

THE RELATIONSHIP BETWEEN THERMAL TREATMENT OF SERPENTINE AND ITS REACTIVITY

ODVISNOST MED TOPLITNO OBDELAVO SERPENTINA IN NJEGOVO AKTIVNOSTJO

Gabriel Sučík¹, Adriana Szabóová¹, L'uboš Popovič¹, Damir Hršak²

¹Technical University of Košice, Faculty of Metallurgy, Department of Ceramics, Park Komenského 3, 04200 Košice, Slovakia

²University of Zagreb, Faculty of Metallurgy, Aleja narodnih heroja, 44103 Sisak, Croatia
gabriel.sucik@tuke.sk

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In this research the effect of the thermal treatment of chrysotile serpentine on the increase in the reactivity during the process of its leaching in a diluted hydrochloric acid was investigated. Measurements were made on samples of 5 g taken from the heap by selecting the fractions of 3–5 mm. The calcination in air of individual samples, required for the analysis, was carried out in an electric muffle furnace at temperatures from 500 to 1100 °C at intervals of 50 °C. The specific surface areas of the calcined samples were measured with the multipoint B.E.T. method and the relative density with a mercury high-pressure porosimeter. The results were related with the yield of Mg²⁺ in an extract of 1 g of a ground serpentine fraction from 0 to 315 µm in 250 cm³ of 0.25 M HCl, taken after 5 min from a reactor stirred at 500 min⁻¹ and at 20 °C. The strong relation between the temperature of the serpentinite calcination and the rate of leaching was confirmed. The specific surface area of the examined serpentine rose from 16.2 m² g⁻¹ at a calcination temperature of 600 °C to the maximum value of 45.2 m² g⁻¹ at a calcination temperature of 700 °C. At this temperature, the degree of dehydroxylation was 82 % and, at the same time, the maximum rate of dissolution of Mg²⁺ was reached. Above this temperature, the specific surface area decreased and, at a temperature of 1100 °C, it fell to a value of 2 m² g⁻¹, which also resulted in a reduction of the yield of Mg²⁺.

Keywords: serpentinite, calcination, specific surface area, apparent porosity, leaching rate, crystallinity

V tem članku je bil preiskovan vpliv toplotne obdelave krizotil serpentina na povečanje reaktivnosti pri procesu izločanja iz raztopine solne kislinske. Meritev so bile izvršene na 5 g vzorcev, vzeti na odlagališču, z ločitvijo frakcije 3–5 mm. Kalcinacija na zraku, posameznih vzorcev za analizo, je bila izvršena v električni retortni peči pri temperaturah od 500 °C do 1100 °C, v intervalih po 50 °C. Specifična površina kalciniranih vzorcev je bila izmerjena z večtočkovno B.E.T. metodo, relativna gostota pa z živo-srebrnim visoko-tlačnim porozimetrom. Rezultati so bili primerjeni z izkoristkom Mg²⁺ pri ekstrakciji iz 1 g osnovne frakcije serpentina z zrnatostjo 0 do 315 µm v 250 cm³ 0,25 M HCl, vzeti po 5 min iz reaktorja s hitrostjo mešanja 500 min⁻¹ pri 20 °C. Potrjena je bila močna odvisnost med temperaturo kalcinacije serpentina in hitrostjo izločanja. Specifična površina preiskovanega serpentina je narasla iz 16,2 m² g⁻¹ pri temperaturi kalcinacije 600 °C na največjo vrednost 45,2 m² g⁻¹ pri temperaturi kalcinacije 700 °C. Pri tej temperaturi je bila stopnja dehidroksilacije 82 % in istočasno je bila dosežena tudi največja hitrost raztopljanja Mg²⁺. Nad to temperaturo se je specifična površina zmanjšala in pri temperaturi 1100 °C padla na 2 m² g⁻¹, kar je vplivalo tudi na zmanjšanje izkoristka Mg²⁺.

Ključne besede: serpentinit, kalcinacija, specifična površina, navidezna poroznost, hitrost izločanja, kristaliničnost

1 INTRODUCTION

The economic efficacy of chemical technologies is closely related with the production speed. The raw material, the subject of this paper and also of earlier papers, is the waste micro-chrysotile material from the Dobšiná area (Slovakia). The aim of the chemical treatment is the production of chemically pure magnesium compounds¹, silica^{2–4} and ferric hydroxide⁵. In the previous papers^{6–8}, the following leaching agents were tested: hydrochloric acid, acetic acid and ammonium chloride. The effect of the leaching-agent concentration and the temperature on the kinetics of the leaching of crude serpentine was monitored.

