

THE DECOMPOSITION OF SERPENTINE BY THERMAL TREATMENT

RAZGRADNJA SERPENTINA PRI TOPLOTNI OBDELAVI

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Prejem rokopisa – received: 2005-03-21; sprejem za objavo – accepted for publication: 2005-11-03

Serpentine, $Mg_3Si_2O_5(OH)_4$, is a suitable raw material for the production of high-purity magnesium oxide and silica. The thermal decomposition of serpentine from the region of Ljeskovac, Croatia was investigated with the aim of establishing the optimum characteristics for acid leaching with pure and fine magnesium oxide and silica powder as the final products. For this purpose it was necessary to break up the crystal structure of the serpentine to obtain free magnesium oxide and silica. The first processing consisted of milling the serpentine to fine powder with a particle size of less than 200 μm and a thermal treatment at the temperature at which the crystal lattice breaks up. From the TG and DTA curves the optimum reaction parameters were established: a heating time of 180 min and a temperature of 660 °C.

Key words: serpentine, thermal decomposition, magnesium oxide and/or silica preparation

Serpentin $Mg_3Si_2O_5(OH)_4$ je primerna surovina za izdelavo čistega magnezijevega in silicijevega oksida. Toplotno razgradnjo serpentina iz Ljeskovca, Hrvatska, smo raziskali s ciljem, da dosežemo optimalne pogoje za luženje, katerega proizvodi sta fina prahova magnezijevega in silicijevega oksida. Da bi se to doseglo, je bilo treba razrešiti kristalno strukturo serpentina in sprostiti oba oksida. Serpentin smo zmleli na delca z velikostjo pod 200 μm in segreti do temperature degradacije kristalne mreže. Iz TG- in DTA-krivulj smo opredelili optimalne reakcijske parametre: čas segrevanja 180 min pri temperaturi 660 °C.

Ključne besede: serpentin, termična razgradnja, priprava, magnezijev oksid, silicijev oksid

1 INTRODUCTION

Serpentine minerals, $Mg_3Si_2O_5(OH)_4$, are widespread and often occur as modified products of olivine and other magnesium-rich silicates. They are found in metamorphic as well as in igneous rocks and occur locally in considerable quantities¹⁻³. The serpentine group includes three closely related minerals: antigorite, lizardite and chrysotile. Basically, they have the same crystal structure and chemical composition, but they differ in the curvature of the lattice planes, which results in antigorite and lizardite being dense or fine-grained and chrysotile being fibrous⁴⁻⁶.

The basis of the crystal structure is a silicate layer connected to a layer of $[MgO_2(OH)_4]$ octahedral. This composite layer is linked to the corresponding layers by weak bonds. Because of misfits between the points connecting the silicate layers and the $[MgO_2(OH)_4]$ octahedral, the composite layers can become bent in waves or shaped into fibres⁷⁻¹¹. In serpentine minerals, Fe and Ni can to some extent replace Mg, while, Al can to a lesser extent replace Si or Mg.

As only free oxides allow the success of the acid leaching process with pure and high-quality magnesium dioxide or/and silica powder as the final products, in this study the thermal decomposition of $Mg_3Si_2O_5(OH)_4$ was determined.

2 EXPERIMENTAL

Original mineral serpentine from the locality Ljeskovac, Croatia was used. The chemical composition of the serpentine powder was determined with a GBC Integra XM ICP analyser. The main constituents of serpentine are SiO_2 (more than 45 %) and MgO (more than 30 %). The dominant admixture is Fe-oxides (more than 10 %). In addition, Al_2O_3 , CaO , Cr_2O_3 and NiO are also present in amounts of more than 0.4 %. The milling process was carried out in a Fritsch Pulverisette 502 ball mill with a heatfield steel chamber, the particle size was assessed using a Fritsch Particle Sizer "analysette 22" and the phase analysis was performed by X-ray diffraction (XRD) with CuK_{α} radiation. A Philips Diffractometer Model MPD 1880 type was used. The differential thermal analysis and thermogravimetric analysis were performed in a MOM Q 1500D derivatograph with a heating rate of 10 °C/min, an air atmosphere, a sample weight of 300 mg and a maximum temperature of 1000 °C. The time, temperature and thermal difference were computer recorded and plotted by means of table processor¹². The inflection points on the curves were very clear and accurate.

