

PROCESSING OF SERPENTINITE TAILINGS TO PURE AMORPHOUS SILICA

[#]ALENA FEDOROČKOVÁ*, PAVEL RASCHMAN*, GABRIEL SUČIK*,
BEATRICE PLEŠINGEROVÁ*, LUBOŠ POPOVIČ*, JAROSLAV BRIANČIN**

**Technical University of Košice, Faculty of Metallurgy, Letná 9, 04200 Košice, Slovak Republic*

***Slovak Academy of Science, Institute of Geotechnics, Watsonova 45, 04353 Kosice, Slovak Republic*

[#]E-mail: alena.fedorockova@tuke.sk

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While the published research papers describe preparation of amorphous silica from water glass or using special methods (e.g. hydrolysis of alkoxides), the present study demonstrates a feasible solution for the cheaper synthesis of highly reactive silica using two-stage (acid and alkaline) leaching of serpentinite ($Mg_3Si_2O_5(OH)_4$).

The alkaline leaching, the purification of sodium metasilicate solution and the effect of impurities on the precipitation of amorphous silica under the conditions of maximum sol stability using HCl, CO_2 and $(NH_4)_2CO_3$ as the precipitating agents were examined in more details.

The prepared samples of silica were of high purity (99.4 % SiO_2 %), did not contain residues of the original raw serpentinite, and the size and shape of the particles were given by the conditions of precipitation. The presence of impurities in the sodium silicate solution had a beneficial effect on the specific surface area - in all cases the values for SiO_2 powders prepared from serpentine were higher than those of SiO_2 prepared from a synthetic solution of Na_2SiO_3 . The specific surface area of SiO_2 samples synthesized under "alkaline" conditions has been much more affected by the presence of impurities if compared to that achieved by "acidic" precipitation.

INTRODUCTION

Amorphous silica is used as a precursor, filler and additive or processing aid in high-technology product formulations such as plastics, synthetic rubbers, catalyst carriers, chemical sensors, adhesives, pesticides, paper, paints and coatings, sealants or insulation materials; it is also used to improve the surfaces and mechanical properties of many materials. Due to its great interest in many applications, the preparation of synthetic amorphous silica has been the subject of extensive research [1-14].

While many authors describe the preparation of amorphous silica by hydrolysis of alkoxides [15-18], in practice the methods based on precipitation of amorphous SiO_2 from water glass are mostly applied [1-3, 11, 16, 19]. An alternative (and cheaper) procedure to prepare highly pure silica powders is through the leaching of serpentinite, because it eliminates such costly operations as melting and high-pressure streams in the water glass route. Serpentinites – the rocks characterized by high contents of silicon oxide (35 - 45 % SiO_2) and magnesium oxide (35 - 40 % MgO), mainly present in form of the mineral serpentine ($Mg_3Si_2O_5(OH)_4$), [20] – are widely spread in nature and, moreover, there are enormous reserves (hundreds of millions tons) of

serpentinite available in the form of tailings from mining of asbestos and chromite deposits [21].

Velinskii and Gusev [21] and Pietriková et al. [22] prepared silica powders by single acid leaching of serpentinite: magnesium (accompanied by other chemically soluble components) was removed by dissolving in an acid and the undissolved (silica-rich) residue was purified by washing [21, 22] and/or ultrasonic and electromagnetic separation [21]. Though the declared purity of the prepared silica products was relatively high (up to 99 % SiO_2), the quality, including specific surface area, particle size distribution or pore size and shape, was generally not comparable with that of synthetic amorphous silica prepared through precipitation.

The present work is focused on hydrometallurgical processing of serpentinite which includes *two-stage* (i.e., acid, using HCl, and alkaline, using NaOH) leaching of serpentinite, followed by purification of the sodium metasilicate solution and precipitation of amorphous silica. The literature reports on the effects of lixiviant concentration, leaching temperature and reagent particle size on the leaching both for the acid leaching [13, 23-25] and alkaline leaching [13, 20]. In order to enhance the leaching rate, mechanical activation [26, 27] or calcination of serpentinite was applied [28, 29]. There are also multiple studies focused on the effects of

experimental conditions of precipitation, i.e. SiO₂:Na₂O molar ratio, pH and additives, such as flocculating agents and/or surfactants, on the characteristics of amorphous silica products, namely purity, specific surface area, pore size and shape [1-3, 13, 16, 19]. However, there is no published literature on the effect of pH and impurities on the precipitation of amorphous silica from concentrated sodium metasilicate solutions prepared from serpentinite without using any flocculating agents or surfactants, to simplify the overall process. These practical aspects were investigated and the experimental results are presented.

