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ISSN 0543-5846
METABK 43 (4) 299-304 (2004)
UDC - UDK 549.4:66.061:628.4=111

PREPARATION OF SiO_2 POWDER THROUGH LEACHING OF SERPENTINE

Received - Primljeno: 2003-11-07
Accepted - Prihvaćeno: 2004-03-25
Preliminary Note - Prethodno priopćenje

In this article, the mechanism of the leaching process of preparing SiO_2 powder is analysed. A number of parameters are discussed, such as the specific surface, the size, the morphology of reactant, the ratio of all reactants, etc. After series of experiments, we successfully obtained high purity silica powder. By implementing the proposed way of chemical treatment of serpentine mineral raw material it is possible to prepare powder with content of SiO_2 up to 99 %. Technology of hydrometallurgical processing of serpentine mineral raw material can be ranked among environmental technologies aimed at the disposal of a waste dump containing asbestos. Besides processing the environmentally unfriendly dump, this technology also results in obtaining lucrative raw materials based on Si and Mg.

Key words: *silicon dioxide, powder, serpentine, leaching*

Pripremanje praha SiO_2 luženjem serpentina. U ovom radu se analizira mehanizam procesa luženja u pripremanju praha SiO_2. Raspravlja se o cijelom nizu parametara kao što su posebna površina, veličina i morfologija reaktanata, omjer svih reaktanata, itd. Nakon niza eksperimenata, dobiven je silicij visoke čistoće u prahu. Primjenjujući predložen način kemijskog tretiranja sirovine za mineral serpentina moguće je pripremiti prah sa sadržajem SiO_2 do 99 %. Tehnologija hidrometalurškog procesiranja sirovine za mineral serpentina može se svrstati među tehnologije s povoljnim utjecajem na okoliš, te je uperena protiv odlaganja otpada koji sadrži azbest. Pored obrade otpadnog materijala štetnog za okoliš, ova tehnologija dovodi do stvaranja unosnih sirovina koje se baziraju na Si i Mg.

Ključne riječi: *silicij dioksid, prah, serpentin, izluživanje*

INTRODUCTION

The paper deals with a new, untraditional technology of obtaining high-purity SiO_2 powder from secondary serpentine mineral raw material. This raw material is deposited in the form of waste dumps, where residues of carcinogenic chryzotile asbestos components also occur. Serpentine raw material is waste generated during processing primary serpentine raw material. The quantity of raw material deposited in dumps is ca 1,3 mil. metric tons with the particle size from 0 to 16 mm (Figure 1.).

SiO_2 powder has found its application in a number of industrial branches. Its particular application is closely connected with its purity, granulometry and physical properties, such as the specific surface, the morphology and the crystal lattice.

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The finest fractions of SiO_2 powder are basic raw material in production of silicate glass, silicon and certain types of optical fibres. SiO_2 powder is used in production of dispersion paints and alkaline water glass, and also as an additive to synthetic masses, winter tyres, in production of grinding and polishing pastes, for grinding rare stones, for polishing and lapping, in civil engineering as an additive to concretes and special plasters, as a pigmentation substance and an additive in production of paper and plastics. The finest fraction is formed by sol-gel products, which are used in production of dispersion paints, for colouring textiles, in production of synthetic leather, lacquers, for drying. SiO_2 is used in production of monosilane SiH_4, which is considered to be a power source of the future. Monosilane is the input raw material in production of solar cells and it has found great use in silicate technologies.

The work summarises the results of research involving physical treatment and hydrometallurgical processing of mineral raw materials. Some factors influencing the chemical treatment of the raw material and the quality of one of products - SiO_2 powder - are analysed.

Figure 1. **Waste dump based on Serpentine**
Slika 1. **Odlagalište otpada baziranog na serpentinu**

CHEMICAL AND MINERALOGICAL COMPOSITION OF SERPENTINE

Serpentine is a major rock-forming mineral and is found as a constituent in many metamorphic and weather igneous rocks. It often colours many of these rocks to a green colour and most rocks that have a green colour probably have serpentine in some amount [1].