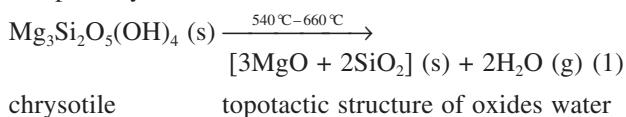
The impacts of the thermal-treatment calcination, where the key parameters were the degree of conversion and the temperature of the dehydroxylation of serpentine, were examined in previous papers^{9–14}. According to these papers, the calcination of serpentine of up to 80 %

resulted in an up to 30-time acceleration of the transfer of Mg²⁺ in the solution compared to the leaching of crude serpentine. The rapidity is attributed to the destruction of the layers of magnesium octahedron and the release of internal links. In addition, there are also changes in the specific surface area and bulk density, relating to the porosity¹⁵. These parameters are directly measurable and, in contrast to the qualitative parameter change in the crystallinity, they may be related to the kinetic parameters of the chemical reactions of the solidus-liquidus type, where the control process is the reaction at the phase interface.

2 EXPERIMENTAL WORK

The measurements of the specific-surface-area and density criteria were implemented on fractions of 3–5 mm. The apparent/open porosity was measured on sam-

ples with a cube shape and a volume of 0.2–0.5 cm³. For the chemical and thermal analysis, the samples were ground in a Mn-steel spherical vibrating chamber. The chemical composition of serpentine was analyzed with ICP OES iCAP6300 and the results are summarized in **Table 1**. By heating the crude serpentine, the thermal dissociation to the origin of the so-called topotactic structure¹⁶ of serpentine anhydride¹⁷ (Equation (1)) occurs in a temperature range of 540–660 °C, which is characterized by a low chemical stability and is accompanied by an increase in the specific surface area and porosity:



By heating them to above 700 °C, the MgO and SiO₂ oxides react with each other on a stable forsterite and amorphous silica¹⁷, stabilizing the structure and increasing the resistance to acids. The chemical reaction is expressed with Equation (2):

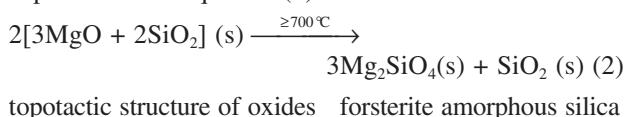


Table 1: Chemical composition of SED serpentine
Tabela 1: Kemijska sestava SED serpentina

MgO	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	NiO	L.O.I.
47.8	28.6	2.4	0.9	5.9	0.3	12.57

The thermochemical processes are identified with a differential thermal analysis and a NETZSCH STA 449F3 Jupiter thermogravimetric instrument, and evaluated in the NETZSCH Proteus program. A graphic recording with characteristic temperature points is shown in **Figure 1** and used for setting the experimental conditions of the calcination.

The calcination in air of 5 g samples of coarse fractions of 3–5 mm was carried out under controlled conditions in an electric muffle furnace at 500–1100 °C, with

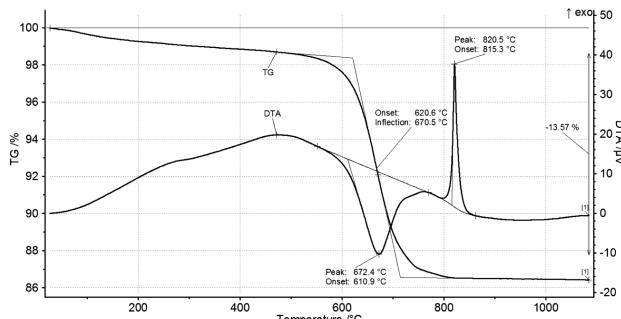


Figure 1: Differential thermal and thermogravimetric analysis of crude serpentine