3 RESULTS AND DISCUSSION

The particle size distribution of the pulverized serpentine is shown in **Figure 1**. The results from the

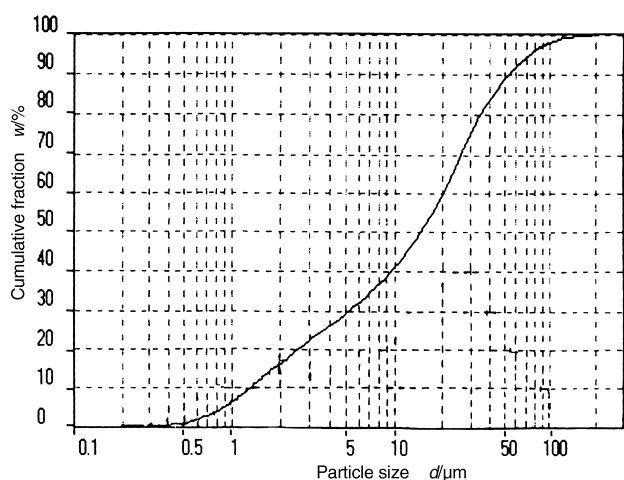


Figure 1: Particle size distribution in serpentine powder
Slika 1: Velikostna porazdelitev zrn v prahu serpentina

serpentine analysis are plotted as an undersized fraction against the particle size.

More than 99.90 % of the particles are less than 150 μm , 90 % of particles are less than 52.91 μm , more than 77.03 % are less than 32 μm , while a cumulative fraction of 50 % is achieved for a particles size of less than 14.58 μm . In this case the term cumulative fraction refers to a particles fraction below the given value.

Only 0.53 % of particles are bigger than 125 μm , and the size of the largest particle is smaller than 200 μm , which means the particle size distribution is optimal for the leaching process¹³. And since more than 10 % of the particles are in the nanosize range we can conclude that the milling process was successfully performed and the

obtained powder size distribution is suitable for differential thermal analysis (DTA).

In general, DTA curves for serpentines are somewhat reminiscent of curves for the kaolinite minerals, except that the endothermic and exothermic reactions follow almost immediately and are virtually without interspace. This is consistent with the general distinction between di- and trioctahedral minerals, the latter usually recrystallizing immediately after dehydroxylation to yield new products. Dehydroxylation appears to occur by an inhomogeneous mechanism^{14,15}.

Serpentine minerals are related both to kaolinite minerals and to chlorites; thus they are the trioctahedral analogues of the kaolinites, but can be readily converted into chlorites. Their chemical composition is much more variable than that of the kaolinite minerals¹⁴.

In **Figure 2** the results of the differential thermal analysis and the thermogravimetric analysis of the serpentine samples before and after thermal treatment are shown. The endothermic peak at 663 $^{\circ}\text{C}$ indicates the decomposition of the crystal lattice of serpentine in the case of the serpentine powder before thermal treatment (DTA 1), and it is absent for the serpentine powder after the thermal treatment (DTA 2). The breaking up of the crystal lattice is accompanied by a 10 % weight loss due to the loss of the chemically bonded water. In both cases the beginning of forsterite formation is indicated by the exothermic peak at nearly 800 $^{\circ}\text{C}$.

To confirm the conclusions obtained from the TG and DTA examinations, XRD analysis was also performed, and in **Figure 3** the X-ray diffractograms of the serpentine powders before and after the thermal treatment are shown.