Serpentine is actually a general name applied to several members of a polymorphic group. These minerals have essentially the same chemistry, but different structures. The following is a list of these minerals, their formulas and symmetry class:
1. Antigorite; $(Mg,Fe)_3Si_2O_5(OH)_4$; monoclinic.
2. Clinochrysotile; $Mg_3Si_2O_5(OH)_4$; monoclinic.
3. Lizardite; $Mg_3Si_2O_5(OH)_4$; trigonal and hexagonal.
4. Orthochrysotile; $Mg_3Si_2O_5(OH)_4$; orthorhombic.
5. Parachrysotile; $(Mg,Fe)_3Si_2O_5(OH)_4$; orthorhombic.

Their differences are minor and almost indistinguishable in hand samples. However, the chrysotile minerals are more likely to form serpentine asbestos, while antigorite and lizardite form cryptocrystalline masses sometimes with a lamellar or micaceous character. Asbestos had been used for years as a fire retarding cloth and in brake linings. Its links to cancer however has led to the development of alternative materials for these purposes.

The mineralogical analysis of the raw material was not made especially for the needs of this study. According to the geological exploration of deposits in surroundings of waste dump the qualitative results of mineralogical analysis are known but the quantitative results are missing.

In literature [2, 3] it is mentioned that basic minerals of the deposit are lizardit and chryzotile, furthermore there are present residues of olivine, enstative before serpentining.

Magnesium in serpentine can be substituted by iron, manganese and nickel. Also there can be found pyroxene and amfibole, ores magnetite, chromite, rarely chromspinelit, minerals Ni and Co.

The theoretical chemical composition of serpentine or chryzotile $3MgO{\cdot}2SiO_2{\cdot}2\,H_2O$ consists of only three MgO, SiO_2 and H_2O, which are represented in 43,63 %, 43,33 % and 13,04 % weight shares. This raw material contains, besides major utility components MgO and SiO_2, also minor components, such as Fe_2O_3 or FeO, Al_2O_3, CaO, Cr_2O_3 and others. Their quantity and quality can significantly influence the resulting properties of final products for which serpentine is used as an input material.

Table 1. shows the chemical composition samples of serpentine raw material taken from two different points of the dump. The results of research presented in the paper were obtained on the raw material whose composition is represented by the sample 1.

Table 1. **Chemical composition of serpentine**
Tablica 1. **Kemijski sastav serpentina**

Component / % by weight	Sample 1	Sample 2
SiO_2	32,56	38,59
MgO	42,73	37,00
Al_2O_3	1,29	1,46
Fe_2O_3	8,67	8,03
Cr_2O_3	0,37	0,38
CaO	1,12	1,22
FeO	1,05	1,15
NiO	0,22	0,25
MnO	0,12	0,11
CoO	0,01	0,01
TiO_2	0,04	0,04
Na_2O	0,02	0,02
K_2O	0,03	0,03
$-H_2O$ (105 °C)	0,79	0,81
Annealing loss	12,41	12,58

SERPENTINE MINERAL RAW MATERIAL PROCESSING

The method of natural serpentine processing makes it possible to obtain utility components from the input raw material and "to program the properties" of intermediate products in relation to their use. The advantage of this procedure is a possibility of influencing the utility properties of intermediate products by a controlled course of individual operations of the technological process (Figure 2.).

The main technological nods of the serpentine processing include physical treatment and hydrometallurgical processing.

Physical treatment of serpentine mineral raw material

a) The physical treatment of serpentine mineral raw material starts with separating the fraction above 1 mm on mechanical gap screens. The utilization of the screen oversizes is more productive and effective in the form of aggregates - crushed material. By analysing the granulometric composition of serpentine raw material, the ratio of the fraction below 1 mm to the fraction above 1 mm was determined as 85,2 : 14,8.

