

Nanoparticles in Experiments on Destruction of Rocks by Explosion

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This paper presents the first (among works known to the authors) experimental study of nanoparticles formed during large-scale chemical explosions. We clarify that the investigated objects are characterized as nanoscale objects (sizes from 1 to 1000 nm) and microscale objects (from 1 to 1000 μm), which allows us to use the classification of particles on the basis of their size. Nanoparticles and microparticles play a significant role in the environment. They can both pollute and clean the atmosphere, because they serve as condensation centers during the formation of poisonous aerosols (SO_2 , NO_x , and others). They also influence the transparency and chemistry of the atmosphere, transport heavy metals and radioactive isotopes, and ultimately influence the climate. Due to the small size and high dispersion, nanoparticles are characterized by high mobility, significant pressure of water vapor, and long lifetime in the atmosphere (approximately 100 days). According to present-day estimates [1], more than 10% of the total mass of fine-dispersed dust and aerosols in the Earth's atmosphere is related to human activity. One of their significant sources is large-scale chemical explosions [2].

We carried out an experimental study of nanoparticles formed during large-scale explosions. Such investigation is interesting from the point of view of revealing the regularities of formation of particles depending on the characteristics of the explosion (type of explosive, specific rate of explosive, and others) and on the type of rock and its physicochemical properties. Ultimately, we can control the formation of nanoparticles during explosions. Crushing of rock into the fine-dispersed state by means of explosion can become one of the commercial methods of producing nanoparticle powder, which can be implemented, for example, as means of protection from some types of biological weapons (see [3], pp. 114–115) or in the solution to

ecological problems related to the pollution of the environment.

Experimental works on the formation of nanoparticles were carried out during explosions in the Fennoscandian granite massif near Vyborg [4]. The rocks contain porphyric phenocrysts (from 3–5 cm to 0.5–2 cm in size) of potassium feldspar (36–43 wt % of the rock mass). The space between the phenocrysts is filled with a coarse- and fine-grained matrix of quartz (23–33%), plagioclase (18–24%), biotite (up to 8%), and hornblende (up to 7%) [5, 6]. Granites of the region are characterized by a homogeneous structure. The velocity of propagation of longitudinal waves at the massif surface is $c_p \approx (5.6\text{--}5.8) \cdot 10^3$ m/s; the density of granite is $\rho \approx (2.6\text{--}2.7) \cdot 10^3$ kg/m³. Disks of pressed trinitrotoluene (200 g) served as the source of explosion. The trinitrotoluene has the following properties: density 1.5 g/cm³; heat of explosion 4120 kJ/kg; detonation rate 6000 m/s; and pressure in the detonation wave $2 \cdot 10^4$ MPa. The explosions were carried out at the surface of a granite massif in an open area.

At first, the sizes of particles were measured in the blast cone after the first explosion using the method of network analysis and optical microscope. Particles with sizes ranging from a few tens of micrometers to 2.5 mm were abundant. The granulometric composition of the destructed medium in this size range is described well by the Rozin–Rammler distribution

$$V(x) = V_0 \exp \left[- \left(\frac{x}{x_0} \right)^n \right],$$

which is characteristic of the case of single crushing (Fig. 1). Here, x is particle size; V_0 is volume of the investigated substance; $V(x)$ is total volume of particles whose volume is greater than x ; x_0 , n are distribution

parameters; and $\langle x \rangle = x_0 \Gamma \left(1 + \frac{1}{n} \right)$ is the mass average

particle size. The obtained value of power in the Rozin–Rammler distribution ($n = 1.15$) corresponds to the values usually observed during explosions of this scale [7–9].

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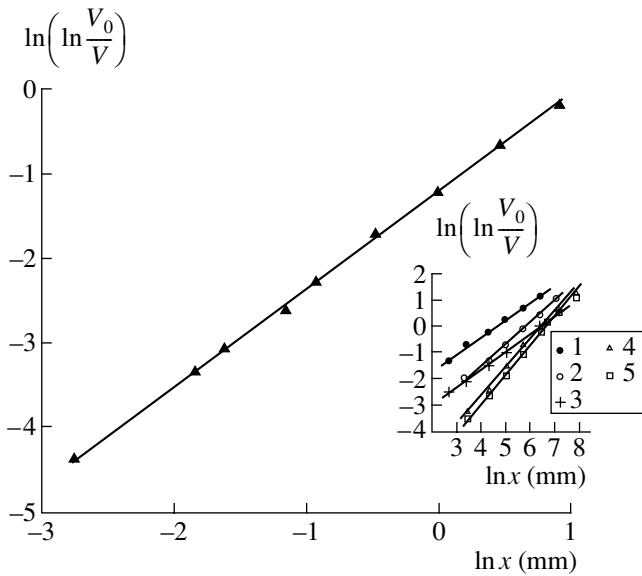


