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CHARACTERISATION OF HIGHLY DISPERSED MAGNESIUM SILICATES PREPARED FROM SILICA SOLS AND SELECTED MAGNESIUM SALTS

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A process of obtaining synthetic magnesium silicate by a precipitation method with the use of silicic acid sols and selected magnesium salts was analysed in order to establish the optimum parameters of the process ensuring getting a product of desired properties. The influence of the following parameters was taken into regard: concentration and type of magnesium salt, concentration of silicic acid sol and direction of reagents supply. The synthetic magnesium silicate was subjected to physico-chemical analysis. The chemical compositions of the products and their crystalline structures were determined. Moreover, the morphology, dispersion and adsorption properties of the products were characterised. The magnesium silicate obtained according to the procedure proposed is highly dispersed, homogeneous and of well-developed surface area.

key words: magnesium silicate, silica sol, precipitation, dispersive characteristics, surface area

1. INTRODUCTION

Silicates belong to the widest spread minerals on the Earth making about 25% of all known minerals. The rocks-forming silicates include: quartz, amphiboles, pyroxenes and micas. Besides their rock-forming role, silicates are the sources of many valuable metals such as nickel, zinc, zircon and lithium and form deposits of many important minerals.

Silicates and aluminosilicates are important raw materials for many industries. They are used in construction, ceramic, paper, rubber, food, pharmaceutical and

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cosmetic industries. Because of their unique physico-chemical properties they are used as selective active adsorbents or polymer fillers (Başçetin, 2010; Carretero, 2010; Villanueva, 2010).

Increasing demand for synthetic silicates of special parameters and properties has stimulated development of new technologies of their production.

One of the best known and documented methods of silica gel production is the sol-gel method. It needs relatively low temperatures and gives products of high purity and homogeneity (Mc Kenzie, 1988). This method belongs to wet ones and requires hydrolysis and condensation of metal alkoxides and inorganic salts.

Another well-known method is based on the ion exchange between the basic ions and protons contained in ≡Si-OH, which permits formation of ≡Si-O-A type bonds (where A is the alkaline metal e.g. Na). The course of hydrolysis and ion exchange depend on the concentration of protons and basic ions in the reaction mixture and influence the concentration of ≡Si-O-A bonds in oligomers. The amorphous Na_2O-SiO_2 powder obtained by the ion-exchange method is the initial product for synthesis of magnesium silicate. The ion exchange between alkali earth ions and sodium in Na_2O-SiO_2 leads to formation of ≡Si-O-M (where M stands for magnesium or calcium ions) (Suda, 1999).

Quite often used are the methods of obtaining synthetic silicates in water systems (Modrzejewska-Sikorska, 2010; Ciesielczyk, 2004). One of them is the standard reaction of precipitation from water-soluble alkaline silicates, e.g. sodium silicate, by addition of a reagent such as mineral acid or magnesium hydroxide (Brew, 2005; El-Naggar, 2007; Ciesielczyk, 2007). A method for obtaining forsterite and enstatite by the two different water processes has been proposed by Andre Douy (Douy, 2002). Irrespective of the type of procedure, the main reaction is hydrolysis of tetraethoxysilane (TEOS) in an aqueous solution of magnesium nitrate.

An alternative method for production of synthetic silicates is that of precipitation in emulsion systems (Kurc, 2008). A typical procedure for obtaining nanoparticle silicates involves preparation of two emulsions (microemulsions); one with metal salt (sodium silicate) and the other with the reducing agent, and their mixing (Bruch, 1997)

Other literature methods for obtaining magnesium silicates described include the hydrothermal method (Goluber, 2005), condensation of gaseous phase to solid state (Brucato, 2002), laser ablation (Fabian, 2000), recovery of magnesium silicate from geothermal brine and that based on the use of A type zeolites (Strack, 1987).

Although silicates occur naturally in many sites over the world, not all deposits are suitable for exploitation because of too high cost and technical difficulties. Moreover, the natural deposits tend to be exhausted, so the interest in production of synthetic magnesium silicate is still vivid. Much effort is made to facilitate their production, decrease the cost and make their production environmentally neutral.

Development of new processes of synthetic magnesium silicate production is aimed at getting products of desired tailored physicochemical properties. The aim of our study was to propose and characterise a new precipitation method of magnesium silicate production.

2. EXPERIMENTAL

2.1. MATERIALS

The main substrate used in the process of magnesium silicate precipitation was silicic acid sol of the commercial name LUDOX® HS-40, purchased from SIGMA–ALDRICH. It is a 40% water solution of SiO_2. The ratio of silica to sodium oxide was 89/101, while the maximum content of SO_4^{2-} in Na_2SO_4 was 0.08%. The concentrations of the silicic acid sol used in our study were 5, 10, 20, 30 and 40%.

