ULTRASONIC METHOD OF PREPARATION FINE-DISPERSED VERMICULITES

AND THERMAL PROPERTIES OF BUILDING MATERIALS

KURBANBAEV SHUKHRAT ERGASHEVICH¹ & MIRZAEV SIROJIDDIN ZAYNIEVICH²

¹Fire Research Centre, Higher Technical School of Fire Safety, Tashkent, Uzbekistan
²Department of Engineering Physics, Tashkent State Technical University, Tashkent, Uzbekistan

ABSTRACT

It is presented the results of studies on preparation of thin and ultra-dispersed vermiculites by ultrasonic method and the study of the influence of formulations based on them on thermal properties building materials.

KEYWORDS: Ultrasonic Grinding of Vermiculite Mineral, Nanparticles of Vermiculite, Thermal Properties of Building Materials

Received: May 19, 2016; Accepted: Jun 10, 2016; Published: Jun 13, 2016; Paper Id.: JMPEJUN20162

INTRODUCTION

In connection with ample opportunities to obtain high quality and high performance materials based on ultra dispersed (nano) particles, the task of developing effective ways of grinding of mineral raw materials and their effective application is important.

The fineness being one of the main characteristics of mineral raw materials, is also an effective tool to control their properties. Since it is known that many substances in fine and especially ultrafine (nano) states exhibit specific properties that are not observed in coarse states.

Obtaining vermiculite powder in a fine form both of fire-resistant and heat-insulating materials is extremely important, because fine fraction (a dispersed phase) is more evenly distributed in dispersion medium (a binder). This fact significantly increases quality, physical and mechanical and flame retardant properties based on these materials. In manufacturing various protective paints (including flame retardants), more fine mineral fraction is retained much longer in the suspension state, which ensures preservation of material quality for a long period of time.

Traditional mechanical methods of grinding of mineral rock, ball mills, pin disintegrators and others enable to obtain high-disparity materials at particularly large interval of time and require large energy consumption. Moreover, percent yield of needed fine fraction is very low, about 50% of the particles of materials dispersed by mechanical means having dimensions of 0.01-0.5 mm, 35% - from 0.5 to 1.0 mm, the remaining being more than 1 mm.

One of the most promising ways of grinding materials is the ultrasonic method. Ultrasound as a powerful source of high-energy is one of the most commonly used methods of influence on the material in order to investigate or change any of the physical parameters of these materials. Meanwhile, ultrasonic grinding method of mineral rock in a relatively short period of time allows to obtain highly dispersed materials.
METHODS AND INSTRUMENTS

This paper presents the results of studies on preparation of thin and ultra (nano) dispersed vermiculites by ultrasonic method and the study of the influence of formulations based on them on thermal properties of building materials (wood and metal).

Thermal studies of obtained dispersed materials were carried out on NETZSCH STA 409 PG/PC. Heating was conducted in the air up to 500°C at 3°C/min.

Using Solver NEXT (Russia) a scanning probe microscope the light phase of the obtained stable suspension of vermiculite was studied.

RESULTS AND DISCUSSIONS

At the first stage of research after coarse and fine grinding vermiculite concentrate (VC) sieve separation into the various fractions was carried out Table 1. The obtained fractions depending on the size of the grains were further used for various materials (flame retardant, heat insulation and fire extinguishing compositions)[1].

<table>
<thead>
<tr>
<th>№</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-4 mm</td>
<td>0,5-1 mm</td>
<td>0,250-0,5 mm</td>
<td>0,160-0,250 mm</td>
<td>0,250≤ mm</td>
<td>0,160≤ mm</td>
<td></td>
</tr>
</tbody>
</table>

To establish optimal formulations of developed materials thermal studies of obtained dispersed vermiculite fractions were carried out on NETZSCH STA 409 PG/PC. It is seen in these thermal images (Figure 1) that with the increase of dispersion from fraction №1 - (0,5 - 1) mm to fractions №2 - (0,250 - 0,5) mm and №3 - 0,160 ≤ mm, the weight loss which is mainly due to evaporation of water is reduced in the following quantitative expressions of 4.64: 4.48: 3.93, respectively, as well as increase in the intensity of endothermic effects with the same order of the samples is observed. But in the second sample №3 endothermic effect within the temperature range of 280-285°C almost completely disappears.

