Fine-Dispersed and Nano Mineral Particles in Mining and Metallurgical Wastes after Commercial and Laboratory Grinding

E. A. Ermolovich, K. A. Izmest'ev, and A. N. Kirilov

National Research University Belgorod State University "BelSU", ul. Pobedy 85, Belgorod, 308015 Russia

Abstract—The paper presents the results of defining the content of fine-grained fractions and nanofractions in mining wastes and the correlation equations for express estimate of powder dispensability. The authors discuss the non-uniqueness of the "fine-grained mineral particles and nanoparticles" notions in scientific literature.

Keywords: mining and metallurgical wastes, dispensability, mining waste recycling in filling mixtures

The World Commission on Environment and Development (1987) with the chairman G. Kh. Brundtland considered the stable development as the satisfaction of needs for the present generation without risk for further generations [1]. To fit the mining and metallurgical industry, the stable development would be impracticable without innovative waste recycling. It is urgent in Russia since the quality of ores here is worse than in foreign countries. During the last two decades, the content of nonferrous metals in ores decreased by 1.3-1.5 times and the content of iron and gold did by 1.25 times, while the fraction of rebellious ores and coal increased from 15 to 40%. In ferrous and nonferrous metal industry, only the volume fraction of mining wastes in the form of solid rocks is more than 210 million m^3 per year, whereas this index for mill tailings exceeds 140 million m^3 per year [2].

Intensification and development of the methods for solving problems of reduction, recycling, reprocessing, and elimination of the negative effect of mining and processing wastes on the environment require a consideration of their dispensability.

It is well-known that the basic properties of matrix, including its activity and hardening rate, are defined by the grinding fineness (dispensability) and grain size distribution of the product to a greater extent than the chemical and mineralogical composition and the presence of some additives [3]. The distribution of metals in mill tailings is concentrated in fine fractions [4-6], while quartz is amassed in the larger ones [4, 5]. The electrodynamic effect for disintegration of mineral complexes is possible at the material fineness, which is no less than 90-100% of the class below 74 μm [2]. Dust dispensability out of tailing dumps defines the negative effect on humans [7] and so on.

Taking into account that the mineral mining-waste materials are reground [8] and the influence of ultradispersed particles appears under creation of new composites even in the concentration 1-1.5% [9, 10], the present authors consider the content of fine-dispersed particles and nanoparticles within technogenic wastes as the currently central problem.

Upon analyzing the literature sources, the question whether the particles qualify as the fine-dispersed fractions is still open to discussion. So according to classification by dispensability level in relation to the size of particles, the systems are coarse-dispersed on the size from 10^{-4} to 10^{-6} m (from

100 to 1 μm) and high-dispersed on the size from 10^{-6} to 10^{-9} m (from 1 to 0.001 μm) [11]. The maximum size of fine-dispersed particles increases up to 120 μm in terms of the grain size analysis [12]. The dispersed products left after rock fracture are considered as fine-dispersed within the range of 10^{-4}-10^{-5} m (from 100 to 10 μm) [13]. In [14], the particles with size of less than 43 μm are taken as fine-dispersed. According to Belarusian construction standards for concrete aggregates and fillers, the fractions containing sieved particles 0,063 mm (63 μm) in size are rated in the fine-dispersed class [15]. Russian standards state the content of fractions with the particle sizes of less than 0.071 mm (71 μm) in the mineral powder [16]. The papers [17, 19] and [18] reported that the fractions with the particle sizes of less than 0.14 mm (140 μm) and 0.074 mm (74 μm) are fine-dispersed. As to classification of gold by sizes, the particles of size 0.1 mm (100 μm) and above belong to visible gold, while the particles of smaller sizes are viewed as fine-dispersed [20]. There is no criterion for determining what system is fine-dispersed and which size allows it to be rated to this class even in PhD students' theses concerning with the properties of fine-dispersed systems and starting materials [21, 22].

The nanodimensional range is also ambiguous in literature. The upper dimensional boundary of condensed matter objects is taken to be at 100 nm according to the nanotechnologies and the sciences of nanostructures and nanomaterials [23]. When the size of structural elements (particles, crystallites, grains) gets to the lower limit, the properties profoundly alter [24-29]. However, the larger particles of not only nanodimensional scale, but of the submicron and even micron scale as well, have such specific properties among the natural mineral phases. The macromineralogy boundary is at 10 μm (10000 nm), or even at 100 μm (100000 nm). Such boundary can have individual value for each particular mineral phase [30]. In some cases, the same material can be nanomaterial or homogeneous material for different applications [31]. Considering the class of mineral particles with unusual properties, the author of [30] proposed to use the term "ultradispersed phases" with combining the nanoparticles and microparticles.

In [8], mining waste mineral nanoparticles are described as the objects with characteristic size of 1-1000 nm. In the dimensional levels of minerals, the nanominerals are found in 10^{-6}-10^{-9} m, i.e., from 1 to 1000 nm as well [32].

Clearly, both experimental and methodical studies should be carried out to enhance the scientific notations. However, the previous experiments showed that nanoparticles, as applied to mineral materials, should be considered within 1-1000 nm since their content here significantly affects the strength of filling mixtures [33].