Slika 1: Diferenčna termična in termogravimetrična analiza surovega serpentina

increments of 50 °C and a dwell time at a particular temperature of 180 min. The samples were inserted into the cold furnace and heated at a rate of 15 °C per minute. With this procedure, 13 samples (SED500– SED1100) were prepared. After the annealing procedure, the residual loss due to annealing (the degree of conversion) and dimensional changes were determined. In the first step of the analysis, the weight and moisture content of each sample were determined on a KERN MLB 50-3N thermobalance, and the geometric volume of mercury was determined on an Amsler 9/593 volume meter. The pore size distribution and the open porosity of the samples were measured with the method of high-pressure mercury porosimetry using automatic Quantachrome porosimeter Poremaster 33. The specific surface areas of S_A samples were measured with a surface-and-pore analyzer through the sorption of nitrogen, with the B.E.T. method. The results were compared with the parameters of the reference sample of unannealed serpentine (SEDraw).

3 RESULTS AND DISCUSSION

The measurement of open porosity π_a of calcined samples SED500 to SED1100 did not confirm the expected correlation between the chemical reactivity in terms of the leaching rate of Mg²⁺ and π_a . It can be claimed that the maximum π_a of almost 20 % was measured on the samples exposed to the temperatures of the forsterite formation with the maximum rate of around 900 °C, with the increase from the temperature of 700 °C in accordance with the forsterite formation¹⁷. On the contrary, at the temperatures in the area of dehydroxylation, $\pi_a = 1.5$ % at the level of raw serpentinite (SEDraw). Intragranular pores had the major proportion, up to 2/3 π_a , as shown in **Figure 2**.

The only noticeable consistency between π_a and specific surface area S_A is the local minimum of 1.5 % and 16 m² g⁻¹ at 600 °C, which could be explained with the closing of the pores due to the impact of the ox-

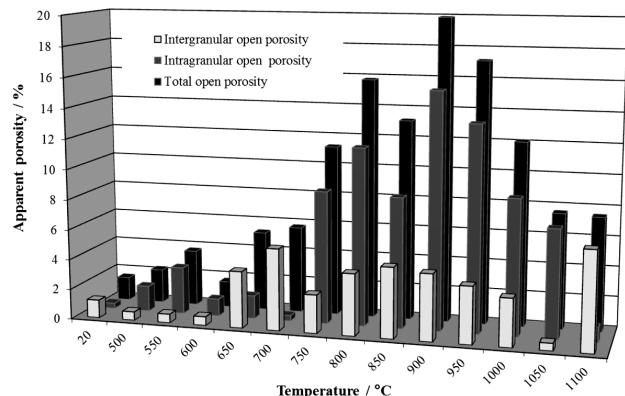


Figure 2: Open porosity and pore character depending on the calcination temperature of SED

Slika 2: Odprta poroznost in značilnost por v odvisnosti od temperature kalcinacije SED

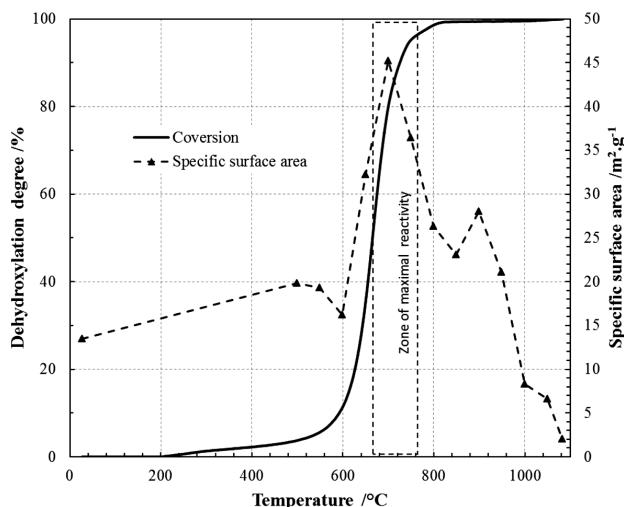


Figure 3: Change in the specific surface of SED depending on the calcination temperature

Slika 3: Spreminjanje specifične površine SED, v odvisnosti od temperature kalcinacije

dizing reactions of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$. Strong correlations between the degree of conversion α and S_A can be found in **Figure 3**. The maximum S_A of $45.2 \text{ m}^2 \text{ g}^{-1}$ was measured for sample SED700 with $\alpha = 82\%$. Increasing the temperature over the recrystallization temperature causes sintering, which is shown as a decrease in π_a and S_A over the value of $2 \text{ m}^2 \text{ g}^{-1}$.

