Preparation and Refinement of Microamorphous Silica

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The application of sulfuric acid for the leaching of serpentinite ore has been investigated in order to prepare the high-purity powder of amorphous SiO_2 with great surface area.

Serpentinite with high content of antigorite was milled to particles under 200 μm in size and then thermally treated with the aim to destroy the crystal structure of antigorite. The highest leaching extent was achieved by H_2SO_4 solution with concentration 5 mol dm^{-3}, while optimum leaching time was 4 h.

Characterization and refinement of the prepared powder were also performed. By the leaching process a good-quality powder of microamorphous silica with 97.36 mass % SiO_2 was prepared, having the surface area 162 $m^2 g^{-1}$ and 71.10 % of particles under 9 μm in size. After a relatively simple refinement procedure, the content of SiO_2 was increased to 98.72 % and BET surface area to 180 $m^2 g^{-1}$.

Microamorphous silicas, which include sols, gels, powders, and porous glasses, generally consist of ultimate particles less than a micron in size or have a specific surface area greater than 3 $m^2 g^{-1}$ [1]. In nature, microamorphous silicas have either been condensed from the vapour phase ejected in volcanic eruptions or deposited from supersaturated solutions in natural waters and in living organisms. It is known that amorphous silica is not truly amorphous but consists of regions of local atomic order, or crystals of extremely small size, which by careful X-ray diffraction studies appear to have the cristobalite structure. Nevertheless, by ordinary diffraction procedures this material gives only a broad band, with no multiple peaks as are ordinarily obtained with macroscopic crystals, and is referred to here as "amorphous".

In recent times, microamorphous silica powders had different fields of application, with few overlapping areas. As modern technology develops, new opportunities for silica proliferate, and new uses are constantly replacing the classic applications soon to become overshadowed by even newer uses [2].

Serpentinite occurs in a large amount on the earth's surface. Many chemical processes for the use of magnesium from serpentinite had been widely investigated. However, serpentinite has not been used effectively in spite of those researches, and has been rarely noted as a raw material for silica production. Great contribution on this field was given by *Kosuge* and collaborators from the National Institute for Resources and Environment, Onogawa, Japan [3—6]. They described the preparation of amorphous silica and siliceous porous material by acid treatment of the ore and studied the surface properties of the products, as well as their potential for industrial usage.

In this paper the treatment of serpentinite ore by acid leaching was studied with the aim to get the powder of pure amorphous SiO_2 with great surface area.

EXPERIMENTAL

Used serpentinite is from "Mokra gora". It is ultrabasic rock, part of "Zlatibor" peridotites zone locality. The main constituents of serpentinite used are SiO_2 and MgO (more than 30 %). The dominant admixture are Fe-oxides. Beside that there are Al_2O_3, CaO, Cr_2O_3, NiO, MnO also present. The main mineral is antigorite (more than 90 %). The method used for microamorphous silica powder preparation involves the leaching of pretreated serpentinite by sulfuric acid in 3-neck glass reactor equipped with an inlet tube, Allinh condenser and mixer. The reactor was situated in an electric heating mantel [7]. The experiments were performed with crushed serpentinite which was milled into fine-sized particles (< 200 μm) and subsequently thermally treated. Thermal treatment of pulverized ore lasted 5 h at the temperature of 550 °C. During the leaching process the suspension was agitated by laboratory mixer. The acidity of H_2SO_4 solution was at pH < 1, the temperature was (107 ± 3) °C, mixing rate was 1000 min^{-1}, serpentinite

mass to H_2SO_4 volume ratio was 1 g : 7.5 cm^3. The concentration of sulfuric acid has been varied between 4 mol dm^{-3} and 6 mol dm^{-3} and the leaching time between 3 h and 7 h. Final product was let to cool to room temperature, then it was vacuum-filtered and successively washed with hot distilled water until the filtrate reaction was negative in regard to the SO_4^{2-} ions presence [8]. Prepared filter cake of amorphous SiO_2 was dried for two days in a laboratory furnace at the temperature of 50 °C.

Obtained silica powder was characterized using X-ray diffraction (XRD) with CuK_α radiation. The Phillips Diffractometer Model MPD 1880 type was used. The particle size was measured by the suspension cell method (CLCELL). The 0.1 M-$Na_4P_2O_7$ aqueous solution deflocculant was used with agitating rate 80 min^{-1}, sonication time 60 s, pause 5 s. The Sympatec Helos equipment at the Institute of Geotechnics of the Slovak Academy of Sciences was used. The Tesla BS 340 scanning electron microscope observations were also performed in order to follow the particle morphology and shape, while chemical composition of microamorphous silica powder was analyzed by the GBC Integra XM ICP analyzer. The mass fraction of SiO_2 was determined by chemical analysis.

RESULTS AND DISCUSSION

Antigorite is the main constituent of serpentinite used in this work. In order to destroy the crystal structure of antigorite, the thermal treatment is necessary. The leaching action of the treated agent could be facilitated.

