdots, c(N, k)],$$

where $k$ is the transition number, $i$ is the cell number, $c$ is the amount of particles with a certain number of graphene layers in the cell, and $N$ is the total amount of cells.

The values of the elements of the initial state vector $S(0)$ of the system are determined by the characteristic of the original graphite and its concentration. The transition of the system from one state to another occurs suddenly during a time interval $\Delta t$. The change in the system over time can be expressed in the following relationships:
\[ S(1) = S(0)P, \]
\[ S(2) = S(1)P, \]
\[ \ldots \ldots \ldots \]
\[ S(i) = S(i-1)P, \]
\[ \ldots \ldots \ldots \]
\[ S(k) = S(k-1)P, \]

where \( P \) is the matrix of transition probabilities.

The matrix \( P \) has the following form:

\[
P = \begin{pmatrix}
p_{11} & p_{12} & \cdots & p_{1n} \\
p_{21} & p_{22} & \cdots & p_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
p_{n1} & p_{n2} & \cdots & p_{nn}
\end{pmatrix}
\]

where \( p_{ij} \) is the probability of transition of particles from the site \( i \) to the site \( j \).

In this model, it is necessary to identify the parameters \( \Delta t \) and \( p_{ij} \). It is logical to assume that the parameter \( \Delta t \) is directly proportional to the angular velocity of rotation of the drum (\( \omega, \text{s}^{-1} \)), because the greater this speed, the more often the particles will fall into the zone between the grinding rods and the inner surface of the drum, where shear exfoliation of these particles is realized.

If \( c \) is the number of particles with a certain number of graphene layers in a cell, then after one delamination cycle, two particles with a smaller number of layers are formed from one particle. Let us assume that the distribution of layers in two particles is equally probable, i.e. if the particle before stratification had 6 layers, then the following combinations are possible with the formation of two particles: 1 layer + 5 layers; 2 layers + 4 layers; 3 layers + 3 layers. Since (to correct \( P_{ii} \)) is the probability that a particle does not fall on a given cycle in the zone of delaminating or the process of delaminating does not occur, the probability can be determined as follows:

\[
p_{i,j} = p_{0i}(N-i),
\]

where \( p_{0i} \) is the probability of the participation of particles of the \( i \)-th cell in the exfoliation process at this transition.

It should be noted that the following condition is always fulfilled:

\[
p_{0i} + p_{ii} = 1,
\]

because at this transition the separation of one particle into two will occur or will not occur and there are no other options.

This model allows you to calculate the concentration of graphene structures in suspension. First of all, it is necessary to decide which particles will be taken into account, in other words, particles with how many layers will be taken into account. For example, it is necessary to calculate the concentration of graphene plates with \( B \) layers or less. Next, you need to determine the number \( N_B \) of the cell in which there are particles whose \( B \) graphene layers. After that, it is necessary to sum the masses of all the particles that are in the cells from \( N_B \) to the \( N \):

\[
M_{BN} = \sum_{i=B}^{N} i \cdot m \cdot c(i),
\]

where \( M_{BN} \) - the mass of particles with the number of layers from \( B \) to \( N \), \( m \) - the mass of one layer of graphene.
The mass concentration of graphene in the suspension $C_{IB}$ is equal to:

$$C_{IB} = \frac{M_{BN}}{M_{S}},$$  \hspace{1cm} (9)

where $M_S$ - the mass of the suspension.

The identification of the parameter of the mathematical model was carried out as follows. When the concentration of graphite in the initial suspension was 10%, the rotational speed of the drum was equal to the critical speed ($\omega_{CR}$):

$$\omega_{CR} = \sqrt{\frac{g}{R}},$$  \hspace{1cm} (10)

g – acceleration of gravity, $R$ – inner radius of the drum.

The concentration of graphene plates with the number of layers from 1 to 15 was determined at a treatment time of 3, 6, 9, 12 and 15 hours. Further, by changing the value of the parameter $p_{i0}$ from 0.1 to 0.9 with a step of 0.1, we found such a value $p_{i0}$ at which the deviations of the calculated values calculated by the formula (9) from the experimental values were minimal.

Since the concentration of graphite in the initial mixture is taken into account in the vector of the initial state, we assumed that when this concentration changes, the numerical value of the parameter should not change. In order for the mathematical model to take into account the speed of rotation of the drum during one transition of the system from one state to another, we adopted the time of one revolution of the drum. Thus, with an increase in the speed of rotation of the drum, the time required for the system to transition from one state to another, that is, the time for transformation of the state vector $S(i-1)$, in accordance with the relations (4) to the state vector $S(i)$ decreases.

So, the model allows a quantitative assessment of the exfoliation process, but the main purpose of creating this model is to study the qualitative patterns of the influence of different parameters on the distribution of particles by the number of graphene layers. Thus, conducting numerical experiments using a mathematical model, we can better understand the process of graphite shear stratification and find new technical solutions to increase the intensity of this process.

Questions about the effect of the diameter of the drum and the coefficient of its filling with the suspension on the intensity of the exfoliation process will be discussed below.