These changes are due to the fact that during grinding vermiculite grains already have time to lose some of the water contained before this process in its interlayer spaces. The disappearance in the sample №3 of a second endothermic effect is due to the fact that with the increase of dispersion the surface area of the material increases repeatedly and at the
same time their activity increases, too. Therefore finer particles of vermiculite almost completely lose all the water contained in them at relatively low temperatures, i.e. at 90.2°C (endothermic effect of sample №3).

On the next stage of the research the effect of the above disperses fractions of vermiculite and new modified vermiculite on fire-retardant effectiveness of coating based on a standard sodium water glass was studied. Temperature measurements results were given of the unheated side of the metal plate coated with the compositions based on sodium water glass and vermiculites stated above. Figure 2 shows the results of measurements of the optimal composition at the following ratios (wt.%): Sodium water glass/vermiculite 80 ÷ 90 and 10 ÷ 20, respectively.

Figure 2 The Dotted Line Is The Furnace Temperature. Compositions: 1 - Sodium Water Glass+ (0, 5 - 1) Mm, VC Fraction; №2 – Sodium Water Glass+ (0,250 – 0,5) Mm VC Fraction; 3 – Sodium Water Glass+ 0,160 ≤ Mm VC Fraction; 4 – 0,160 ≤ Mm VC Fraction + Concentrated Phosphoric Acid + Sodium Water Glass to Complete Neutralization of the Acid; 5 – 0,160 ≤ Mm VC Fraction + Concentrated Nitric Acid + Sodium Water Glass to Complete Neutralization of the Acid.

Figure 2 show that coating based on compositions (numbered from 1 to 5) significantly reduces the temperature of a metal plate. However, to obtain high decorative properties and high flame retardant properties of paints more highly dispersed vermiculite fractions are more suitable. These are compositions №3 - Sodium water glass + 0,160 ≤ mm VC fraction; №4 - 0,160 ≤ mm VC fraction + concentrated phosphoric acid + Sodium water glass to complete neutralization of the acid; №5 - 0,160 ≤ mm VC fraction + concentrated nitric acid + Sodium water glass to complete neutralization of the acid.

Further, at the next step fraction №6 in Table 1 was used to obtain more fine fractions of vermiculite mineral using ultrasound.

The physical nature of the action of ultrasound reduces to formation of cavitation bubbles in the tested systems, the cleavage of which leads to development of huge pressures that generate a powerful impact and intensification of physical and chemical processes. These effects include a shock wave, influence of temperature, electrical and photochemical phenomena contributing to mechanical failure, breakage of chemical, molecular and supramolecular bonds of various kinds of substances and disperse systems [2, 3].
The feature of this method is that ultrasonic dispersing mineral rock is not carried out as the mechanical grinding and mixing of all the mineral particles as well as the selective force on the border splicing mineral grains, which break down in the first place, complex composite assemblies, consisting of particles of various minerals. Thus there is the breaking of bonds, mechanical fasteners grains of different minerals. Sami grains of these minerals specified time are saved to non-destructive because their strength exceeds the strength of the forces of intergranular bonds. Therefore, by controlling the duration of the acoustic fields in this case can be directed force on the ultrasonic milling complex mineral aggregates to form particles of vermiculite minerals and impurity particles (various micas, hydroxides, etc.). Volumetric efficiency separation of mineral particles and impurities occur in subsequent process cycles (for example, by acid activation) [1-3].

The peculiarity of this method is that ultrasonic dispersing of mineral rock is carried out not as mechanical grinding and mixing of all the mineral particles but as selective force on the border of splicing mineral grains, which breaks down first and foremost, complex composite assemblies, consisting of particles of various minerals. In this case there occurs breaking of bonds, which mechanically fastener grains of different minerals. The grains of these minerals preserve without any destruction for the specified time, because their strength exceeds the strength of the forces of intergranular bonds. Therefore, by controlling the duration of the acoustic fields in this case ultrasonic force impact can be directed on milling complex mineral aggregates to form particles of vermiculite and impurity minerals (various micas, hydroxides etc.). Volumetric separation of productive mineral particles and impurities occur in subsequent process cycles (for example, by acid activation) [1-3].