THEORETICAL

The scheme of the proposed process is shown in Figure 1.

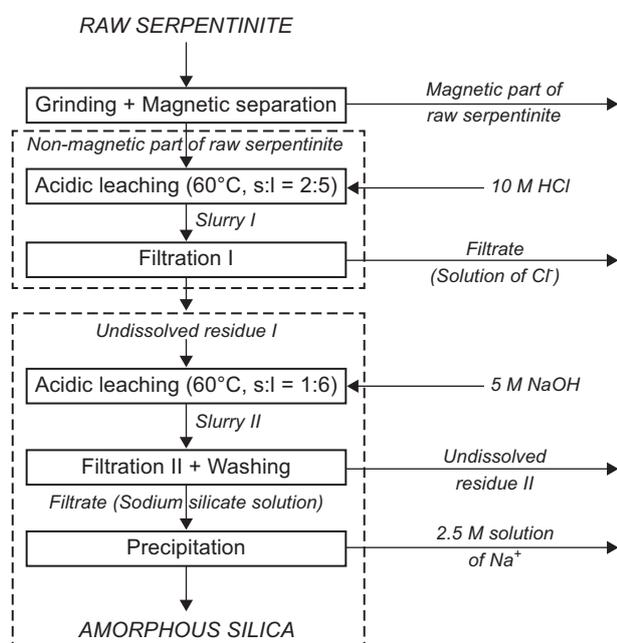
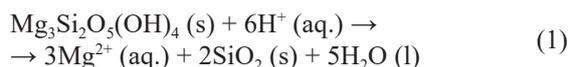


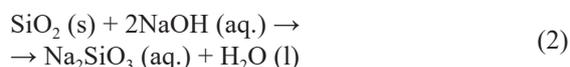
Figure 1. Two stage process of amorphous silica synthesis from serpentinite.

At first, the magnesium (accompanied by other chemically soluble components) is dissolved in an acid (reaction 1) to give the silica concentrate, i.e. the undissolved (silica-rich) residue I

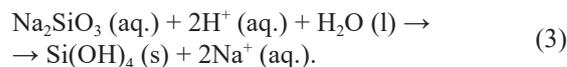


Commonly used acids are hydrochloric acid [13, 23, 24, 30] and sulphuric acid [27, 31, 32].

The silica-rich residue (concentrate) after acid leaching is a feed for *alkaline leaching* (reaction 2) to prepare a raw sodium metasilicate solution.



The sodium metasilicate solution is then purified and acidified, to give silicic acid (reaction 3) and finally amorphous silica:



It is known that stable partially polymerised silicic acid, characterised by ultimate silica particles [16] and long gel time [11, 14, 16], is formed when the reaction (acidulation of aqueous sodium silicate solution) is carried out at pH ≈ 1-4. As the pH increases (pH > pH_{ZPC} ≈ 2.0), the dissociation of the surface hydroxyl groups (reaction 4) results in formation of negatively charged particles and, subsequently, less aggregation [16, 33].



Reaching pH = 10.5 the particles can depolymerize, become less stable and dissolve to form sodium silicate [16]. In general, the sol has a maximum stability with the longest gelling time at pH 1.0 - 4.0 and over 9.0, and a minimum stability with rapid gelling at pH 5.0 - 8.0 [5, 11, 14, 34].

Since the synthesis of amorphous silica by the neutralization of sodium silicate solutions with acid (reaction 3) is conventionally carried out at pH = 8 [1-3], the surfactants and/or salts must be applied to reduce the electrostatic repulsion among primary silica particles.

The proposed technological process will be acceptable if it is simple and cheap, it is able to use concentrated solutions and provide the final product of a high and stable quality. Taking into account all the information listed above, it is hypothesized that:

- Amorphous SiO₂ characterised by long gel time and high specific surface area could be synthesized at 1.0 ≤ pH ≤ 4.0, without the use of flocculants.
- Converting the silicic substance into the solution (Equation 2) and subsequent precipitation (Equation 3) remove any impact of the original raw-materials on the nature of the final product. In such a case, the physico-chemical parameters of silica prepared using the proposed procedure could be comparable with those of synthetic amorphous silica synthesised from water glass, depending on the efficiency of the purification of the concentrated raw sodium metasilicate solution. Furthermore, final product of approximately constant quality could be obtained from serpentinites with slightly different chemical and phase composition.