The present authors aimed to define the contents of individual fine-dispersed fractions and nanofractions in mining and metallurgical wastes of different grinding and find their relations to the average size of powder particles. The introduction showed how important the influence of these parameters is. To define the distribution of the particles over fractions are not necessarily possible with using the laser analyzer, while a demand for the express determination can emerge during solution of different problems concerning with the processing of wastes and the elimination of their negative effect on the environment. Specifically, the impact of the content of various fractions under design of hardened filling mixtures for the area of worked-out rooms was taken into account [33, 34]. All the given wastes were used as the components of filling composites. The versatility of approximating curves is proved in actual practice. The idea is that the content of fractions does not depend on the type of wastes, but does on the average size of powder particles, which is easily defined even by sieve analysis. These relationships are recommended to be applied due to high approximation reliability.

The size distribution of powder particles of technogenic wastes was studied using the laser diffraction-type particle size analyzer Analysette 22 NanoTec. The measurement was carried out with ultrasonic dispersion of powders in liquid by means of the FR 1.27.2009.06762 method (“Method of measuring the particle sizes in suspensions, emulsions and aerosols in the nanometer and colloid ranges with using dynamic light scattering”):

1. Measurement range: the maximum range is within 0.1-1021.87 μm since the size of powder particles is initially unknown.
2. Measuring parameters: the duration of the measurement is, on average, 50 scans.
3. Measuring the background is carried out before each test to decrease the influence of the measuring liquid. Any pollution after previous measurement is stated to eliminate its negative effect on the next result.
4. Measuring the size distribution of particles: a sample matter of volume 5 ml is poured into the module for dispersion in 500 ml of liquid. The liquid dispersion module provides the automatically operated washing. The powder of the given type is examined with using the ultrasonic generator. The measurement starts as soon as the absorption reaches the specified value.
5. Results. The differential and cumulative curves for particle size distribution are obtained.

The present paper contains the research on the waste products from the wet magnetic separation of ferruginous quartzites, all kinds of which were obtained by grinding with commercial equipment of Kombinat KMAruda JSC that is in service today. The term “commercial grinding” is thus used instead of grinding on the laboratory installations. Moreover, the commercial grinding is characterized by the cement grinding fineness, i.e., by the current average size of cement particles, which is 30—35 μm. By the ultrafine grinding is meant the average size of grinded product, which is less than 20 μm [35]. Such grinding was carried out on the laboratory vibratory disc mill RS200 and ball mill SHLM.

— The particle distribution was defined with using the following mining and metallurgical wastes:
— The commercial ground granulated blast-furnace slag (metallurgical waste);
— The ultrafine ground granulated blast-furnace slag;
— The waste products of ultrafine ground dolomite detritus;
— The waste products of ultrafine ground limestone detritus;
— The current waste products from the wet magnetic separation of ferruginous quartzite;
— The waste products from the wet magnetic separation of ferruginous quartzite, sand fraction;
— The waste products from the wet magnetic separation of ferruginous quartzite, slag fraction;
— The waste products from the wet magnetic separation of ferruginous quartzite with using the flocculating agent Magnofloc 155;
— The old waste products from the wet magnetic separation of ferruginous quartzites out of the tailing dump; and
— The converter slag (metallurgical waste).

The results of defining the content of fine-dispersed particles and nanoparticles in mining and metallurgical waste powders are presented in the table.

The content of fine-dispersed particles and nanoparticles in mining and metallurgical wastes

Wastes	Particle sizes, μm							
	0-0.2	0-0.5	0-1	0-3	0-5	0-10	0-43	0-71
	The content of fractions out of the total volume of a sample, %							
Commercial ground granulated blast-furnace slag, *d* = 31.87 μm	0	0.69	3.72	13.44	17.98	30.23	69.12	93.1
Ultrafine ground granulated blast-furnace slag, *d* = 17.87 μm	0	0.67	3.66	15.09	21.22	38.11	92.95	99.96
Waste products of ultrafine ground dolomite detritus, *d*=35.18 μm	0	0.67	3.13	9.92	12.84	20.77	59.95	95.34
Waste products of ultrafine ground limestone detritus, *d*=6.07 μm	0	1.74	10.44	42.2	54.37	80.04	100.00	100.00
Current waste products from the wet magnetic separation of ferruginous quartzites, *d* = 29.71 μm	0.14	0.55	2.62	11.83	16.24	27.44	69.17	96.47
Old waste products from the wet magnetic separation of ferruginous quartzites, *d* = 75.76 μm	0	0.22	1.08	4.82	6.1	10.65	36.48	65.11
Waste products from the wet magnetic separation of ferruginous quartzite with using the flocculating agent Magnofloc 155, *d* = 30.68 μm	0	0.49	2.73	12.54	17.43	30.29	71.74	94.57
Waste products from the wet magnetic separation of ferruginous quartzite, sand fraction, *d* = 88.17 μm	0.1	0.14	0.61	2.06	2.40	3.37	11.54	38.02
Waste products from the wet magnetic separation of ferruginous quartzites, slag fraction, *d* = 23.39 μm	0	0.51	2.62	12.27	17.20	30.35	84.00	99.89
Converter slag, *d* = 3.67 μm	0.06	12.29	28.41	56.29	71.27	93.06	100.00	100.00