For more efficient use of acoustic power at ultrasonic grinding a special pulp - slurry of mineral particles in the water at a ratio (wt. %) of 0,1 ÷ 1,0 to 99,9 ÷ 99,0 respectively, is prepared. The pulp, as mentioned above consists of pre-crushed vermiculite mineral rock (fraction № 6 Table 1) and water. The acoustic vibrator in a form of a metal plate, oscillating at certain frequency is input into the slurry and dispersing the material is performed. Preliminary experiments on grinding mineral clays using various vibrators oscillating at a relatively wide range of frequencies (16-26 kHz) have shown that the acoustic power developed by them around 1.0-1.2 kW/kg, the most effective dispersion of the raw vermiculite clay takes place during operation in the range of 22.6 - 23.8 kHz.

To improve the efficiency of ultrasonic dispersion process of vermiculite rock a few alkaline and acidic activators were tested that were administered in small quantities in the dispersed medium. The main positive action of such activators is that by changing electrochemical state of the surface of crushed materials, they allow the fluid (in this case it is water) to penetrate more efficiently and at greater depths (by micro cracks, pores, dislocations, defects and other disorders of material structure) inside the mineral vermiculite grains. In this case, the explosive effect of the acoustic waves is much bigger and more efficient than in the absence of activators. We investigated a number of compounds, such as H₃PO₄, H₂SO₄, HNO₃, HCl, Na₂SO₄, NaHSO₃, Na₂SiO₃, Na₂CO₃, NaOH, and KOH. The experiments have shown that strongly acidic and strongly alkaline reagents showed the strongest impact on the efficiency of dispersing vermiculite rock. Moreover, it has become known out of the research, that addition of hundredths of a percent (of the mass of crushed rocks) of these substances is enough to get the same crushing effect, which was shown, for example, by a few percent of Na₂CO₃.

Now it should be noted that strongly acidic reagents such as H₃PO₄, H₂SO₄ и HNO₃, as it is known from the analysis of the scientific literature on these materials [4] and from our own studies [5], reinforce the processes of vermiculite dispersion and by chemical interaction of structural units of this mineral. Moreover, it has become known out of own studies that by
changing the concentration of acid and conditions of interaction it is possible to control these processes.

The experiments on chipping raw vermiculite showed that the optimal concentration of activation additive based on the Na$_2$SiO$_3$, at which destruction of complex mineral complexes occurs most efficiently at the range of 0.006 wt.% of the weight of the material to be grounded (Fig.3). Thus, about 70% of crushed particles have the size of 4.0-12.0 microns (disperesion time - 25 min). It should be noted that at raw vermiculite dispersion during the same time without addition of Na$_2$SiO$_3$ the most particles have sizes from 10 to 30 microns. Activation additive, thereby increasing the effectiveness of dispersion approximately to two-three times. It also should be noted that when increasing the amount of activator Na$_2$SiO$_3$ introduced to the pulp at more than 0.006 wt. %, grinding efficiency of raw vermiculite decreases.

![Figure 3: Dependence of the Bulk Viscosity of Clay Suspensions of Vermiculite on the amount of Na$_2$SiO$_3$ Alkaline Activator Introduced. In this Case, the Viscosity of the Medium Shown in the Figure below is Determined by Its Degree of Dispersion](image)

In 24-25 min after dispersing slurry is a suspension of solid particles in water. After 10-12 min of settling upper slurry comprises a very small powder fraction having the size of 0.4-1.0 microns (about 15%). In its central part large portion of mineral particles having an average size of 2 to 12 micrometers (50-55% of all particles), and at the bottom (near the bottom of the vessel), the largest particles are collected up to 15 - 30 microns (about 35%). Obviously, the more fractions with high dispersion of particles in the mineral powder, the better initial weight of substances will be divided into components of the entire fraction. The finest fraction is virtually pure vermiculite mineral with a minimum content of impurity minerals.

When grinding the expanded vermiculite at approximately the same grinding conditions porous laminated vermiculite was obtained with a particle size of from 0.5 to 2.5 microns, i.e. much more fine powder. This difference is mainly determined by the fact that the expanded vermiculite presents a porous material. Because of such high porosity such vermiculite is relatively easily exfoliated into tiny particles with the size of about 1 micron. While grinding of raw vermiculite – of more solid and dense rocks - is much more difficult process and takes place at more rigid regimes. Therefore, at the same time of dispersion the average sizes of the obtained particles of raw vermiculite constitute the bulk of 5-12 mm (instead of 0.5-2.5 microns for porous vermiculite).