EXPERIMENTAL

Material

Bulk material obtained from the mining and processing of serpentinite at Dobšiná, Slovakia was used in the present study. Mineral phases identified by X-ray diffraction analysis (XRD) were: lizardite, chrysotile, calcite, magnetite, and orthopyroxene.

A sample of serpentinite with particle sizes of up to 150 μm (Figure 2) was prepared by grinding, dry-screening and magnetic separation as shown in Figure 1.

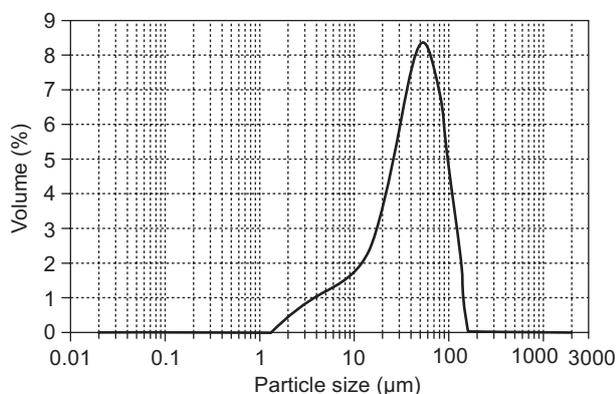


Figure 2. Particle size distribution of the serpentinite sample.

After magnetic separation, the non-magnetic part of raw serpentinite was treated in 10 M hydrochloric acid to obtain a solid residue (referred to as undissolved residue I) as a source of silica. This residue was then washed in water until the pH value reached neutrality.

Methods

Preparation of the sodium metasilicate solution

Sodium metasilicate solution ($\text{SiO}_2 : \text{Na}_2\text{O}$ molar ratio = 1:1) was prepared by alkaline leaching of the silica concentrate (i.e., undissolved residue I) in 5 M NaOH at 60°C and filtration. Apart from silicon, other accompanying elements, e.g., aluminium, iron, calcium, magnesium, nickel, etc. present as impurities were determined in the filtrate using AAS analysis. The cake (referred to as undissolved residue II) was then washed by 2×250 ml of distilled water. The washing water was added to the filtrate and the undissolved residue II was analysed using atomic absorption spectrometry (AAS).

Preparation of the silica samples

Samples of synthetic amorphous silica were synthesized in compliance with chemical reaction 3 using HCl, CO_2 and $(\text{NH}_4)_2\text{CO}_3$ as precipitating agents. To stimulate the aggregation of primary silica particles without using additives, we carried out the synthesis of amorphous SiO_2 from a concentrated metasilicate solution at pH = 1.0 (using HCl) and over 9.0 (using CO_2 or $(\text{NH}_4)_2\text{CO}_3$), i.e. under the conditions of maximum sol stability.

The synthesis of silica gel using HCl was carried out by adding a thin stream of 2.5 M aqueous solution of sodium metasilicate into the bulk of intensively stirred (800 s^{-1}) 10 M aqueous solution of hydrochloric acid.

In the case of silica synthesis through the carbonization reaction, CO_2 ($p_{\text{CO}_2} = 1.3 \times 10^5 \text{ Pa}$) was introduced into the bottom of the reactor with a continuously – stirred Na_2SiO_3 solution. When the pH of the solution was stabilized, the gas flow was switched over to N_2 to remove free CO_2 from the reactor. Precipitation using ammonium carbonate was carried out by adding a powdered $(\text{NH}_4)_2\text{CO}_3$ into the Na_2SiO_3 solution at the molar ratio 1.5 : 1.

In all experiments the temperature was kept at about 22°C. Finally, the synthesized silica was washed to remove sodium ions, filtered, dried at 110°C, and ground.

Characterization of the silica samples

XRD patterns for the synthesized samples were recorded on a powder diffractometer (X'Pert PRO) using CoK_α radiation (1.78901 Å) with Ni filter. Scanning electron microscopy (SEM, TESCAN MIRA 3) was used to investigate the morphologies of the silica powders. The Energy dispersive X-ray spectroscopy (EDS) system attached with the SEM allows for qualitative and quantitative elemental analysis, point analysis and the spatial distribution of elements using X-ray mapping. The specific surface area was determined using the B.E.T. nitrogen adsorption technique (NOVA 1000 Quantachrome Instrument). The purity of final products was verified by ICP-OES analysis.