Although there are several variables that are important in the preparing of microamorphous silica, only two of them were changed: the concentration of sulfuric acid and the leaching time. The other parameters like pH, the temperature during nucleation process, the choice of method how to disperse the reactants and for bringing them together, were kept constant.

In order to find out if there is a possibility to increase $w(SiO_2)$ in the powder, the following four-step refinement procedure was performed.

1. $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$
2. $Na_2SiO_3 + CO_2 \rightarrow Na_2CO_3 + H_2SiO_3$ (gel)
3. H_2SiO_3 (gel) $\rightarrow SiO_2 + H_2O$
4. Milling

In the first step the microamorphous silica was transformed into Na_2SiO_3 using NaOH as a precursor. During the second step gaseous CO_2 was introduced into the reaction vessel at pressure 300 kPa so that H_2SiO_3 gel resulted. The third step involved thermal dissociation of H_2SiO_3 for 1 h at 1050 °C. Finally, the SiO_2 prepared in the third step was pulverized in one-ball vibrating mill under the air atmosphere. After 1 h the milling process was interrupted and resulting SiO_2 powder analyzed again for chemical composition and BET surface. It is obvious that the refinement procedure resulted in silica powder with improved characteristics: the content of SiO_2 was increased from 97.36 % to 98.72 %, while the data from BET surface analysis gave the value of 180 $m^2\ g^{-1}$ for the refined product. This specific surface area is about 11 % greater than that of non-refined SiO_2 powder.

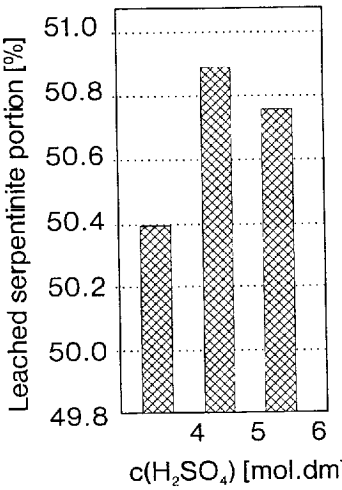

Fig. 1. The influence of sulfuric acid concentration on leached serpentinite portion. Leaching time was 4 h.

The experiments showed that SiO_2 extraction is affected by the combination of leaching time and sulfuric acid concentration. Therefore, it is important to establish a balance between providing sufficient acid and leaching time. Preliminary investigations showed that promising results, *i.e.* high SiO_2 extractions were obtained during a 4 h leaching process [7]. Hitherto, having this parameter as optimum, the experiments were performed with the aim to establish the beneficial sulfuric acid concentration. Fig. 1 shows that 5 mol dm^{-3} H_2SO_4 gave the highest leaching extent with 50.9 mass % SiO_2.

The chemical composition of microamorphous silica powder is shown in Table 1.

Fig. 2 shows a typical X-ray diffraction pattern for the amorphous silica. The absence of any characteristic peaks and the scattering on XRD-diffractogram showed

Table 1. The Chemical Composition of Microamorphous Silica Powder

Component	w/%
SiO_2	97.36
CaO	0.56
Fe_2O_3	0.25
MgO	0.20
Al_2O_3	0.11
Cr_2O_3	0.08
Other	1.44

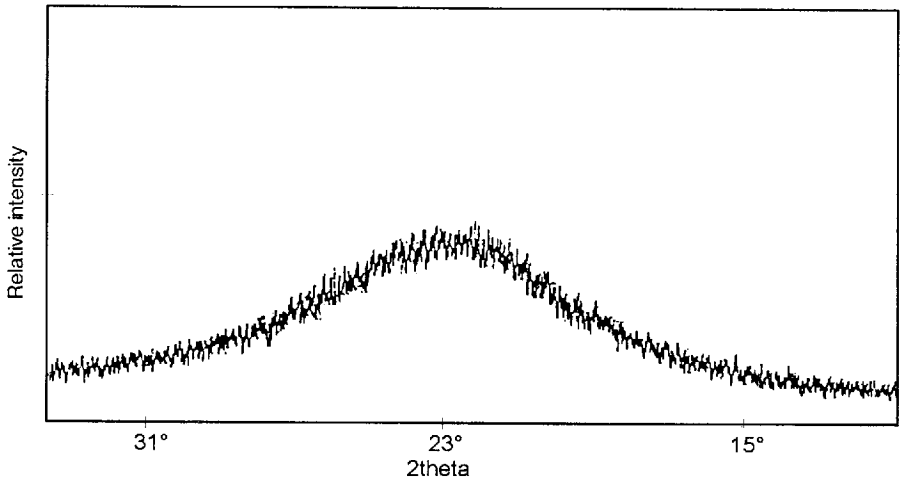

Fig. 2. X-Ray scattering of microamorphous silica powder.

that the synthesis conditions were able to control the morphology of silica as well as the efficiency of the leaching process. The value 97.36 mass % of SiO_2 from Table 1 confirmed such conclusion.

The morphology of the samples was observed with a scanning electron microscope. Fig. 3 shows a SEM photograph of the silica powder. It can be seen that fine powders are obtained by leaching procedure performed, *i.e.* the powder consists of approximately microsized particles. They are not perfectly spherical and monosized. Near-round shaped particles on the photograph differ in size, ranging mostly from 5 to 15 μm.