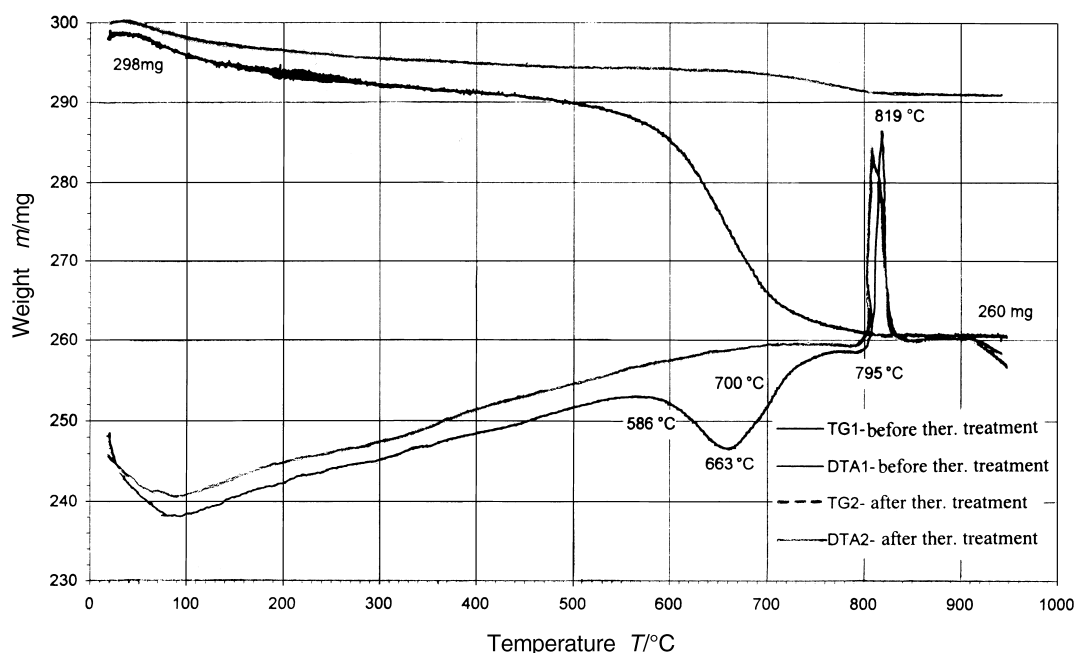


Figure 2: Curves from DTA and TG analyses of serpentine powder before and after thermal treatment
Slika 2: Krivulje analize prahu serpentina DTA in TG pred toplotno obdelavo in po njej