RESULTS AND DISCUSSION

While acid leaching has been used in the present study to prepare a silica concentrate, the feed for the second stage of the overall process, the alkaline leaching of the undissolved residue I, purification of the sodium metasilicate solution and precipitation of silica are the main focus of the study.

Nature of leach residue after acid leaching

The results of chemical analyses of dried raw serpentinite and undissolved residue I obtained by atomic absorption spectrometry (AAS) are summarized in Table 1. (L.O.I. of raw serpentinite and undissolved residue I is comprised of chemically bound water in serpentinite and carbon dioxide in calcite, and physically bound water).

It was found out that an important role in determining the purity of synthesized SiO_2 is played by the analytical method used. Quantitative elemental microanalysis (EDS) in our case reported only the presence of silicon and oxygen (Figures 3a-d) and the silica concentrate appeared to be seemingly pure SiO_2 . However, according to the results in Table 1, the purity of the SiO_2 concentrate was 87.2 % which, calculated to an anhydrous state, was about 96 % SiO_2 . The main accompanying elements were magnesium, aluminium and iron.

Table 1. Chemical composition of serpentinite prior to and after acid leaching (10 M HCl; process temperature 60°C; solid: liquid ratio = 2:5).

Sample	Chemical composition (wt. %)							
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	NiO	Cr ₂ O ₃	L.O.I.
Non-magnetic part of raw serpentinite	38.2	1.2	37.3	5.7	1.4	0.1	0.3	14.1
Undissolved residue I (silica concentrate)	1.54	0.08	87.2	0.4	0.8	0.02	0.04	9.2

Velinskii and Gusev [21], and Pietriková et al. [22] consider the undissolved residue I as a final product, that is pure SiO₂. Although it would be possible to increase slightly the SiO₂ content by extending the leaching period, other SiO₂ characteristics could not be improved significantly. Figure 3a shows the different size and shape of the particles, in particular the residues of the original fibrous structure of chrysotile, which is ascribed to the nature of the raw serpentine used. Significant amount of serpentine phase remaining in the residue after acid leaching is caused by the strong diffusion resistance of the inert silica layer, inhibiting the complete conversion of serpentine phase [13].

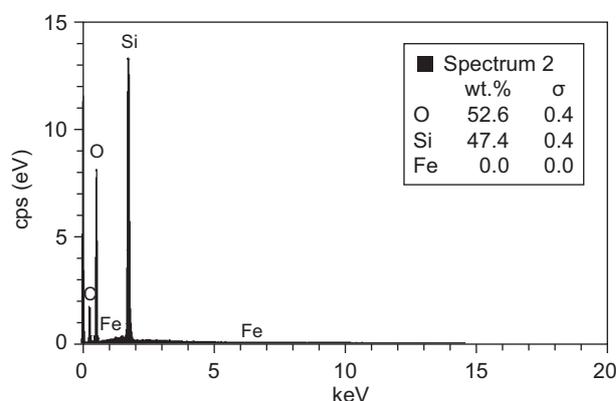
Preparation of sodium metasilicate solution

To prepare concentrated solution of sodium metasilicate, the silica concentrate (undissolved residue I) was subjected to alkaline leaching (reaction 2). The chemical composition of sodium metasilicate solution is shown in Table 2.

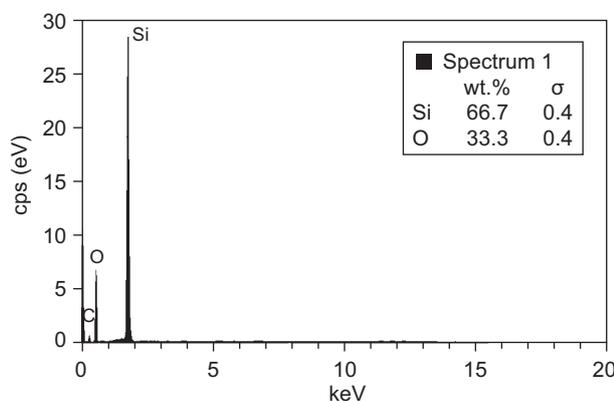
By alkaline leaching of the silica concentrate a portion of accompanying elements passed into the solution, and the rest of them remained undissolved in the form of insoluble residue II (5.9 wt. % undissolved residue I), which was removed by filtration. The chemical composition of the filter cake (the undissolved residue II) is found to be as follows (in wt. %): 62.3 % SiO₂, 9.8 % MgO; 1.4 % Fe₂O₃; 21.7 % Al₂O₃; 2.8 %CaO; 0.80 % TiO₂.