The precipitating reagents used were solutions of magnesium sulphate ($MgSO_4{\cdot}7H_2O$) of 1.67 g/cm^3 in density, magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$) of 1.46 g/cm^3 in density and magnesium chloride ($MgCl_2{\cdot}6H_2O$) of 1.57 g/cm^3 in density, all made by POCh SA. The magnesium salts were used in the form of solutions of 5, 10, 20, 30 and 40% concentrations.

2.2. METHODS OF STUDIES

Precipitation of synthetic highly dispersed magnesium silicates was conducted at room temperature in a reactor of 1000 cm^3 in volume, equipped with a mechanical stirrer CAT R18 (1000-1600 rpm.). Silicic acid sol (200 cm^3) was supplied at the constant rate of 5 cm^3/min to the reactor already containing a proper magnesium salt (200 cm^3) with the help of a peristaltic pump type ISM 833A, made by ISMATEC. The effect of the reverse direction of supply on the final product properties was also studied. At the second stage of the process the product was filtered off under reduced pressure. To remove the traces of the salts the precipitate was twice washed with hot water. After filtration the product was dried in a stationary drier at 105°C for 24 h.

The first step of the products characterisation was determination of their chemical composition. To this aim magnesium silicate was leached in a solution of HCl/H_2O (1/1) to remove $MgCl_2$. The solution obtained contained the silica precipitate which was separated by gravitational method and washed with distilled water. The content of silicon dioxide was determined by the weight analysis. In the filtrate obtained after leaching the percent contents of magnesium and some small amounts of calcium, sodium and potassium coming from the silicic acid sol solution, were determined by the absorption atomic spectrometry (AAS) on a PU 9100X spectrophotometer made by UNICAM. The crystalline structures of the magnesium silicate samples obtained were established by the WAXS method on a horizontal diffractometer TUR–M–62. Morphology and microstructure of the silicates were assessed on the basis of SEM photographs taken with a VO40 type scanning electron microscope made by Zeiss. SEM images permit concluding about the character of agglomerations and degree of dispersion. The particle size distributions (dispersion degree) were determined with the use of a Mastersizer 2000 instrument, made by Malvern Instruments Ltd.

The adsorption properties of the samples were estimated with the help of an ASAP 2020 instrument made by Micromeritics Instruments Co.

3. RESULT AND DISCUSSION

Results of determination of the chemical composition of the samples obtained by the AAS method and weight analysis are given in Table 1. According to the results the main components of synthetic magnesium silicates are silicon dioxide and magnesium oxide. The other components are the trace amounts of the salts used (K_2O, Na_2O, CaO) left after washing. The chemical composition of the samples obtained was compared with that of the natural magnesium silicate – the natural talc contained SiO_2 46.4÷63.4%, MgO 24.3÷31.9%, CaO 0.4÷13%.

Analysis of the data characterising the samples obtained has shown that only sample 2, that is magnesium silicate obtained from a 5% magnesium sulphate and 30% sol, has the composition similar to that of the natural magnesium silicate. Such a chemical composition ensures good quality of the precipitated samples. Samples 1, 3 (obtained with the use of magnesium sulphate(VI)) and samples 11, 12 (obtained with the use of magnesium chloride) have compositions different from that of the natural talc, but their content of main oxides (SiO_2 and MgO) is comparable. The lowest percent content of SiO_2 (44.4%) and the highest percent contribution of MgO (52.1%) were found in sample 13 obtained with the use of 5% $MgCl_2$ and 20% SiO_2. The highest content of SiO_2 (77.2%) was found in sample 28 obtained with the use of 10% $Mg(NO_3)_2$ and 20% SiO_2. In this sample the content of MgO was 19.3% and the moisture content was 8.5%. The moisture content in all samples varied from 8.5 to 9.4%.

On the basis of the WAXS studies (intensity distribution curves $I=f(\Theta)$) the maximum intensity for the samples studied is a few tens times lower than for the crystalline samples. This observation means that the magnesium silicates obtained are fully amorphous. An exemplary WAXS pattern recorded for sample 5 is shown in Fig. 1.