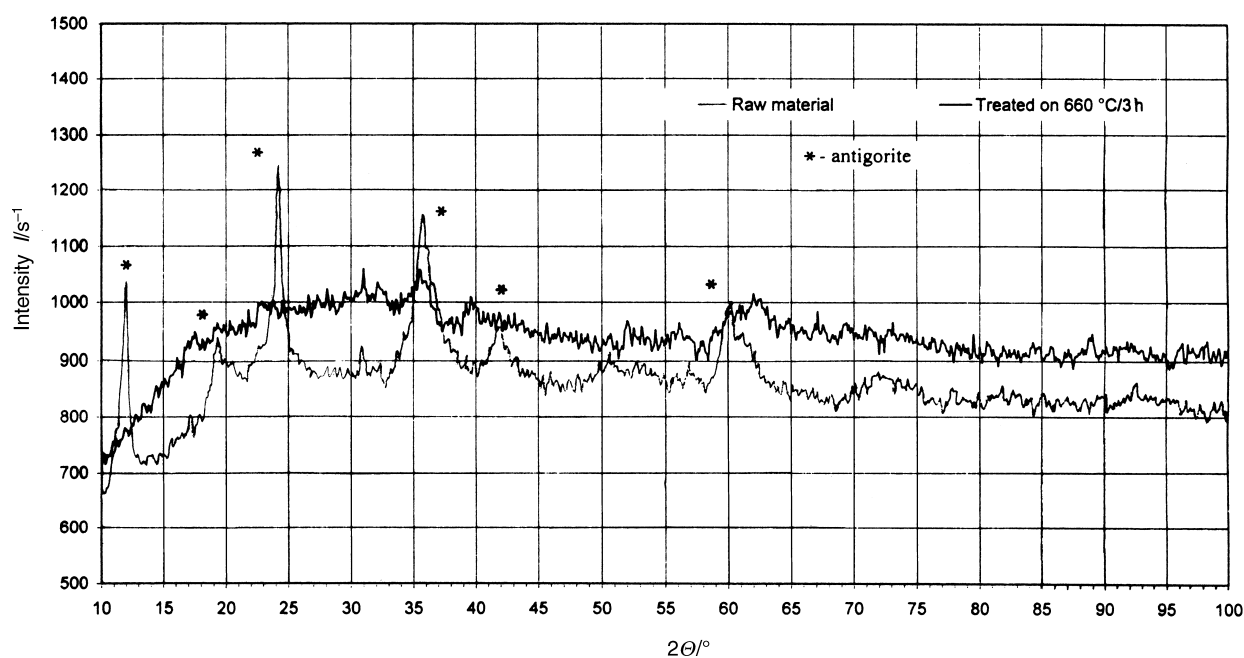


Figure 3: XRD diffractograms of serpentine powder before and after thermal treatment

Slika 3: XRD-difraktogrami prahu serpentina pred toplotno obdelavo in po njej

The XRD pattern of the serpentine powder before the thermal treatment indicates that the serpentine is mainly in the form of antigorite. The absence of any significant characteristic peaks in the XRD pattern of the serpentine powder after the thermal treatment indicates that the thermal breaking up of the crystal lattice of the serpentine was successfully performed.

4 CONCLUSION

The raw material used in this study was the mineral serpentine, $Mg_3Si_2O_5(OH)_4$, from the region of Ljeskovac, Croatia. Using a thermal treatment, the original crystal lattice was broken up and an amorphous mixture of free oxides, magnesium oxide and silica was obtained, which is suitable for pulp leaching processing.

The optimum parameters for the serpentine's thermal treatment were established: a reaction time of 180 min and a temperature of 660 °C guarantee that the process of breaking up of the mineral lattice is performed with the lowest consumption of energy.

5 LITERATURE

¹D. W. Hyndman, *Petrology of Igneous and Metamorphic Rocks*, McGraw-Hill Book Company, 2nd ed., New York 1985, 550–562

²P. Tapan, *Indian Miner.* 47 (1993), 151–156

³W. A. Deer, R. A. Howie and J. Zussman, *An Introduction to the Rock-Forming Minerals*, Longman Scientific & Technical, 2nd ed., Hong Kong 1993, 554–555

⁴R. L. Carlson, D. J. Miller, *Geophys. Res. Lett.* 24 (1997), 457–460

⁵A. Hall, *Igneous Petrology*, Longman Scientific & Technical, 2nd ed., Malaysia 1998, 463

⁶H. Blatt, R. J. Tracy, *Petrology: Igneous, Sedimentary, and Metamorphic*, W. H. Freeman and Company, 2nd ed., New York 1996, 439

⁷O. Johnsen, *Photographic Guide to Minerals of the World*, Oxford University Press, Oxford 2002, 334

⁸A. M. Amer, *Modell. Meas. Control. C.* 48 (1995), 25–41

⁹E. Dinelli, A. Lombini, A. Simoni, C. Ferrari, *Mineral. Petrogr. Acta* 40 (1997), 241–255

¹⁰H. Feng, *Huaxue Shijie*, 37 (1996), 11–13

¹¹U. G. Gasse, R. A. Dahlgren, *Soil Sci.* 158 (1994), 409–420

¹²G. Sučik, J. Durišin, T. Kuffa, *Pripojenie Derivatografu Q1500D na PC AT/XT (Connection of Derivatograph Q1500D to PC AT/XT)*, Booklet of XIII. Conference on Thermal Analysis and Calorimetry – TERMANAL'94, Stara Lesná, 1994

¹³K. Kosuge, K. Simada, A. Tsunashima, *Chem. Mater.* 7 (1995), 2241–2246

¹⁴R. C. Mackenzie, *Differential Thermal Analysis*, Academic Press, 2nd ed., London 1970, 526–37

¹⁵G. Sučik, D. Hršak, *DTA a rafinácia serpentinu*, Booklet of XVI. Conference on Thermal Analysis and Calorimetry – TERMANAL 2003, Stará Lesná, 2003