The reactivity of ground calcinate was tested for fractions of $0\text{--}315 \mu\text{m}$. **Figure 4** shows a graphical representation of the function of the yield of Mg^{2+} $\alpha_{\text{Mg}} = f(\alpha, T)$ in intervals of (10, 20 and 60) min. From this dependence it follows that for the maximum efficiency

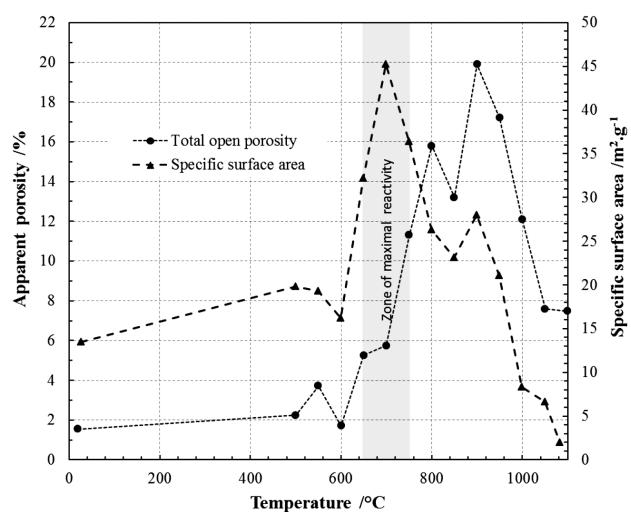


Figure 5: Comparison of the total open porosity and specific surface area as the function of temperature

Slika 5: Primerjava skupne odprte poroznosti in specifične površine v odvisnosti od temperature

of leaching, it is necessary to calcine serpentine so that a conversion of about 80 % is achieved and the calcination temperature is in a range from 600 to 700 °C. This will also guarantee the maximum surface area, which is an important parameter affecting the kinetics of the leaching. On the other hand, a porosity increase does not indicate a leaching improvement because of the structure stabilization due to the transformation to forsterite as shown in **Figure 5**.

4 CONCLUSION

The chemical reactivity of calcined serpentine depends primarily on the degree of structural crystallinity. The leaching rate of the forsterite-crystal phase is similar to the leaching rate of crude serpentine. It makes the thermal activation meaningless.

The reactive serpentine formation at temperatures of 600–700 °C does not significantly depend on the dwell time, unlike in the case of higher temperatures. At a temperature above 700 °C, a partial forsterite formation takes place.

At the temperature above 700 °C, the apparent porosity increases, but the specific surface decreases. This phenomenon is related to the recrystallization, the overall contraction of the volume and the sintering.

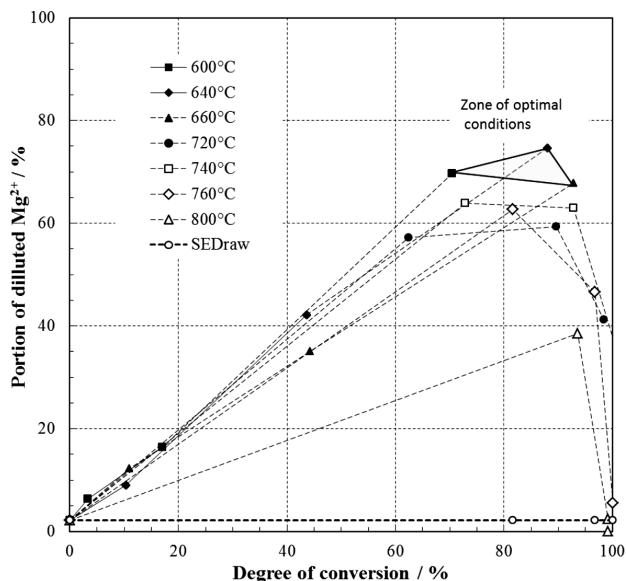


Figure 4: Dependence of the dissolution efficiency of magnesium depending on the calcination condition for serpentinite (SED)

Slika 4: Odvisnost učinkovitosti raztopljanja magnezija od pogojev pri kalcinaciji serpentina (SED)

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