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STATISTICAL METHOD FOR DETERMINATION OF THE SPECIFIC SURFACE OF POWDERS AND BULK MATERIALS

STATISTICKÁ METODA PRO URČOVÁNÍ MĚRNÝCH POVRCHŮ PRÁŠKŮ A SYPKÝCH MATERIÁLŮ

Abstract

Calculation methods for determination of the specific surface of powders and bulk materials often follow approximation of the ideal particle surface, most often the smooth sphere. During calculations of the specific powder surface the character of the probability distribution that controls the size of powder particles is not taken into account. This is the logarithmic-normal distribution. Usually, even the dispersion of particle sizes from the average size is not taken into account, in spite of the fact that the average particle size does not correspond to the particle size belonging to the average surface or volume. The current status of these problems is described in this article. The mentioned shortcomings in the calculation of the specific surface of powder particles can be eliminated by the method of calculation that uses the statistical-mathematical tools suggested by the authors of this article. The fact that both powders and bulk materials have a logarithmic-normal distribution of the probability of particle sizes is taken into account. The method that enables the calculation of the specific surface of powders and bulk materials is the subject of this article.

Abstrakt

V technickém a přírodovědeckém výzkumu je velmi často nutné znát hodnoty měrných povrchů prášků či sypkých hmot. Prvním stupněm takového výpočtu je pak aproximace zrn některým geometrickým útvarem s hladkým povrchem, nejčastěji hladkou koulí. Nejenom samotná aproximace způsobuje chybu stanovení měrného povrchu a dalších parametrů materiálu. Při výpočtu měrného povrchu prášku se dále nepřihlíží k charakteru rozdělení pravděpodobnosti, kterým se rozměr částic prášků a sypkých hmot řídí. Jedná o logaritmicko-normální rozdělení. V článku je navržena statistická metoda zpřesňující výpočet měrných povrchů prášků a sypkých hmot a jsou prezentovány také další statistické parametry těchto materiálů.

1 INTRODUCTION

The work presented in this article is focused on explaining the possibility of a statistical approach for calculation of the specific surface of powders and bulk materials [1]. The specific surface signifies the surface related to the unit of weight or volume of a given powder. This quantity is measured while looking for absorbents, during determination of the surface energy of solid materials, etc. The size of a surface area can be determined by two methods. One of them is use of an apparatus for determination of the real size of surfaces by the BET method based on gas adsorption [2]. The other

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method, usable wherever it is sufficient to determine the size of the surface approximating its structure by a smooth plane, is based on statistical-mathematical calculations. The authors of this article focus on making this statistical-mathematical approach more exact.

2 THEORY

Observing particles under a microscope, irregular shapes can be seen [3]. In order to determine the specific surfaces of these particles by the statistical and mathematical methods more easily, the irregular shapes are replaced by well-defined geometrical shape, the sphere, throughout the presented input analysis [4]. This approximation is used also in laser analyzers used for grain size analysis – detected powder particles are considered to be spheres. Each simplification causes inaccuracies, however. But during determination of the specific surfaces of powders and bulk materials simplification is necessary, and it is therefore possible to accept it. A photograph from a microscope (Fig. 1) shows a shape difference between almandine (garnet) minerals with the size interval (100-800) μm and bulk zirconium with the size interval (50-300) μm. It is evident that the particles are irregular [5]. Nevertheless, approximation by spheres is possible. It is apparent that zirconium particles are rounder than almandine ones. However, the shapes and complexity of particle surfaces depend also on the technological processing of the material.