Fig. 1. Experimental distribution of particles obtained after the first explosion and the theoretical Rozin–Rammler distribution. Granulometric composition of the demolished rocks during excavating explosion [8] is shown in the inset (in straightening coordinates characteristic of the Rozin–Rammler distribution). Sites: (1) Cabriolet; (2) Dugout; (3) Denni Boy; (4) Pre Scuner Charles; (5) Salky.

The number of nanoparticles formed after the first explosion was insufficient for a representative study of their distribution by sizes. Therefore, we carried out three sequential explosions at the same site; i.e., the charge for the second explosion was located in the blast cone of the first explosion and the charge for the third explosion was located in the blast cone of the second explosion. Fibrous dust collectors (AFA-RSP-10 Petryanov filters) each fixed between two disks were placed at the expansion boundary of gaseous product expansion at 1 m above the Earth’s surface so that their plane was perpendicular to the direction of the explosive charge.

Nanoparticles and microparticles collected on the filter fibers and in the blast cone formed after three explosions were analyzed. In order to control the experiment, we also analyzed filters not subjected to the influence of explosions but located in the same area before explosions (hereafter, unaltered filters). The sizes of particles were measured using an MBS-10 optical microscope, JEOLS scanning electron microscope, and EM-125 transmitting electron microscope. The particles collected in the blast cone formed after three explosions were also used to plot the size distribution of particles. The data were obtained using optical and scanning electron microscopic images. We determined the sizes of approximately 1000 particles, which is sufficient for statistical analysis.

The general size range of particles collected on the filter fibers was from 20 nm to 240 μm. Classification of particles by their shape allows us to distinguish two

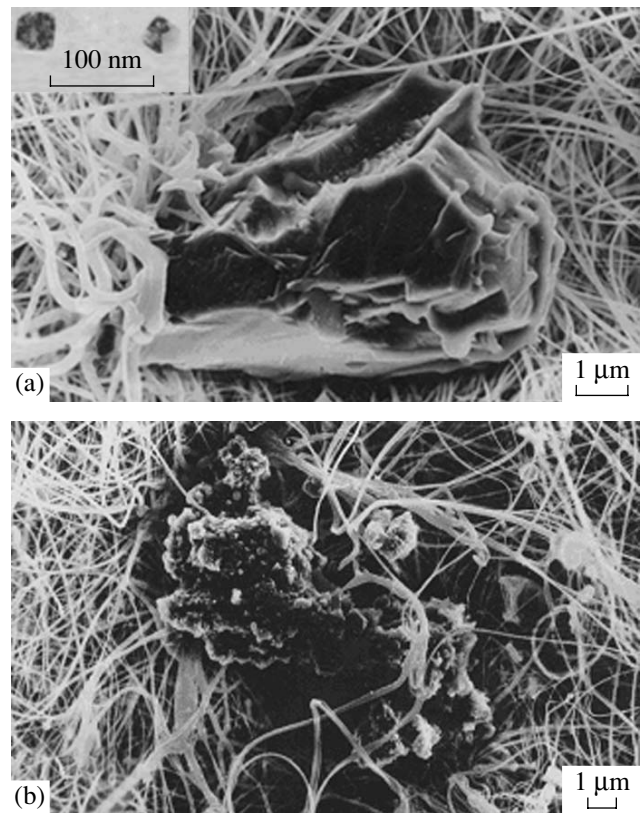


Fig. 2. Scanning electron microscopic images of particles on filter fibers. The figure shows examples of (a) individual splinter-type particles and (b) aggregations of particles of various sizes (from 30 nm to 5 μm) in one relatively dense conglomerate. One can see nanometer particles of the droplet type (b) at the surface of larger particles. The major images were obtained with a JEOLS scanning electron microscope. The image in the upper left-hand corner of the figure (a) was obtained with an EM-125 transmitting electron microscope.

main types: (i) splinter-type particles with size exceeding 50 nm (Fig. 2a); (ii) droplet-type particles (size from 20 nm to 5 μm) and their conglomerates (Fig. 2b). It is possible to state that the particles found on the filter fibers were formed immediately after explosions because such particles were not found in the analysis of unaltered filters.