The experiments on optimization of temperature regimes of dispersion process showed that at too high acoustic bath cooling, in which dispersion of the material occurs, the intensity of the grinding process is markedly reduced - obviously, because the role of temperature as the enhancer of physical and chemical processes originating in the
pulp reduces. Empirically it has been found that the optimum temperature at which the process of crushing rock under the action of the acoustic field is sufficiently effective and together with this, operating elements of magnetostrictive transducers (vibrators) are at the suitable temperature mode for continuous operation, at the range of 55-65°C. It is clearly seen that the optimal temperatures for effective grinding of raw vermiculite are more stringent (10-15°C) than for crushing porous vermiculite maintained at the first stage of study (45-50°C).

As it was shown by experiments on grinding vermiculite rock to obtain its effective dispersion much more stringent operating parameters (frequency of acoustic field, pulp temperature, concentration of activation additives et al.) are required. The experiments on optimization of the temperature conditions of the process of dispersing the crude vermiculite showed that, at excessively high acoustic cooling bath, in which dispersion of rock takes place, the intensity of grinding process is markedly reduced - obviously, because the role of temperature as the enhancer of physical and chemical processes originating in the pulp reduces.

For further study on the acid activation and purification of vermiculite from impurities almost all the pulp is used, in addition to the pulp quickly deposited and located at the bottom part. The pulp is discharged into a separate container where its chemical activation is produced by weak acid solutions. When activated, for example using 4-6% aqueous solutions of hydrochloric acid a significant portion of the impurity iron and titanium oxides is transferred in the liquid phase. The solution then becomes of yellow-green color. After settlement for 15-20 minutes a yellow-green solution is drained and the remaining mass is pushed through a thick cloth. The resulting creamy mass is spread on a flat surface and subject to extra drying - natural drying in the sun or in the oven.

Further investigations allowed getting nanofluids based on mineral vermiculite; a method for their preparation was developed.

Further, using Solver NEXT (Russia), a scanning probe microscope the light phase of the obtained stable suspension of vermiculite was studied. The images (Figure 4) of the topography of the surface of the vermiculite nanoparticles were obtained and the grain size distribution of particles was calculated.

Figure 4 shows (left) that surface topography of vermiculite particles indicates that by one of the parameters (h - height) the maximum value is within 250 nm. From the second shot (right) it can be seen that the particle size
distribution is within the range from 50 to 400 nm. The maximum content has the particles with a size of 250 ÷ 300 nm.

To obtain stable suspensions of vermiculite (nanofluid) with finely divided particles it was needed to examine their influence on combustibility of wood-based materials, as well as carry out an assessment of their extinguishing properties.

To evaluate fire-fighting properties we have developed a way to assess these qualities [6]. The suspensions containing vermiculite mineral nanoparticles obtained in the course of these studies, served as the basis for obtaining new extinguishing agents, more effective than ordinary water liquid. Later, Figure 5 shows the results of studies on the impact of these suspensions on flammability of wood. In this figure: 1 line, it is an indicator of exhaust gas temperature versus time, a timber sample is treated with ordinary water. Lines 2-1 and 2-2 are indicators of discharge gas temperatures, depending on the time, treated with vermiculite suspensions. In this sample 2-2 is an indicator of wood sample treated with suspension obtained based on vermiculite nanoparticles. Comparing lines 2-1 and 2-2 shows that at relatively low consumption of vermiculite-containing suspensions it is possible to achieve the same indicators as in sample 2-1. Sample 2-1 is indicators of wood samples treated with bentonite-vermiculite suspension [6].

From the above data it may be stated that the obtained stable suspensions with superfine particles of vermiculites are more effective for obtaining liquid extinguishing agents than ordinary suspensions.

![Figure 5: Temperature Dependence of the Heat Flow Leaving the Ceramic Tube from the Observation Time](image)

**CONCLUSIONS**

Thus, if at the first stage of the research the focus was made on preparation and study of thermal properties of fine and ultra dispersed vermiculites as a flame retardant fillers, in the second stage of study the main part of the experiments was carried out to assess the fire retardant qualities of paints and fire-extinguishing properties of the materials. For example, fire tests of wood strips coated with the same paints showed that a thin film of fireproofing paint containing 15% of finely divided vermiculite is much more effective and longer (about 2-3 times) opposed to the flame than the film of paint made on the basis of other mineral clays, such as, kaolin. Moreover, a protective film based on powder of raw vermiculite is 40-50% more active in its counteracting to flame compared to the paint containing porous powder of vermiculite.
REFERENCES