More precise data concerning the particle size distribution are obtained by particle size analysis of SiO_2 powder. Namely, such testing is critically important at many stages of research and fabrication and in a range of applications, covering dry powders, suspensions, aerosols, emulsions, and sprays. Therefore, the following figure illustrates the results from SiO_2 analysis plotted as undersized fraction against the particle size.

From Fig. 4 it can be seen that more than 50 % of particles are under 5 μm in size, more than 2/3 (71.1 %) under 9 μm, while cumulative fraction of 80.93 % was obtained for the particles under 15 μm. Cumulative fraction means particles fraction under given value.

Only 8.49 % of particles were of size over 30 μm. Among them, the greatest particle size found is 103 μm, but fraction with dimensions 87—103 μm is present only within 0.04 %. It is important to note that 11.94 % of particles are in the range of nano-size. The surface area of this SiO_2 powder was found to be 162 $m^2\ g^{-1}$. Additional chemical treatment in a multiphase system and subsequent milling of solid product increased this value.

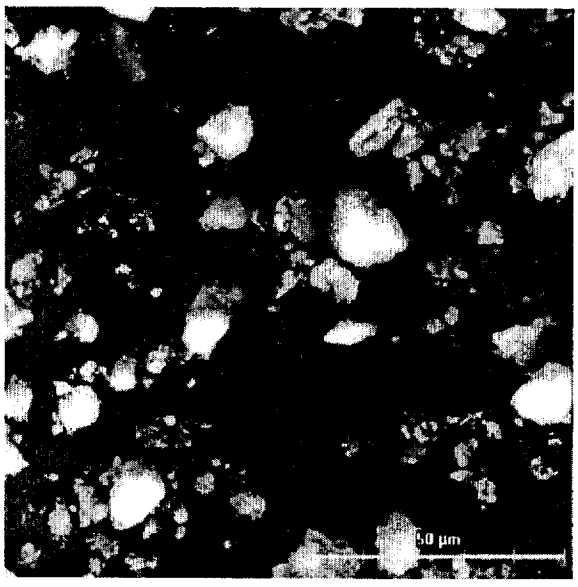

Fig. 3. SEM image of the microamorphous particles.

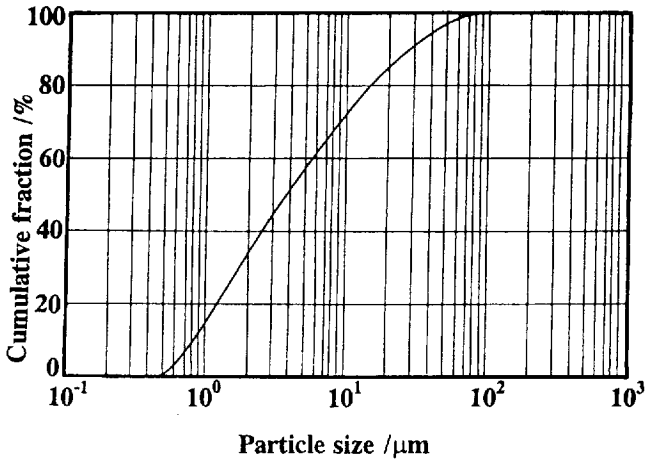

Fig. 4. Particle size distribution in microamorphous silica powder.

The results in this work indicate that prepared and refined microamorphous silica powder, because of its high SiO_2 content and large specific surface area could be a very useful material for wide industrial application [4, 9]. One of several possibilities could be exploitation in ceramics industry as precursor for producing of silicium nitride powders or whiskers, silicium carbide, and sialons.

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REFERENCES

1. Iler, R. K., *The Chemistry of Silica.* Wiley, New York, 1979.
2. Bergna, H. E., *Colloid Chemistry of Silica: An Overview, Advances in Chemistry,* Series 234. American Chemical Society, Washington, D. C., 1994.
3. Kosuge, K., Simada, K., and Tsunashima, A., *Advanced Utilization of Serpentinite.* Report of the National Institute for Resources and Environment No. 18, January 1997.
4. Kosuge, K., Simada, K., Tsunashima, A., and Otsuka, R., *J. Mining Mater. Process. Inst. Japan 108*, 443 (1992).
5. Kosuge, K., Simada, K., and Tsunashima, A., *Chem. Mater. 7*, 2241 (1995).
6. Kosuge, K., Simada, K., Tsunashima, A., and Otsuka, R., *Nippon Kagaku Kaishi 4*, 335 (1993).
7. Hršak, D., Malina, J., and Orlić, D., *Kem. Ind. 50*, 663 (2001).
8. Hršak, D., *DrSc. Thesis*. University of Zagreb, Zagreb, Croatia, 2001.
9. Navrotsky, A., in *Silica* (Heaney, P. J., Prewitt, C. T., and Gibbs, G. V., Editors), pp. 309—329. Mineralogical Society of America, Washington, D.C., BookCrafters, Chelsea, Michigan, 1994.