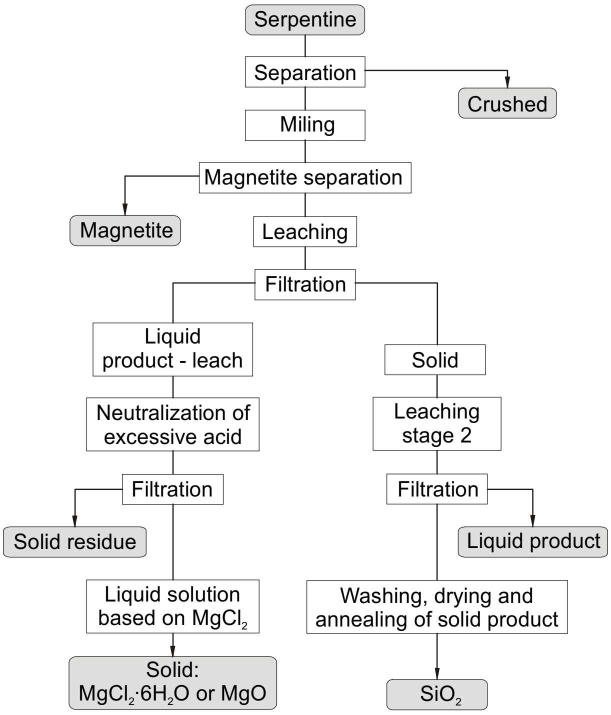

Figure 2. **Scheme of serpentine processing**
Slika 2. **Shema obrade serpentina**

b) The homogenisation and milling before the hydrometallurgical (chemical) processing of serpentine, which guarantees the top grain size level, the defined granulometry and the chemical homogeneity of treated material, significantly influence the reproducibility of the technological process of raw material processing [4, 5]. For chemical treatment, material milled in ball mills to a grain size below 0,25 mm is used. Table 2. shows the grain composition of milled material. The particle size below 40 μm was determined using a sedimentograph of SEISHIN company. It results from the data in Table 2. that over 80 % by weight of milled serpentine used in the experiments was below 20 μm. The specific surface of milled serpentine determined using BET method is 15,93 m^2/g.
c) Removal of ferric components is one of important problems in processing the raw material, because the aim is to obtain a chemically pure SiO_2 product. A reduction of the iron content in the charge before the chemical reaction has also a significant effect on the reduction of consumption of the used acid. The removal of ferric components is made by dry or wet electromagnetic separation, electrostatic separation or separation in heavy liquids and suspensions.

Table 2. **Grain compositions of raw material and product - SiO_2 powder**
Tablica 2. **Sastav zrna sirovine i materijala - prah SiO_2**

Grain class / μm	Weight yield / %			
	Sample 1		SiO_2	
	γ_i	$\Sigma\gamma_i$	γ_i	$\Sigma\gamma_i$
< 2	-	-	48,22	
2 - 10	-	-	31,68	79,90
< 10	39,10	-	-	-
10 - 20	43,42	82,52	15,85	95,75
20 - 30	12,92	95,44	3,54	99,29
30 - 40	2,14	97,58	0,71	100,00
> 40	2,42	100,00	-	-
Σ	100,00		100,00	

The results of dry electromagnetic separation [6] show that it is possible to remove 60 - 65 % iron from the input material using common means, while the material loss is ca 30 % by weight. By increasing the saturating current intensity, an increase of the weight recovery and the yield take place, as well as an unfavourable increase of the weight recovery. In wet magnetic separation, better results can be expected as regards the purity of products; however, the application of this method is debatable due to the formation of clusters of asbestos fibres. The uniform distribution of magnetite grains within the whole volume of serpentine is unfavourable from the practical point of view.

The experimental results indicate the unsuitability of the application of magnetic separation in the industrial processing of serpentine. One of possible solutions of the problem is the separation of magnetite using permanent magnets. This method saves some amount of acid, however, the content of the resulting SiO_2 product is increased by as little as ca 1,5 % (Figure 4.). Magnetite obtained by separation from serpentine using permanent magnets has a min. content of 97 % and the specific surface determined using BET method of 8,14 m^2/g. Magnetite powder can be used as a by-product without any further treatment.