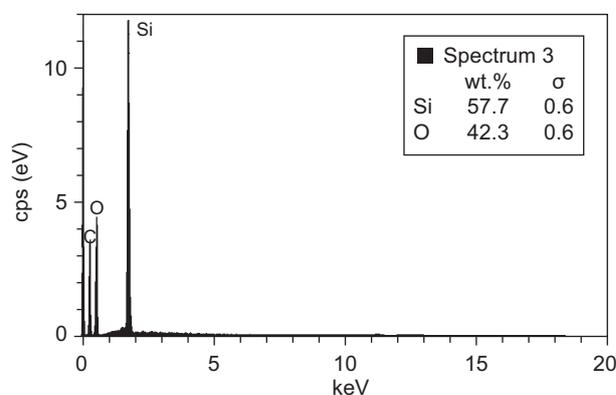
a) SEM image of undissolved residue I



c) EDS spectrum of undissolved residue I



b) EDS spectrum of undissolved residue I



d) EDS spectrum of undissolved residue I

Figure 3. a) SEM micrograph; b-d) results of X-ray microanalysis of undissolved residue I.

Table 2. Chemical composition of a concentrated sodium metasilicate solution prepared by alkaline leaching of undissolved residue I (5 M NaOH; process temperature 60°C; solid: liquid ratio = 1:6) and filtration.

Sample	pH	Chemical composition (g·l ⁻¹)							
		Si ⁴⁺	Al ³⁺	Ca ²⁺	Fe ²⁺ + Fe ³⁺	Mg ²⁺	Ni ²⁺	Cr ³⁺	Ti ⁴⁺
Sodium silicate solution	13.8	69.4	0.030	0.017	0.062	0.077	0.02	0.003	0.014

Precipitation of amorphous silica samples and their characterization

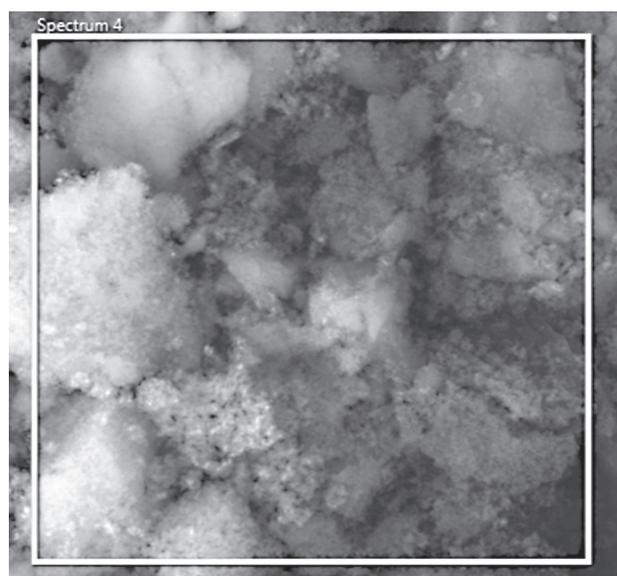
SEM micrographs and the results of elemental analysis of the SiO₂ powders synthesized using HCl, CO₂ and (NH₄)₂CO₃ are given in Figure 4a-c. The values of specific surface area (S_A) and characteristics of pores are summarized in Table 3.