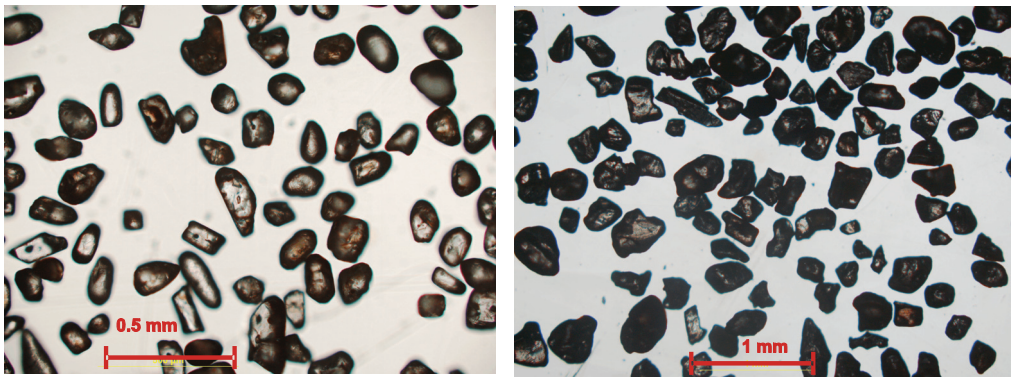

Fig. 1 Minerals in bulk state: zirconium on the left, almandine on the right

2.1 Application of logarithmic-normal distribution theory to powders

It is generally known that the size of the material or powder particles d_i is controlled by the logarithmic-normal distribution [2, 6], i.e. by normal distribution of quantities $\ln(d_i)$. This distribution is coherent in real cases. The sizes of different particles can be ascertained by microscopic observation or by laser grain size analyzers. However, there are other methods of determining particle size [7].

Based on knowledge of the expression for a logarithmic-normal distribution of powder particle sizes [6] the transformation of a random quantity d_i to the size distribution of surfaces or volumes of a given powder can be performed [8]. For the given geometrical shapes of particles the following relationship [6] is valid between the sought quantity Z and the random quantity X_i

$$Z = kX_1^{a_1} X_2^{a_2} \ldots X_n^{a_n} \tag{1}$$

Z is the sought quantity (surface or volume), k is a constant, X_j are independent quantities (e.g. a sphere diameter, the side of a cube, the height of a cylinder and so on) and a_j are exponents, $j \in \{1,\ldots,n\}$.

The average volume or surface of a general particle shape can then be determined [6] by the equation:

$$E_Z = k \cdot \exp\left[\sum_{j=1}^{n}\left(a_j \mu_j + \frac{1}{2} a_j^2 \sigma_j^2\right)\right] \tag{2}$$

where μ_j is a logarithmic average value of the quantity X_j, σ^2 is a logarithmic dispersion, and a_j are exponents.

For the average value of a spherical particle volume [6] the following is valid:

$$E_V = \frac{\pi}{6} \exp\left(3\mu + 4.5\sigma^2\right) \tag{3}$$

The average value of a spherical particle surface [6] is determined by the equation

$$E_S = \pi \exp\left(2\mu + 2\sigma^2\right) \tag{4}$$

The μ parameter is a logarithmic average particle value (grain diameter) defined as

$$\mu = \frac{\sum_{i=1}^{n} \ln d_i}{n} = \ln(d_{0.5}) \tag{5}$$

where d_i are particle sizes, n is the number of measured particles and $d_{0.5}$ is the median. The parameter σ^2 is the logarithmic dispersion defined by the expression (6)

$$\sigma^2 = \frac{\sum_{i=1}^{n} (\ln d_i - \mu)^2}{n-1} \tag{6}$$

It follows from the presented relationships that the average particle size $\bar{d}$ does not belong to the particle with an average surface or an average volume.

2.2 Traditional approaches to calculation of specific surfaces of powders

The general definition of the specific powder surface S_S is expressed by the equation

$$S_S = \frac{S}{m} \tag{7}$$

where S is the total surface of the powder and m is the powder weight.

The simplest way to express specific surfaces results from knowledge of the average size of powder particles [2, 9, 10, 11, 12]. The specific surface of the spherical particles is then calculated as follows:

$$S_S = \frac{S}{m} = 6 \cdot \frac{N\pi\bar{d}^2}{N\rho\pi\bar{d}^3} = \frac{6}{\rho\bar{d}} \tag{8}$$

N is the total number of particles and ρ is the material density.