Hydrometallurgical method of serpentine processing using hydrochloric acid

The leaching of serpentine is a relatively complex chemical reaction of a liquid (acidic agent) with a multi-component solid substance. During the reaction, individual components of the solid substance react with acid with different rates. During the hydrometallurgical process of serpentine processing, the soluble share, which is mainly based on magnesium, is leached from the solid phase by the action of acid, while some solid components of serpentine are chemically dissolved more quickly than others. The solid, insoluble phase - SiO_2 - is separated from the mineral by leaching and then it can be subjected to further refining. The leaching chemistry can be described in a simplified way as follows:

$$xMgO \cdot ySiO_2 \cdot zH_2O\ (s) + 2HCl(l) \Rightarrow$$
$$xMgCl_2(l) + ySiO_2\ (s) + zH_2O(l)$$

By leaching with acid, the soluble components of serpentine are dissolved into a leach. The liquid leach mainly consists of $MgCl_2$, but it also contains chlorides of another's metals. The leaching efficiency of the mentioned parts of raw material indirectly influences the achieved purity of silicon dioxide.

Physically treated serpentine is conveyed into a laboratory isothermal reactor of high-grade acid-proof steel, where the perfect mixing of the suspension is provided for the whole time of supplying serpentine and the reaction. Besides the heating possibility, the reactor must also meet the abrasive resistance requirement.

The mixing efficiency is improved by the exothermal course of the reaction accompanied with vigorous evolution of reaction gases.

After separating the liquid phase - leachate - on a filter press, the solid product is washed with hot water, while wastewater is neutralized. After washing for several times and decanting the refined SiO_2, the product is dried at 105 °C for 2 h and heated at 1000 °C for 2 h (test procedure DIN 55921). During heating OH^- bound water is released in an amount of ca 6,5 %. The time of heating is determined by monitoring the water loss down to zero. The SiO_2 powder obtained in such a way is one of lucrative, industrially utilizable products of hydrometallurgical processing of the mineral raw material, whose content of SiO_2 in product ranges from 97 to 99 %.

The chemical process took place in a chemical reactor in a continuous way. The working mode of the reactor was adapted to the expected operating conditions. Since it is a heterogeneous process, the whole reaction rate is a result of the mutual action of chemical reactions and transport actions, while it is also necessary to take into account the absorption and desorption of the reacting gas (hot vapours with increased contents of CO_2, H_2O and HCl). These circumstances can influence the accuracy of laboratory and operating measurements to a various extent. It is therefore necessary to consider them in assessing the reliability of experiments, as well as in determining the reaction efficiency and the conversion rate. In leaching the dissoluble share from serpentine, the following factors of the process were monitored:

- concentration of hydrochloric acid (18, 20 and 25 %). It was taken into account that despite an increased efficiency of leaching when using excessive acid in one-stage leaching, for potential utilization of the leach, as well as for economic reasons, it is more advantageous to apply multi-stage leaching;
- reaction time. We monitored the actual reaction time, influenced by the time necessary for adding the input raw material into the reactor and the filtration time. The serpentine leaching time in the experiments made was 1 h and 2 h;
- the fraction size of the input charge - milled serpentine. The finer grain, the greater its reactivity;
- chemical composition of the input charge of serpentine;
- the reactions were made under isothermal conditions at 105 °C under reflux.

The above-mentioned parameters have an effect on the overall efficiency of the reaction, the consumption of water used for washing SiO_2, the savings of acid and the quality of the solid product after the reaction, i.e. the achieved purity of SiO_2.

Since there is no generally applicable guide for the optimum way of leaching mineral raw material, the kinetics of the hydrometallurgical serpentine processing, i.e. the rate and mechanism of the process, was assessed based on direct experiments. When studying the leaching kinetics, a procedure was chosen where individual measurements and experiments were evaluated gradually. The results of preceding reaction conditions were used in choosing further measurements [7, 4, 5].

RESULT ANALYSIS AND DISCUSSION

The hydrometallurgical serpentine processing consists in an action of acid on soluble mineral components and the subsequent leaching of the soluble share from the solid phase; as a result, SiO_2 powder is obtained. Besides silicon oxide, a liquid product based on magnesium is also a utility component, whose processing is described in [5, 8].