At the next stage of the study, the particle size distributions were determined for the magnesium silicate samples obtained. The curves for the samples precipitated from magnesium sulphate and 10% solution of SiO_2 sol shown in Fig. 2a indicate that these samples contain particles of diameters varying in a very wide range. A similar result was observed for the samples whose curves are shown in Fig. 2. The particle size distribution curves obtained for samples precipitated with the use of 5% $MgCl_2$ (sample 14) and with the use of 10% $Mg(NO_3)_2$ solutions (sample 29) were found to coincide to a large degree. The particle size distribution obtained for sample 19 obtained with 10% $MgCl_2$ solution was found significantly different from that of sample 14 obtained with 5% $MgCl_2$ solution. Analysis of the values of D[4,3] (mean diameter by volume) reveals that the diameter of particles in the whole sample volume increases (the sample is less homogeneous) with increasing concentration of the salt used for precipitation of this sample. This relation was observed for the samples obtained using magnesium sulphate (in sample 4 the mean diameter was 27.46 μm, while in sample 9 it was 32.7 μm) and using magnesium chloride (in sample 14 the mean diameter is 18.9 μm, while in sample 19 it is 24.5 μm). No such relation was found for the samples obtained using magnesium nitrate as magnesium silicate was not obtained using 5% $Mg(NO_3)_2$ and 10% SiO_2 solutions.

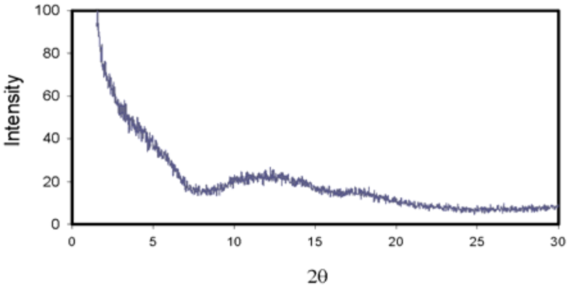


Fig.1. WAXS pattern of magnesium silicate – sample 5 (precipitated from 5% $MgSO_4$ and 5% SiO_2 sol)

As follows from Fig. 2, the particle size distributions obtained for the samples produced with the use of 20% SiO_2 and 5% $Mg(NO_3)_2$ (sample 23), 5% $MgCl_2$ (sample 13) and 10% $MgSO_4$ (sample 8) are similar. For sample 23 the mean particle diameter in the whole sample volume is 21.9 μm, for sample 13 it is 22.5 μm, while for sample 8 is 23.6 μm. In sample 23, 10% volume contribution is brought by the particles of diameter below 4.1 μm, for samples 13 and 8 the same volume contribution is brought by the particles of diameters below 3.9 μm and 3.9 μm, respectively, 50% volume contribution is brought by the particles of diameters below 15.0 μm, for samples 13 and 8 the analogous values are 14.9 μm and 15.7 μm and 90% volume contribution is brought by agglomerates of the diameters below 50.3 μm, for samples 13 and 8 the analogous values are 52.7 μm and 55.3 μm, respectively. A narrow range of particle diameters was obtained for magnesium silicate obtained with the use of 20% or 10% SiO_2 sol and 10% solutions of magnesium chloride or magnesium nitrate, Fig. 2a.

Interesting results were obtained for the product obtained with the use of 30% sol and the magnesium salts studied in different concentrations. Practically all particle size distribution curves overlapped (Fig. 2c), which means that high concentration of sol causes that the particles of magnesium silicate vary in the same range irrespective of the use of different salts in different concentrations.

Figure 2d presents particle size distributions obtained for synthetic magnesium silicate precipitated from a solution of 40% SiO_2 sol and different magnesium salts. For all samples narrow ranges of particle diameters variation were noted. Similarly as for the products precipitated with the use of 5, 10 and 30% of SiO_2 sol, also when using 40% sol solution the greatest mean diameter in the whole sample volume (of 25.5 μm) was obtained for sample 1 precipitated with 5% solution of $MgSO_4$. In this sample the particles of diameters below 4.9 μm brought 10% volume contribution, those of diameters below 18.8 μm 50% contribution, while the agglomerations of diameters below 56.1 μm a 90% contribution. For the other products obtained with the use of 40% sol solution, the volume contributions of particular fractions were different than for sample 1.