3. Experiment

First of all, we investigated the movement of rods in the cross section of a smooth rotating drum with a diameter of 400 mm. Earlier [13], we found that the rods periodically rise up with the rotating drum, and then slide down to the starting position. Shift effects on particles of graphite can occur only when the rods slide down. High-speed video showed that the rods do not always slide on the inner surface of a rotating drum, but sometimes rotate. When the rods rotate about their own axis, shear forces on the particles do not act and there is no exfoliation process. Thus, during one revolution of the drum, only for a very short period of time, the separation of particles of graphite occurs and low-layer graphene is formed. The result is a low intensity shear exfoliation process. We have developed a rod drum mill design in which the rods are interconnected by a flexible cable and they cannot rotate about their own axes [13]. So the rods periodically rise up and then slide down. A new problem was that the time for lifting the rods up and the time they were sliding down were approximately the same. Thus, half the residence time of the rods in the rotating drum of the process of exfoliation of graphite does not occur. We solved this problem by connecting the rods with the base, as shown in figure 1. In this embodiment, the rods all the time slide relative to the inner surface of the rotating drum. It should be noted that the sliding of the rods occurs even when the rotational speed of the drum is greater than the critical speed ($\omega_{CR}$).

In our opinion, at the best option, the speed of rotation of the drum should be maximum, and the number of rods should be such that they occupy one-fourth of the circumference of the drum, as shown in figure 1. We found that at the speed of rotation of the drum 1.5 from the critical speed, rods
slide well on the inner surface of the drum. We used these recommendations during the process of exfoliating graphite in a laboratory mill.

Experiments with real exfoliation of graphite were carried out on a laboratory ball mill with rods (figure 2), performed in accordance with [13].

Figure 1. Rods connected by a flexible cable in a rotating drum.

Figure 2. Laboratory ball mill (a) and grinding rods (b).

Experiments were performed in the following sequence. Previously, using the paddle mixer, the initial suspension was prepared from graphite powder and synthetic oil. In the experiments used crystalline graphite brand GS-2. The mass concentration of graphite was varied from 5 mg / ml to 30 mg / ml. This suspension was loaded into the drum, where there were grinding rods. The number of rods varied from 3 to 12. The rods were used in three diameters: 8, 10, and 12 mm. The speed of rotation of the drum was changed from 28 to 140 rpm.

Every three hours the drum was stopped, three samples of the suspension were taken. These samples were centrifuged, the precipitate was removed and the concentration of graphene structures was determined. Since there are no proven methods for determining graphcone concentration in oil, we developed a new method. This method is based on the difference in the density of oil and graphene: the density of oil is about 800 kg / m; The density of graphene is about 2000 kg / m. The
concentration was determined as follows. We measured 25 ml of the suspension with an accuracy of 0.04 ml and weighed this suspension with an accuracy of 0.0001 g. The percentage concentration of graphene was determined as follows:

$$c_G = \left(\frac{G_S - \gamma_D V_S}{\gamma_O V_S}\right) \cdot 100 / G_S$$

(11)

where $G_S$ is the weight of the sample suspension, mg; $\gamma_O$ - real oil density, mg / ml; $V_S$ - sample volume, ml.

If the concentration value is multiplied by the total volume of the suspension, which we get after centrifuging and removing the sediment and divide by the processing time in the drum, then we obtain the performance value.

4. Results and discussion

Figure 3 shows the characteristic dependence of productivity on the concentration of graphite in the initial suspension. In this case, the speed of rotation of the drum was equal to the critical, and the processing time of the suspension is 15 hours. We used the performance values at graphite concentration in the initial suspension 10% to determine the numerical value of the parameter ($p_{i0}$) and then calculate using the formula (6) the remaining elements of the transition probability matrix (5). These values were used in calculating the performance of a rod drum mill at other values of its rotational speed. Figure 4 shows the characteristic dependencies of performance on the relative speed of rotation of the drum. In this case, straight lines are the calculation according to the mathematical model for a laboratory drum with a diameter of 160 mm and relative speeds of rotation ($\omega / \omega_{CR}$) 1, 1.25, 0.5, respectively. The concentration of graphite in the initial mixture was 10%. It can be seen that the calculated dependences 1, 2, and 3 are in satisfactory agreement with the experimental data, those confirm the assumptions we made in deriving the formula.

Figure 3. The dependence of the performance of the mill on the concentration of graphite in the initial suspension.
The results of the experiments that we conducted with different numbers of rods showed that with an increase in the number of rods, the intensity of the exfoliation process increases, but we have not yet managed to find a relationship that adequately describes the effect of the number of rods on the intensity of graphene concentration in the finished suspension.

**Conclusion**

A mathematical model of the process of liquid-phase exfoliation of graphite is considered and the problem of identifying its parameters is solved. Conducted experimental studies to determine the effect of concentration graphite in the original suspension and the speed of rotation of the rotor on the performance of the rod drum mill. It has been established that the proposed mathematical model adequately describes the actual process of exfoliation of graphite and can be used to determine the parameters of the mill and the modes of its operation, which are necessary for ensuring a given performance.

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