From the presented results it follows that:

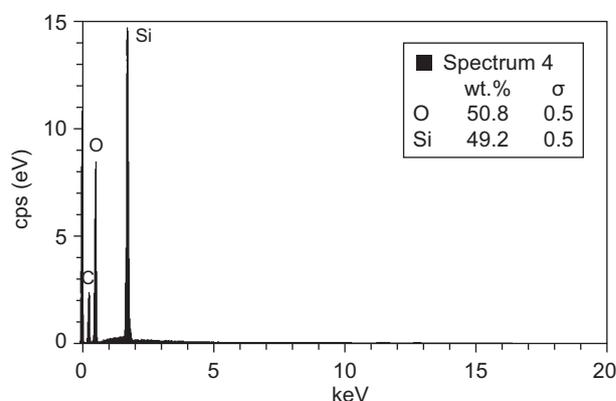
- Total yield of silicon in the overall process was 90 - 91 %.
- The prepared samples of synthetic silica were of high purity (99.4 % SiO₂), no residues of the original fibrous structure of chrysotile could have been observed. It was therefore concluded that the size and shape of the silica particles are governed by the precipitation (Figures 4a-c). As reported earlier, the synthesized SiO₂ powders had an amorphous structure [35]. With regard to purity, EDS of the sample precipitated using HCl showed only the presence of silicon and oxygen (Figure 4a). In the case of samples prepared by the precipitation using CO₂ and (NH₄)₂CO₃, residual amounts of non-washed out sodium also were observed (Figures 4b, 4c). These findings correlate well with the results of other authors. Bai et al. [13] report that the lower the pH of precipitation, the lower

the total amount of impurities in the final product. Lee et al. [5] observed that washing of wet gel under acidic conditions (at pH ≈ 2.5) was more effective to reduce residual amounts of salts.

- Considering the microporosity and the mesopore size distribution of the final SiO₂ powders, the values presented in Table 3 suggest that the vast majority (~99 %) of pores are smaller than 30 nm while micropores with diameter lower than 2 nm are practically present only in silica precipitated by HCl.
- The specific surface area (S_{BET}) of the silica powders presented in Table 3 achieved the values lower than those of the SiO₂ powders synthesized by precipitation from water glass in the presence of a surfactant (which is about 690 m²·g⁻¹ [1-3]). But at this point it is worth mentioning the drawbacks of the “water glass” procedure which are the expense of the surfactant and thermal treatment associated with its removal [1]. On the other hand, the samples synthesized in this work were characterized by significantly higher specific surface area if compared to those prepared from serpentinite by single acid leaching (340 m²·g⁻¹ [22]). The use of carbon dioxide and ammonium carbonate as acidifying agents resulted in less specific surface area and more impurity than hydrochloric acid (as shown in the Table 3 and Figure 4). The specific surface area of prepared silica powders (392 m²·g⁻¹ using CO₂ and 414 m²·g⁻¹ using (NH₄)₂CO₃) correlates well with that reported by Bai et al. [13] (349 m²·g⁻¹) and was two times greater than that observed for silica prepared from water glass (210 m²·g⁻¹ [19]).



a) HCl

Figure 4. SEM micrographs and the results of the elemental X-ray microanalysis of the synthesized SiO₂ powders (acidifying agent used: a) HCl; b) CO₂; c) (NH₄)₂CO₃). (continue on next page)