Using approximation of the results of experimental investigations into 21 samples, the following correlation dependences of the content of fine-dispersed particles and nanoparticles on the average size of powder particles of mining wastes within the range of 3-90 μm are stated:

$$C = a\exp(bd) + c\ .$$

Here, C is the content of fraction out of the total volume of a sample %; d is the average size of particles, μm; a is the variable parameter, which is 357.224 (for the fraction size of less than 0.5 μm (500 nm)); 148.879 (for the fraction size of less than 1 μm (1000 nm)); 83.9592 (for the fraction size of less than 3 μm); 95.9956 (for the fraction size of less than 5 μm); 97.7641(for the fraction size of less than 10 μm); 170.854 (for the fraction size of less than 43 μm); b is the variable parameter, which is 0.9286 (for the fraction size of less than 0.5 μm); 0.4777 (for the fraction size of less than 1 μm); 0.1549 (for the fraction size of less than 3 μm); 0.1329 (for the fraction size of less than 5 μm); 0.0706 (for the fraction size of less than 10 μm); 0,0098 (for the fraction size of less than 43 μm); and c is the variable parameter, which is 0.4626 (for the fraction size of less than 0.5 μm); 2.5468 (for the fraction size of less than 1 μm); 8.4449 (for the fraction size of less than 3 μm); 10.9282 (for the fraction size of less than 5 μm); 12.4084 (for the fraction size of less than 10 μm); 55.6281 (for the fraction size of less than 43 μm).

Figure 1 shows the relationship between the content of fraction with the size of less than 10 μm and the average size of powder particles of mining and metallurgical wastes.

The stated relationships can be applied to the express estimate of dispensability of mining wastes. For example, it is useful in design of filling mixtures for the area of worked-out rooms or prediction of the parameters of dusting heaps and tailing dumps.

The waste products after dressing the ferruginous quartzites (d = 69.16 μm; the silicon dioxide, about 68-70% (hardness according to the Mohs scale is 7) and ferrous oxides, 20-25% (hardness according to the Mohs scale is 5.5-6.5) prevail) were subjected to wet grinding in isopropyl alcohol by using the planetary mill Pulverisette 5 during 12 h with further centrifugation. As a result, the material containing mining waste particles with the average size of 150 nm was obtained (Fig. 2). The geometric size of particles was defined by means of the transmission electron microscope Jeol JEM-2100 in terms of averaging 50 measurement data; the length of the room was 100 cm in that. Figure 2 shows the particles with the size from 10 nm. The further research will be aimed at studying the given material and its effect on the properties of new composites.

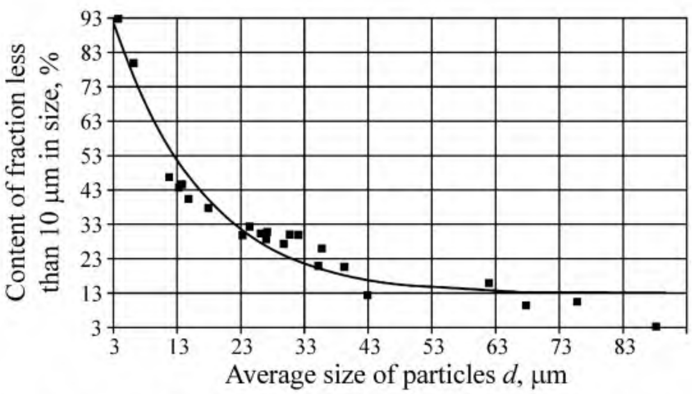

Fig. 1. The relationship between the content of fraction with the size of less than 10 μm and the average size of powder particles. The approximation reliability is R^2 = 0,988, 0.970; 0.943; 0.934; 0.940; 0.957 for fractions of less than 0.5, 1, 3, 5, 10, 43 μm.

Fig. 2. Powder of waste products from dressing the ferruginous quartzites of KMA (Kursk magnetic anomaly) after grinding on the planetary mill and further centrifugation.

CONCLUSIONS

1. The presence of mining wastes becomes a key factor for providing the environmental safety of the country.

2. The up-to-date main technology solutions for eliminating the negative effect of technogenic wastes require the consideration of their dispensability.

3. The class of mineral particles (fine-dispersed fractions or nanofractions) is still a point open to question. Both experimental and methodical studies should be carried out to enhance the scientific notations.

4. Using approximation of the obtained experimental data, the correlation dependences of the content of fine-dispersed fractions and nanofractions on the average size of powder particles of technogenic wastes within the range of 3-90 μm in exponential form, are stated.

5. The express estimate of dispensability of mineral wastes at the design of filling composites for making the artificial masses and for the control of dusting heaps and tailings dumps can be implemented in terms of the resultant relationships.

6. The laboratory grinding of waste products from dressing the ferruginous quartzites (hardness according to the Mohs scale is up to 7) on the planetary mill made possible to obtain the material containing particles of average size 150 nm. Thus it can be used for creating new composites.

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