OC-50: Exfoliation and Size Reduction Treatment of Vermiculite by Ultrasound Irradiation

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Vermiculite, a lamellar hydrated aluminum iron magnesium silicate, has the unusual property of exfoliating, when submitted to a thermal shock, due to the inter-lamellar generation of steam or by reaction with H_2O_2 through its decomposition (Muromtsev et al., 1990). In its exfoliated state, vermiculite shows very interesting properties such as low bulk density, low thermal conductivity and comparatively high melting point (1240–1430°C), high absorbency, high specific surface area and cation exchange properties. Other benefits are its chemical inertness, endurance, and environmental safety. However, several industrial and agricultural applications, require an important particle size reduction and/or exfoliation of the vermiculites. The reduction of particle size can be achieved by ultrasonic treatment to obtain micrometric vermiculite (Wiewiora et al., 2003). Though submicrometric size were obtained by ultrasonic treatment at 20 kHz, the needed sonication time was very long (t>80 hours) (Wiewiora et al., 2003). In this work, we have explored the effects of ultrasound at 20 kHz on thermally exfoliated vermiculite mineral (fine grade 3 mm size; provided by “Comptoir des Minéraux et Matières Premières”, France; originating from Yuli, China) either in water or in H_2O_2 (35%) using different types of reactors and irradiating systems, in order to better understand the effect of sonication on the structure and the chemical properties of the vermiculite. Various irradiating devices: probe sonicator in cylindrical or “rosette” reactor, and sonitube® (ultrasonic continuous flow processing); were tested in order to optimize the reduction size while reducing working time, and to scale up the production of micrometric sized vermiculite.

The sonication experiments of vermiculite dispersions were conducted on lab-scale using either an ultrasonic probe (500 W, diameter 19 mm or 13 mm, Sonics and Materials) in a cylinder reactor or in a “rosette” type reactor (60 mL water or 35% H_2O_2 suspensions cooled at 25°C by circulating cryogenic fluid). On pilot-scale, experiments were conducted in an ultrasonic tube (850 W sonitube®, active volume 700 mL, internal diameter 50 mm) supplied by continuous closed flow (100 L/min) of 2.5 L H_2O_2 (17%) vermiculite suspensions at T=44°C. The sonicated vermiculite particles were characterized by laser granulometry, Scanning Electron Microscopy (SEM) coupled to X-ray microanalysis, X-ray diffraction, infrared spectroscopy, and nitrogen adsorption measurements at 77 K. The surface properties of the vermiculite particles were studied by pH measurements and zeta potential analyses.

The laser granulometry characterization has shown that whatever the ultrasonic device, the vermiculite size distribution was sonication-time and power dependent and controlled by the solid mass fraction of the suspension.

The ultrasonic treatment of the vermiculite by probe irradiation in conventional cylindrical reactor was compared in two solvents: H_2O_2, and water (for sonication time in the range 1-12 hours). The ultrasonic treatment of the vermiculite in H_2O_2 or water was performed in this reactor-type for various durations. The sonication was found to be more effective for the size reduction and the exfoliation in the hydrogen peroxide than in water. Impurities of Ti were observed by Energy Dispersive Spectroscopy due to the erosion of the probe (Ti-6Al-4V alloy). In both media, an exfoliation and a size reduction were observed after only 1 h of ultrasonic treatment by Scanning Electron Microscopy (SEM), X-ray diffraction, and nitrogen adsorption measurements at 77 K. X-ray diffraction studies showed the absence of damage in crystals structure after sonication and a reduction of crystallites size along the basal direction *(00l*). The different ultrasonic treatments also induced modifications of the surface properties of the vermiculite particles, brought out by BET surface measurements, infrared spectroscopy, pH modifications of the materials and zeta potential analyses. Sonication of the vermiculites yielded to the formation of carbonate anions from the dissolved CO_2, and hydroxide anions released from the clay layers. The long ultrasound irradiation of the vermiculite in hydrogen peroxide (> 5h) generated the decrease of the surface charge, pointed out by pH and zeta potential modifications, allowing an aggregation of the submicron particles (Nguyen et al. , 2012).

The smallest submicometric particle size distributions (d_{50} ~ 1 μm) were obtained by sonication in the “rosette” reactor of vermiculite suspensions at lower mass solid % (1 %) in hydrogen peroxide or water suspension

(Figure 1). These particle size distributions were found bimodal with modes at ~ 0.2 μm and ~ 2 μm. The de-airing of the water suspensions by Argon prior to the sonication allowed an additional decrease of the particle size reinforcing the mode at ~ 0.2 μm in the particle size distribution. Moreover the increase of the temperature of the suspensions from 20°C to 90°C improved the reduction size efficiency.

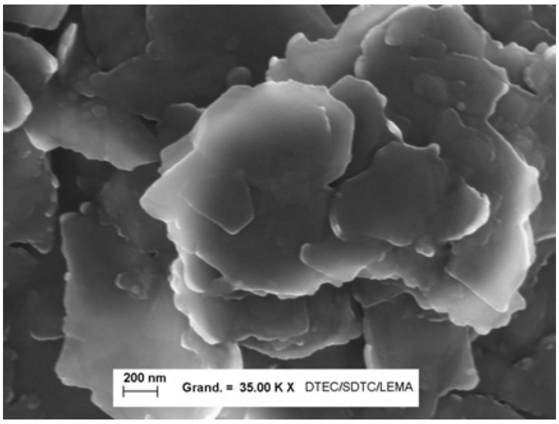

Figure 1: SEM image of the vermiculite particles sonicated for 5 h, in "rosette" reactor, from H_2O_2 (35%) vermiculite suspension (Solid fraction=1%).

The scale up for production of micrometric vermiculite particles was tested using sonitube® system coupled to closed flow (20 mass solid % suspension) for the production of about 600 g of micrometric vermiculite. After 5 h of sonication, particules of 20 μm median size (d_{50}) were obtained. Median sizes lower than 10 μm were attained after 20 h of sonitube® irradiation.

Aknowledgment
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References

Muromtsev V.A, Zolotukhina N.M., Mamina A.K, Inorganic Materials, X-ray, IR spectroscopic, and chemical analysis of products of reaction between vermiculite and hydrogen peroxide, 1990, 26, 868.

Wiewiora A.,. Perez-Rodriguez J.L, Perez-Maqueda L.A., Drapala J., Particle size distribution in sonicated high- and low-charge vermiculites, Applied Clay Science, 2003, 24, 51.

Nguyen A. N., Reinert L., Lévêque J-M., Beziat A., Dehaudt P., Juliaa J-F., Duclaux L., Preparation and characterization of micron and submicron-sized vermiculite powder by ultrasonic irradiation, Applied Clay Science, 2012, to be published.