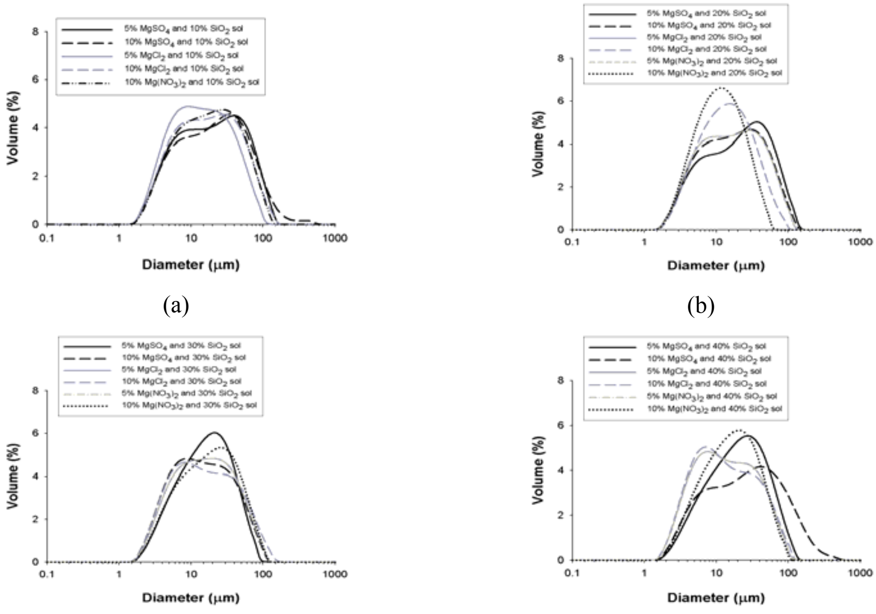
Morphology of the magnesium silicate samples obtained was evaluated on the basis of SEM images. Selected images of $MgO \cdot SiO_2$ are shown in Fig. 3. The SEM images presented confirm that the samples are built of particles whose sizes correspond to those indicated by the relevant particle size distributions and whose shapes are irregular.

Adsorption properties of the samples studied were characterised on the basis of the nitrogen adsorption/desorption isotherms. Figure 4 presents the relation between the volume of nitrogen adsorbed on samples 5, 19 and 29 versus relative pressure. The isotherms recorded for sample 5 precipitated with 5% $MgSO_4$ and 5% SiO_2 and sample 29 precipitated with the use of 10% $Mg(NO_3)_2$ and 10% SiO_2 are very similar. The amount of nitrogen adsorbed increases slowly up to p/p_0 of 0.8. For higher p/p_0 values the adsorption of nitrogen rapidly increases to reach a maximum of 570 cm^3/g at $p/p_0=1$ for sample 5, while for sample 29 to reach a maximum of 540 cm^3/g at $p/p_0=1$. The isotherm recorded for sample 19 precipitated with the use of 10% $MgCl_2$ and 10% SiO_2 solutions has a different character. The amounts of adsorbed nitrogen are initially much smaller than for samples 5 and 29, but for relative pressure values greater than $p/p_0=0.8$ this amount rapidly increases to reach a maximum of 470 cm^3/g at $p/p_0=1$. The adsorption capacity of sample 19 is much smaller than that of sample 5, for which the maximum amount of adsorbed nitrogen is 570 cm^3/g.

The greatest porosity and thus largest specific surface area was found for the samples precipitated with the use of magnesium sulphate and magnesium chloride. All the samples of synthetic magnesium silicate were classified as mesoporous. The largest specific surface area of 513 m^2/g and the greatest pore volume of 0.7 cm^3/g were determined for sample 5, which indicates that this silicate shows the greatest surface activity. The same pore volume was found for sample 29, but its specific surface area was smaller 412 m^2/g. The smallest specific surface area was measured for sample 19 precipitated with the use of 10% magnesium chloride and 10% SiO_2 sol. The pore volume of this sample was also smaller than those of the samples precipitated with magnesium sulphate or magnesium chloride. The mean pore diameter found for these three samples was similar and varied from 5.0 to 5.4 nm.