Figure 3 allows us to compare the experimental size distribution of nanoparticles with the Kolmogorov distribution [7]

$$\Phi(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^t \exp\left(-\frac{y^2}{2}\right) dy,$$

which characterizes the size distribution of particles in the case of multiple crushing. Here, x is the particle size; $\Phi(t)$ is the probability to find a particle with size smaller than x ; $t = \frac{\ln x - \ln x_0}{\ln \sigma}$; x_0, σ are parameters of

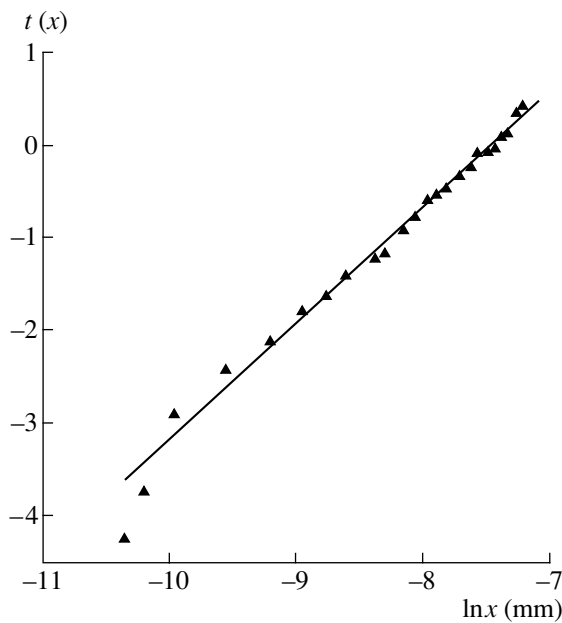


Fig. 3. Experimental distribution of nanoparticles compared with the Kolmogorov distribution.

distribution; and $\langle x \rangle = x_0$ is the mass average size of the particle. It appears that the experimental distribution agrees well with the Kolmogorov distribution for the particles with sizes smaller than 900 nm (corresponding to the values $\ln x < -7$ in Fig. 3). Taking into account that the Kolmogorov distribution characterizes the case of multiple crushing, one can conclude that a significant part of smaller particles was formed as a result of crushing of larger particles during the second and third explosions. A significant decrease in the mass of nanoparticles with the decrease of their sizes is caused, in particular, by an increase in the strength of particles with decrease of their size. It is worth noting that the correspondence of the experimental data to the Kolmogorov distribution becomes invalid in the range of particle size less than 100 nm. The causes of this phenomenon deserve special study.

Along with the visual study of the shape of micro-particles and nanoparticles and compilation of their grain size distribution, we also performed chemical analysis of 20 particles of the splinter type (size from 30 μm to 2 mm) collected in the blast cone after the third explosion. The microprobe analysis was performed with a JSM-35C scanning electron microscope equipped with Zink 860 X-ray spectrometer and Si (Li) detector. The analysis showed that approximately 60% of the total chemical composition belongs to oxygen; ~25%, to Si; ~10%, to Al, Ca, Na, and K; and ~5%, to other substances. The mineralogical composition of the particles based on their chemical composition includes quartz (SiO_2), potassium feldspar KAlSi_3O_8 , and two modifications of plagioclase $\{\text{Na,Ca}\}\text{AlSi}_3\text{O}_8$. The investigated fragments (size from 30 μm to 2 mm) con-

sist of one, two, or three different minerals. If the particle size decreases, then the presence of one mineral becomes a characteristic feature. The obtained chemical and mineralogical compositions of particles do not contradict the composition of rapakivi granite of the Vyborg pluton [5, 6]. We could not study the mineralogical composition of the droplet-type particles due to their small size and insufficient quantity.

Thus, we have demonstrated the possibility of the formation of nanoparticles during large-scale chemical explosions. The minimal size of particles formed in such explosions is 20 nm. Classification of particles by their shape allows us to distinguish two main types: splinter-type particles (size >50 nm) and droplet-type particles (size from 20 nm to 5 μm). The splinter-type particles are formed as a result of crushing of the rocks of the granite massif. A significant part of nanoparticles is formed as a result of crushing of larger particles of the first explosion during the subsequent explosions. The droplet-type particles can be formed as a result of melting of rocks and condensation of gaseous products of the explosion on the filter fibers of the filters. This is suggested, in particular, by the small sizes of such particles.

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