THE RELATIONSHIP BETWEEN THERMAL TREATMENT OF SERPENTINE AND ITS REACTIVITY

ODVISNOST MED TOPLITNO OBDELAVO SERPENTINA IN NJEGOVO AKTIVNOSTJO

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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 area of the calcined samples was 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 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 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 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 samples were measured with the multipoint B.E.T. method and the relative density with a mercury high-pressure porosimeter. V tem članku je bil preiskovan vpliv toplotne obdelave krizotil serpentina na povečanje reaktivnosti pri procesu izložanja iz rastopine solne kisline. Meritve so bile izvršene na 5 g vzorcev, vzetih iz odlagališča, z ločitvijo frakcije 3–5 mm. Kalcinacija na zraku, posameznih vzorcev za analizo, je bila izvršena v električni retorni peći 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-šločnim porosimetrometrom. Rezultati so bili primerjani z izkoristkom Mg²⁺ pri ekstrakciji iz 1 g osnovno frakcije serpentina z zrastanjem €0 do 315 μm 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 izložanja. Specifična površina preiskovanega serpentina je narasla iz 16,2 m² g⁻¹ pri temperaturi kalcinacije 600 °C do največje vrednosti 45,2 m² g⁻¹ pri temperaturi 1100 °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⁺.

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

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 compounds, 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 compounds, 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 compounds, closely related with the production speed.

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. 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 porosity. 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-
samples 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 structure⁶ of serpentine anhydride (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:

\[
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 (s) \xrightarrow{540–660 \degree C} [3\text{MgO} + 2\text{SiO}_2] (s) + 2\text{H}_2\text{O} (g) \quad (1)
\]

topotactic structure of oxides water

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):

\[
2[3\text{MgO} + 2\text{SiO}_2] (s) \xrightarrow{700 \degree C} 3\text{Mg}_2\text{Si}_4\text{O}_9(s) + \text{SiO}_2 (s) \quad (2)
\]

topotactic structure of oxides forsterite amorphous silica

<table>
<thead>
<tr>
<th>MgO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>NiO</th>
<th>L.O.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.8</td>
<td>28.6</td>
<td>2.4</td>
<td>0.9</td>
<td>5.9</td>
<td>0.3</td>
<td>12.57</td>
</tr>
</tbody>
</table>

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 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 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 \(\pi_o\) of calcined samples SED500 to SED1100 did not confirm the expected correlation between the chemical reactivity in terms of the leaching rate of Mg\(^{2+}\) and \(\pi_o\). It can be claimed that the maximum \(\pi_o\) 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, \(\pi_o = 1.5 \%\) at the level of raw serpentinite (SEDraw). Intragranular pores had the major proportion, up to 2/3 \(\pi_o\), as shown in Figure 2.

The only noticeable consistency between \(\pi_o\) 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-
dizing reactions of \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \). Strong correlations between the degree of conversion \( \alpha \) and \( S_\lambda \) can be found in Figure 3. The maximum \( S_\lambda \) of 45.2 m\(^2\) 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 \( \pi_\alpha \) and \( S_\lambda \) over the value of 2 m\(^2\) g\(^{-1}\).

The reactivity of ground calcinite was tested for fractions of 0–315 μm. 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 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.

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5 REFERENCES

15. B. Plešingerová, K. K. Tkáčová, L. Turčániová, Transactions of the Technical University of Košice, 4 (1994) 1, 79