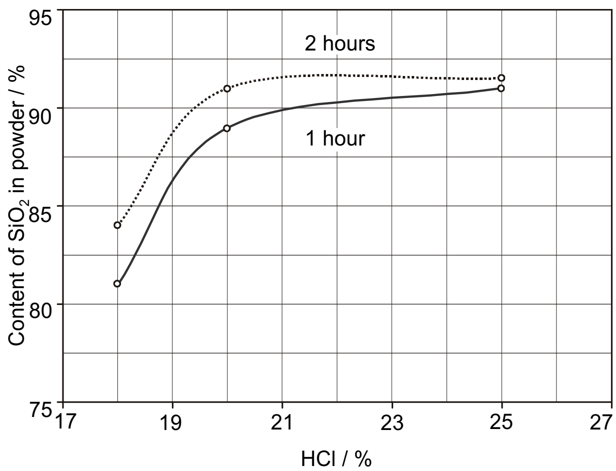

Figure 3. **Effect of HCl concentration and leaching time on content of SiO_2 in powder**

Slika 3. **Efekt koncentracije HCl i trajanja luženja na sadržaj SiO_2 u prahu**

The effective study of the one-stage leaching of serpentine represents a combination of the experiment and the subsequent evaluation of measured results with the aim to formulate an image of the course of the process:

a) Influence of the concentration of hydrochloric acid and the reaction time on the achieved content of SiO_2 in product (Figure 3.).

The content of the SiO_2 in product obtained by leaching serpentine in 18 % HCl for 1 hour is ca 81 %. By increasing the concentration from 18 to 25 %, the content of the SiO_2 in product increases by 10 % with the same reaction time. The effect of the extension of the leaching time on the content of the SiO_2 in product is the most significant at 18 and 20 % concentrations.

b) Effect of the HCl concentration and the magnetic separation on the content of the SiO_2 in product (Figure 4.).

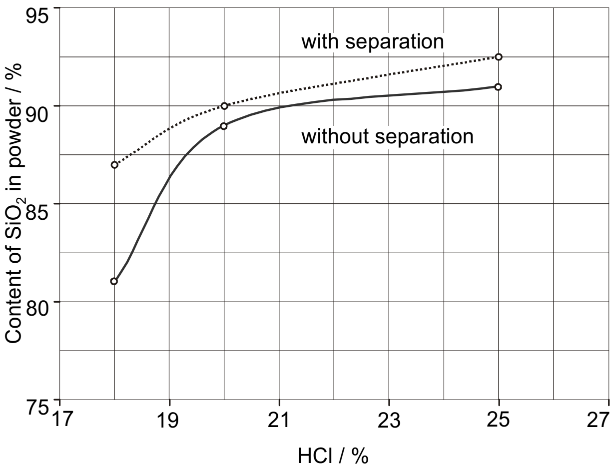

Figure 4. **Effect of HCl concentration and magnetic separation on content of the SiO_2 in product**
Slika 4. **Efekt koncentracije HCl i magnetne separacije na sadržaj SiO_2 u proizvodu**

By the wet separation of magnetite using permanent magnets, the charge weight decreases by ca 30 % and the acid consumption decreases. After magnetic separation at 1 hour leaching in 20 and 25 % HCl concentration the content of the resulting SiO_2 product is increased by as little as ca 1,5 % in compare with leaching without magnetic separation.

c) Effect of the acid concentration and the magnetic separation on the reaction efficiency (Figure 5.).

The noticeable effect of the acid concentration on reaction efficiency (stage conversion) was registered at 1 hour leaching after magnetic separation. The highest reaction yield was recorded in leaching serpentine with magnetic separation using 20 and 25 % HCl.

d) Refining of SiO_2.

An increase in the refining effect on a higher content of SiO_2 (min 99 %) can be achieved using the second stage of leaching at the some conditions as the first stage of leaching and after annealing at 1000 °C. By refining, it is possible to obtain a min. content of annealed SiO_2 of ca 99 %.