Particle size distribution is often disregarded in practical applications. In better cases [10, 12] knowledge of the particle distribution in individual discrete size fractions is used

$$S_S = \frac{6}{\rho} \sum_{i=1}^{n} \frac{1}{\bar{d}_i} \tag{9}$$

where $\bar{d}_i$ is the average value of the particle size of the i-th fraction. The fractions are most often obtained by a sieve analysis and depend on the parameters of the sieves used. The expression (9) is acceptable not only for distributions with the log-normal distribution, but also for manmade prepared powders that do not have the log-normal distribution.

However, these approaches have three basic shortcomings, which can significantly distort the correct value of the specific surface:

1. The average particle size is not directly related to the average volume or the average surface of particles (this is valid also for the normal distribution). A particle with the average size has a mean size $\bar{d} = \exp\left(\mu + 0.5\sigma^2\right)$, a particle with the average surface has a mean size $\bar{d}_S = \exp\left(\mu + \sigma^2\right)$ and a particle with the average volume has a mean size $\bar{d}_V = \exp\left(\mu + 1.5\sigma^2\right)$.
2. There is no quantity that would characterize a dispersion of d_i values in the expressions (8) and (9).
3. Distribution of powder particle sizes is not governed by the normal distribution.

2.3 Proposal of a statistical method for calculation of the specific surfaces of powders

The team of authors of this article suggests the fundamental use of statistical-mathematical tools for calculation of the specific surfaces. Using the expressions (3) and (4), the main expression (10) is derived for powders and bulk materials with spherical particles

$$S_S = \frac{S}{m} = \frac{NE_S}{\rho NE_V} = \frac{6}{\rho \cdot \exp\left(\mu + 2.5\sigma^2\right)}. \tag{10}$$

The aforementioned calculation respects the logarithmic-normal distribution of powder and bulk material particle sizes and also the dispersion of the given distribution. As will be shown later, in specific cases this approach significantly changes the values of the specific surfaces of powders in comparison with the traditional methods of calculation mentioned above.

2.4 Graphical comparison of theoretical approaches

The difference between the usually used equation (8) and the newly proposed equation (10) is presented in Figure 2, which graphically compares the values of the specific surfaces of almandine mineral powder ρ = 4,080 kg/m^3, average particle size 100 μm determined use the two approaches mentioned above. The x-axis shows the value of the 90% fractile of particle size, indicated in the technical literature by the symbol $d_{0.9}$. The x values smoothly vary the dispersion σ^2 of the particle size of a hypothetical powder. The y-axis shows the values of the specific powder surface S_S with a certain dispersion of particle sizes from the average particle size $\bar{d}$. The unit m^2/g is used in the graph for a specific surface and the presented results because it is one of the units very frequently used in both the technical and the scientific literature (apart cm^2/g) and it is more suitable for values set in the cases analyzed in this paper.

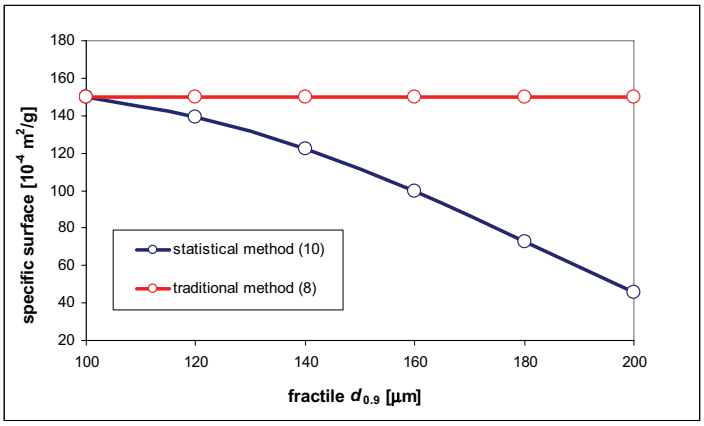

Fig. 2. Graphical comparison of methods for determination of specific surfaces of powders