Table 1. Chemical composition of synthetic magnesium silicates

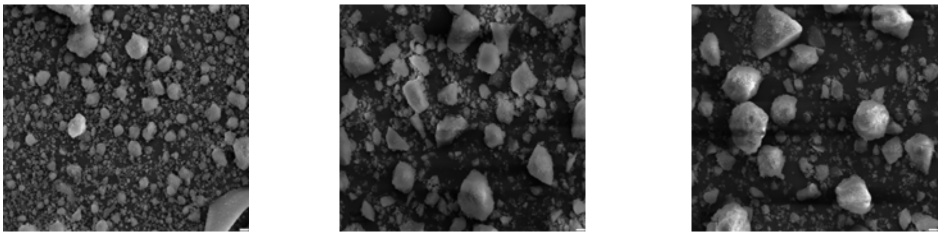
Sample no.	Concentration of magnesium salt (%)	Concentration of SiO_2 sol (%)	Precipitation direction	Contents (%)		
				SiO_2	MgO	H_2O
1	5	40	Silica sol to $MgSO_4$	59.1	36.8	9.1
2	5	30		62.7	33.2	9.1
3	5	20		58.2	37.8	9.0
4	5	10		75.2	21.3	8.5
5	5	5		69.6	26.6	8.8
6	10	40		77.1	19.3	8.6
7	10	30		70.7	25.3	9.0
8	10	20		70.4	25.5	9.1
9	10	10		71.0	24.9	9.1
10	10	5		55.8	40.2	9.0
11	5	40	Silica sol to $MgCl_2$	58.5	37.5	9.0
12	5	30		66.2	30.0	8.8
13	5	20		44.4	52.1	8.5
14	5	10		72.4	24.1	8.5
15	5	5		49.8	46.2	9.0
16	10	40		47.8	48.3	8.9
17	10	30		45.7	50.4	8.9
18	10	20		71.5	24.5	9.0
19	10	10		49.2	47.3	8.5
20	10	5		-	-	-
21	5	40	Silica sol to $Mg(NO_3)_2$	-	-	-
22	5	30		76.4	18.8	8.9
23	5	20		52.9	43.1	9.0
24	5	10		-	-	-
25	5	5		-	-	-
26	10	40		76.5	19.7	8.8
27	10	30		73.6	22.9	8.5
28	10	20		77.2	19.3	8.5
29	10	10		75.9	19.7	9.4
30	10	5		-	-	-



(a) (b)

(c) (d)

Fig. 2. PSD's of magnesium silicate – samples precipitated from (a) 10, (b) 20, (c) 30 and (d) 40% silica sol solution and different types and concentrations of magnesium salts



(a) (b) (c)

Fig. 3. SEM photographs of magnesium silicate – samples (a) 5, (b) 19 and (c) 29

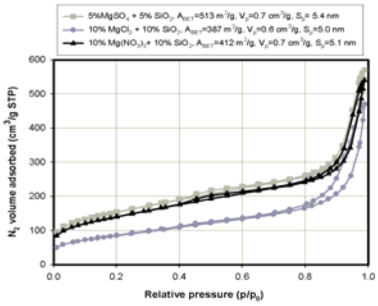


Fig. 4. N_2 adsorption/desorption isotherms of synthetic magnesium silicates (samples 5, 19 and 29)

3. CONCLUSION

According to the presented and discussed results, the character of synthetic magnesium silicate obtained by the method of precipitation based on silica sols is determined by the type of magnesium salt used. The process performed for SiO_2 sols of low concentrations permits getting products of higher degree of dispersion. The best physico-chemical properties have been revealed by sample 5 (obtained with the use of 5% $MgSO_4$ and 5% SiO_2 sole solutions), sample 19 (10% $MgCl_2$ and 10% SiO_2 sol) and sample 29 (10% $Mg(NO_3)_2$ and 10% SiO_2 sol). The experiments performed for the reversed direction of reagents supply, i.e. when sol was supplied to a proper magnesium salt, have proved that under such conditions the method does not guarantee obtaining the product desired, and moreover, when the precipitating agent is magnesium nitrate or magnesium chloride, the product is impossible to get.

The dispersion character of the synthetic magnesium silicate obtained has been shown to be determined by the type of magnesium salt used in the process of precipitation and its concentration. The use of magnesium salt at a lower concentration leads to obtaining a more dispersed product. It has been shown that synthetic magnesium silicates of particles whose diameters vary in a narrow range are obtained when using SiO_2 sol of high concentrations, 30 or 40%. The best-developed specific surface area (BET) and the greatest pore volume (513 m^2/g) have been found for sample 5, which shows the highest surface activity. The results have confirmed the possibility of using magnesium silicates as selective adsorbents.

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Przedstawiono rezultaty badań nad otrzymywaniem syntetycznego krzemianu magnezu metodą strąceniową w oparciu o zole kwasu krzemowego i wybrane związki magnezu. Istotnym zagadnieniem realizowanej tematyki było dobranie podstawowych parametrów prowadzenia procesu strącania, celem uzyskania produktu o jak najlepszych właściwościach fizykochemicznych. W trakcie badań przeanalizowano następujące parametry procesu: stężenie i rodzaj soli magnezu, stężenie zolu kwasu krzemowego, kierunek dozowania reagentów. Dodatkowo otrzymany syntetyczny krzemian magnezu poddany został analizie fizykochemicznej.

słowa kluczowe: krzemian magnezu, zol krzemionkowy, wytrącanie, charakterystyka dyspersji, pole powierzchni