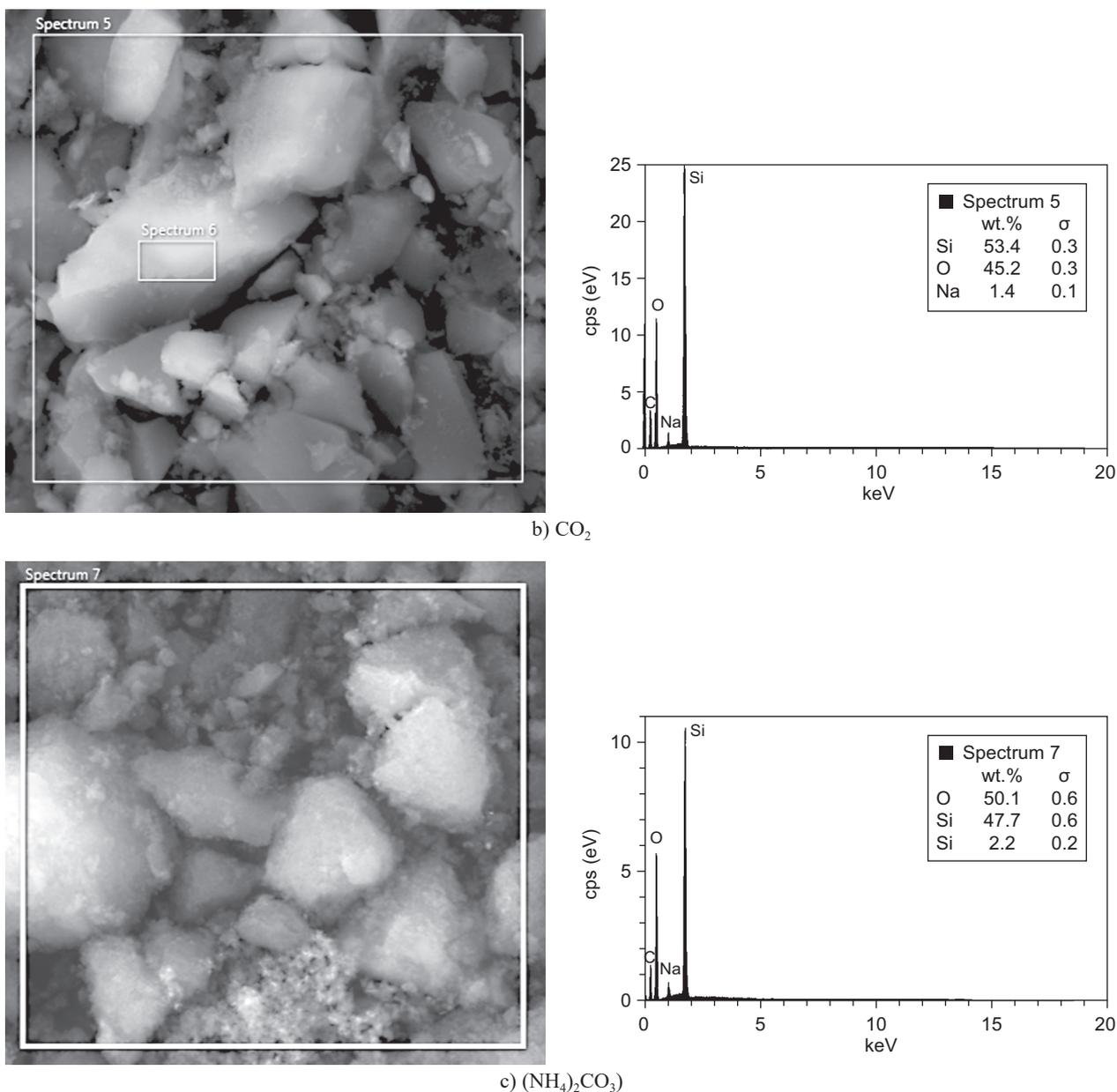


Figure 4. SEM micrographs and the results of the elemental X-ray microanalysis of the synthesized SiO₂ powders (acidifying agent used: a) HCl; b) CO₂; c) (NH₄)₂CO₃).

Table 3. The specific surface area and characteristics of pores of synthesized SiO₂ powders.

Silica properties		Precipitation agents		
		HCl (aq)	(NH ₄) ₂ CO ₃ (s)	CO ₂ (g)
Reaction conditions	pH _{final}	1.0	10.7	10.0
	p(CO ₂) [10 ⁵ Pa]	–	–	1.3
Specific surface area (S _{BET}) [m ² ·g ⁻¹]		541	414	392
Fraction of pores (in vol. %) with diameter:	< 2 nm	28	2	0
	2-10 nm	33	52	21
	10-20 nm	21	26	52
	20-30 nm	17	20	27

- e) To verify the effect of accompanying species (impurities) on the specific surface area of SiO₂ products, reference samples were prepared by precipitation from a synthetic solution of Na₂SiO₃ (with a mole Na₂O:SiO₂ ratio = 1:1) prepared by dissolving SiO₂ powder of purity p.a. in a concentrated solution of pure NaOH. From the comparison illustrated by Figure 5 it follows that the presence of impurities (specified in Table 2) seems to have a beneficial effect on the specific surface area; in all cases the values of the specific surface area of SiO₂ powders prepared from serpentinite were higher than those of SiO₂ prepared from a synthetic solution of Na₂SiO₃. More significant effect of impurities was observed when the precipitation was performed under alkaline conditions (using CO₂ and (NH₄)₂CO₃) as indicated in Figure 5. This is in agreement with results valid for alkaline media only, showing that impurities such as Na or Al may be picked up and then occluded inside the colloidal particles, forming there microcavities [16].
- f) In practical terms, it is important that the final product has a stable quality even when raw-materials with a slightly varying composition are used. From Figure 5 it can be seen that the synthesis of amorphous SiO₂ by precipitation at pH = 1 is more advantageous

from the technological point of view, because the characteristics of synthesized SiO₂ powders are less sensitive to the presence of impurities in the sodium metasilicate solution. Furthermore, long gel times (circa 18 h) observed under acidic conditions offer longer manipulation times in the final stage of the technological process.