The size of the specific surface S_S determined by the equation (10) depends on the logarithmic dispersion σ^2 . For clarity, the dependency of the specific surface on the fractile $d_{0.9}$ is shown in Figure 2. We can derive the relationship between quantities σ^2 and $d_{0.9}$ from the generally known relationship for values of the distribution function of standardized normal distribution

$$F(d_{0.9}) = \Phi\left[\left(\ln d_{0.9} - \mu\right)/\sigma\right] \tag{11}$$

where $F(d_i)$ is the tabulated value of the distribution function of the normal distribution, since the logarithmic values of d_i have a normal distribution. The quantity $\Phi(d_{\text{norm}})$ shows the size of the distribution function of the standardized normal distribution and d_{norm} is then the standardized value of d_i. For $d_{0.9}$ and the normal distribution the table value d_{norm}=1.29 is valid.

With the exception of the hypothetical case, when all the particles have the same size, the quantitative differences between specific surface values determined by the two methods can be observed (see Figure 2). According to Figure 2, the specific surface for $d_{0.9}$ with the value 200 μm determined from the equation (8) is 3.3 times larger than the one calculated by the equation (10). Other cases can show even bigger differences. For example, the hypothetical average particle size of almandine powder, i.e. 49.2 nm with $d_{0.9}$=100 nm (median $d_{0.5}$=10 nm), yields the value calculated from the equation (8), 29.9 m^2/g, and from the equation (10) only 0.051 m^2/g, which is 586 times lower. Therefore, it is correct to use the equation (10), not (8) for similar calculations. The equation (8) overestimates the specific surface size, in some cases very significantly. Using this new knowledge it will apparently be possible to clarify a discrepancy between surface energies determined by different theoretical and experimental procedures [13].

2.5 Discussion

If it is necessary to find the size of a real specific surface of a powder or bulk material for experimental reasons, knowledge gained from fractal geometry can be utilized, according to which a smooth surface has the dimension $D = 2$ and the real surface dimension in the interval $2 \le D < 3$ [14, 15]. Using this piece of knowledge the authors of this article suggest transformation of the equation (10) to the more complex shape that satisfies the requirements of fractal theory. The general function relationship can be expressed in this form

$$S_S = f\left(\mu, \sigma^2, D, \rho\right). \tag{12}$$

For the specific surface S_S measured by the BET method, the fractal dimension of the powder surface D can be calculated. Consequently, it is possible to determine the size of a specific surface of the powder from the same material, using knowledge of the parameters of particle size distribution μ and σ^2 . The advantage of this procedure lies in the ability to calculate the real specific surfaces by application of the distribution parameters. Subsequently, there is no need to perform many time-consuming and financially demanding measurements, as in the case of the BET method.

3 CONCLUSIONS

The authors have demonstrated the possibility of using statistical-mathematical tools for determination of the specific surfaces of powders and bulk materials. During such calculations it is always necessary to respect the logarithmic-normal distribution of sizes of powder particles. Using a simpler relationship, shown as the equation (8), the experimenters could commit errors depending on the size of dispersion of the powder particle sizes. This causes overestimation of the specific surface size. The approximation of particles by spheres is often used in the practice of technical and natural sciences and it is acceptable in the majority of cases. However, such approximation always introduces a certain error into the result, since natural particles have very complicated shapes. The error then becomes larger when the particles are flatter and, consequently, smaller in volume and smoother of surface than round ones. However, this does not change the principle of the method described in this

article. Some applications of this knowledge to powders with the general shape of particles (non-spherical) were indicated. The average surface and volume can be calculated using the general equation (2). The derived main equation (10) can also be related to the generally known fractal theory. The result of such a relationship can then be used for calculation of the specific surfaces respecting their real segmentation. A more exact description of such an approach deserves a deeper analysis. Therefore, it is not a part of this article.

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