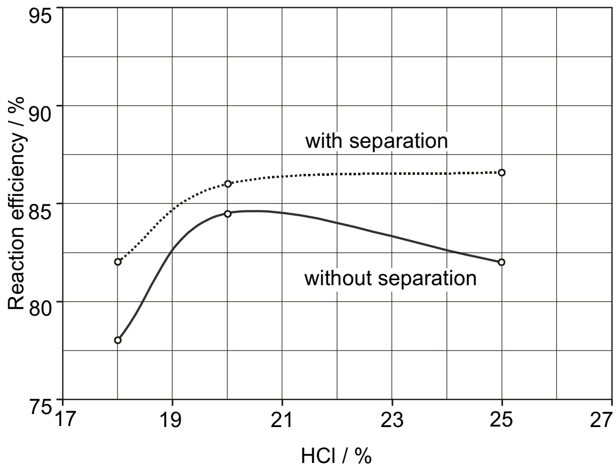

Figure 5. **Effect of acid concentration and magnetic separation on reaction efficiency**
Slika 5. **Efekt koncentracije kiseline i magnetne separacije na učinkovitost reakcije**

e) The physical properties of SiO_2 powder:
- specific surface of not heated SiO_2 determined using BET method is 340 m^2/g,
- crystal lattice determined by X ray diffraction analysis is tetragonal,
- the granulometric composition of SiO_2 obtained by hydrometallurgical processing of the serpentine mineral raw material before annealing and determined using a sedimentograph of SEISHIN is shown in Figure 6. The weight yield of grain class under 0,1 μm is ca 50 %.

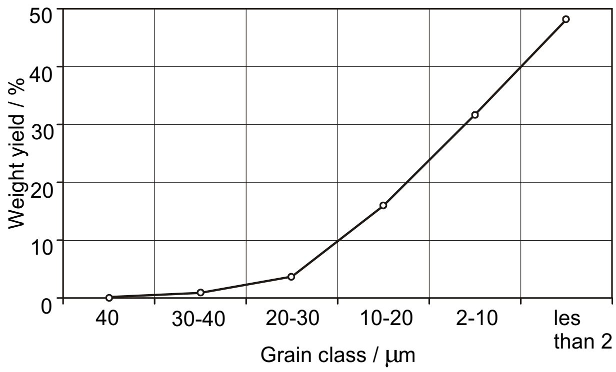

Figure 6. **Granulometric composition of SiO_2 powder**
Slika 6. **Granulometrijski sastav praha SiO_2**

CONCLUSION

By implementing the proposed way of chemical treatment of serpentine mineral raw material it is possible to prepare powder with content of SiO_2 up to 99 %. The mentioned technology of hydrometallurgical processing of secondary serpentine mineral raw material can be ranked among environmental technologies aimed at the disposal of a waste dump containing asbestos. Besides processing the environmentally unfriendly dump, this technology also results in obtaining lucrative raw materials based on Si and Mg. This technology can also be applied to other deposits with a similar chemical, mineralogical and grain composition.

Partial conclusions of the technological procedure:

1. The chemical composition of the input material, the acid concentration and the leaching temperature and time are crucial factors of the leaching kinetics. The highest reaction efficiency was recorded in the action of 25 % HCl with the solid to liquid phase ratio of 1:4.
2. The optimum leaching time is 1 hour. By increasing the leaching time above 2 hours, the reaction efficiency does not increase any more. The effect of the leaching time is more significant at lower concentrations.
3. The reaction temperature must not fall below 105 °C. Considering the fact that the reaction is exothermal, the reaction temperature can be influenced by batching the input raw material and by mixing.
4. The efficiency of the chemical reaction after the leaching stage 1 is 78 to 84 %, after the leaching stage 2 the content increases by ca 6 %. The application of excessive acid in the solution is not effective from the viewpoint of the further utilization of the leach, as well as from the economic point of view. By wet separation of magnetite powder using permanent magnets, ca 30 % of weight is removed, while the content of SiO_2 increased by as little as 1,5 %.
5. The OH^- bound water loss by heating at 1000 °C / 2h ranges from 6,5 to 8 %.

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