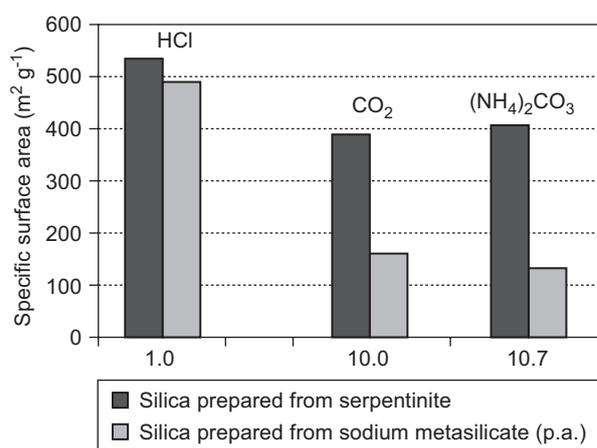


Figure 5. Influence of impurities on the specific surface area of synthesized SiO₂ samples.

Table 4. Comparison of process parameters used in the present work and in work of Bai et al. [13], and properties of final products.

		Present work	Bai et al. [13]
Process parameters used			
Process	Raw-materials (feed) used	serpentinite	serpentinite
	Acid leaching	10 M HCl	1-2 M HCl
		60°C	24 - 80°C
		S:L = 2:5	S:L = (40g : 1000 ml) = 1:25
	Alkaline leaching	5M NaOH	0.1 - 0.3 M NaOH
		60°C	24 - 40°C
		S:L = 1:6	S:L = (0.1g : 40 ml) = 1:400
	Precipitation	Concentration of the sodium metasilicate solution (C _{Si4+}) = 69.4 g·l ⁻¹	Concentration of the sodium metasilicate solution (C _{Si4+}) = 1.17 g·l ⁻¹
		Acidifying (precipitating) agent: CO ₂	Acidifying (precipitating) agent: CO ₂
		pH = 10.0	pH = 7.7 - 10.0
22°C		24 - 80°C	
Characteristics of final product			
Product	Structure	amorphous	amorphous
	Purity SiO ₂ in wt. % (depends on the efficiency of washing)	99.4	up to 97.7
	Specific surface area (S _{BET}) in m ² ·g ⁻¹	392	349
	System of pores	Mesoporous, narrow pore distribution – average pore diameter approx. 15 nm	Mesoporous, narrow pore distribution – average pore diameter approx. 10 nm

Comparing the results obtained for precipitation using CO₂ in the present work with those presented by Bai et al. [13], we found that the final products characterized by very similar purity, pore diameter and specific surface area can be prepared by the proposed procedure from different serpentinite raw-materials and under different (technological) conditions – for more details see Table 4.

This observation leads us to conclude that the hypothesis about the possibility of the proposed procedure to produce final product of stable quality from serpentinites with slightly different chemical and phase composition may be eligible.

CONCLUSIONS

From the presented results it follows that:

- Amorphous silica with high purity (99.4 %) was synthesized from serpentinite by a two stage leaching and precipitation.
- Highly reactive product with surface area from 392 m²·g⁻¹ to 541 m²·g⁻¹, depending on the precipitating (acidifying) agent used, was obtained.
- When the precipitation is carried out at pH = 1 or pH > 9 (i.e., under conditions of maximum sol stability), no additives have to be used, thus allowing lower operating costs. Furthermore, long gel times observed under acidic conditions offer longer manipulation times in the final stage of the technological process.
- The presence of impurities in the sodium metasilicate solution had a beneficial effect on the specific surface area, especially under “alkaline” conditions.
- The specific surface area of SiO₂ samples synthesized under “acidic” conditions was practically insensitive to the presence of impurities if compared to that achieved under “alkaline” precipitation. Hence, the synthesis of amorphous SiO₂ under highly acidic conditions (i.e. at pH = 1) is more advantageous from the technological point of view, so offering the chance to produce final product of stable quality from serpentinites with slightly different chemical and phase composition.

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