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Physicochemical studies on precipitated magnesium silicates

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Abstract In this study, an attempt was made to obtain highly dispersed magnesium silicates which could be employed as polymer fillers or active adsorbents. Due to numerous applications of magnesium silicates and silicates of other metals, three procedures were suggested for production of their synthetic equivalents. The precipitation processes were optimized in respect to temperature, reagent dosing rate, rate of mixing them, substrate concentration, etc. In the process of magnesium silicate precipitation 5% solutions of sodium metasilicate (water glass) and magnesium sulphate(VI) were used. In order to broaden application range of synthetic magnesium silicates they were subjected to surface hydrophobization (for the purpose non-ionic surfactants were used) and surface modification (using silane pro-adhesive compounds). All the unmodified and modified samples were subjected to a broad physicochemical analysis. Chemical composition of unmodified magnesium silicates was determined using atomic adsorption spectrometry. In addition particle diameters were estimated in all the samples. Effective particle diameter, polydispersity were defined, particle size distributions were estimated using dynamic light scattering (DLS technique). Principal adsorptive properties were established to check up whether the obtained in laboratory synthetic magnesium silicates can be applied as adsorbents. This was executed by determination of nitrogen adsorption/desorption isotherms on the surface of magnesium silicates. Moreover, taking advantage of the isotherms, specific surface area, diameter and volume of pores were estimated.

Introduction

Development of new technologies and improvement of the already existing ones requires not only novel equipment but also new materials of strictly defined properties. Such a situation can be noted in cases of obtaining new nanomaterials, applied as active adsorbents of polymer fillers. A synthetic magnesium silicate certainly represents one of such materials. Literature reports published till now indicate that natural magnesium silicates (e.g., talc, enstatite, diopsite) are widely used as adsorbents of numerous ions such as ions of lead or calcium [1], of polysaccharides [2], as potentiometric sensors of hydrogen ions [3], in production of ceramics [4] or for sorption of atmospheric CO_2 [5]. Physicochemical properties of such minerals are well recognized [6, 7]. In addition, frequently articles appear which discuss natural silicates of other metals and their application. Similarly to magnesium silicate, they are used in several disciplines [8–12]. Resembling magnesium silicate in structure, clinoptyolite is used to recover cerium from radioctive waste materials and to adsorb Nd^{3+} ions [13]. Stratified natural silicates are also used as carriers of plant protection agents [14].

Similarities in structure between natural and synthetic silicates point to their similar application potential. Several investigators have described

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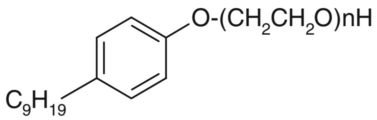
procedures for production of synthetic silicates [15, 16], their properties [17–21] and effects of surface modification [22–25]. Most frequently, silicate fillers are obtained acting with a soluble salt of respective metal on sodium metasilicate [26]. Procedures aimed at optimization of the production process and of surface modification should yield products of strictly defined physicochemical parameters and should broaden the application range of synthetic magnesium silicates and silicates of other metals.

Experimental details

Materials

In order to obtain synthetic magnesium silicates the following substrates were used: 5% solution of magnesium sulphate(VI), $MgSO_4 \cdot 7H_2O$ (POCh S.A.) and sodium metasilicate (5% aqueous solution in respect to content of SiO_2). The aqueos sodium metasilicate solution of SiO_2/Na_2O molar ratio $M_S = 3.3$, Na_2O – 8.8%, SiO_2 – 28.5%, density – 1.38 g/dm^3 produced by VITROSILICON S.A. was applied.

Alteration in surface activity of magnesium silicate was implemented using reaction with non-ionic surfactants and silane coupling agents. For the purpose the following compounds were applied: from the group of non-ionic surfactants: oxyethylenated unsaturated fatty alcohols (Rokanols K3 and K7) of the general formula $RO(CH_2CH_2O)_nH$ (where R is alkil group which may contains different hydrocarbons chains from 16 to 22 carbon atoms) as well as nonylphenylpolyoxyethyleneglycol ethers (Rokafenols N3, N6 and N9) of the following general formula:



where $n_{aver.}$ = around 3, $n_{aver.}$ = around 6 or $n_{aver.}$ = around 9. The above non-ionic surfactants were produced by PCC Rokita S.A.

Out of the group of silane pro-adhesive compounds, produced by UniSil, the following agents were used: *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15)—$H_2N(CH_2)_2NH(CH_2)_3\ Si(OCH_3)_3$, octyltriethoxysilane (U-222)—$CH_3(CH_2)_7Si(OC_2H_5)_3$, 3-chloropropyltrimethoxysilane (U-311)—$Cl(CH_2)_3Si(OCH_3)_3$, 3-methacryloxypropyltrimethoxysilane (U-511)—$CH_2{=}C(CH_3)\ COO(CH_2)_3Si(OCH_3)_3$, vinyltrimethoxysilane (U-611)—$CH_2{=}CHSi(OCH_3)_3$.

Procedures and methods

Production of synthetic magnesium silicates

The process of precipiting highly dispersed magnesium silicates was conducted in a round bottom flask, of 0.5 dm^3 capacity, equipped with a top stirrer (2000 rpm). The reactive system was maintained in a thermostat. The substrates were dosed to the flask at the constant rate of 2.3 cm^3/min, using a PP2B-15 type peristaltic pump. The process was conducted at the temperature of 20, 40, 60 or 80 °C.

Three procedures were suggested to produce magnesium silicate (Fig. 1).

The product obtained following the precipitation was subjected to filtration under vacuum. The obtained sediment was dried at the temperature of 105 °C for 24 h. The so prepared samples were subjected to physicochemical analysis.

Surface modification of synthetic magnesium silicates

The above presented procedure for precipitation of magnesium silicates was supplemented by dosing of a modifier, aimed to alter surface character of the fillers. Appropriate amount of a modifying agent was added to the reactive system at the moment when dosing of sodium metasilicate solution just ended. The entire flask content (together with the modifier) continued to be mixed for 20 min. Subsequently, the procedure progressed analogously as in the case of production of unmodified magnesium silicates, i.e., the products were subjected to filtration, washed and dried.

Respective modifying agents were dosed in 1, 3 or 5 weight parts per the amount of SiO_2 introduced with the sodium metasilicate solution. When calculating the weight parts, volume of Na_2SiO_3, its modulus and concentration were taken into account.

Physicochemical properties of the obtained magnesium silicates

Silicon dioxide content in studied samples was estimated by a weighing method. Apart from SiO_2 content, contents of Mg, Ca, Na and K in the magnesium silicate sample (calculated in the form of respective oxides of the metals) were estimated employing atomic absorption spectrometry.

Following the precipitation, the silicas were subjected to physicochemical tests, their bulk densities as well as water, dibutyl phthalate and paraffin oil absorbing capacities were estimated. The bulk densities

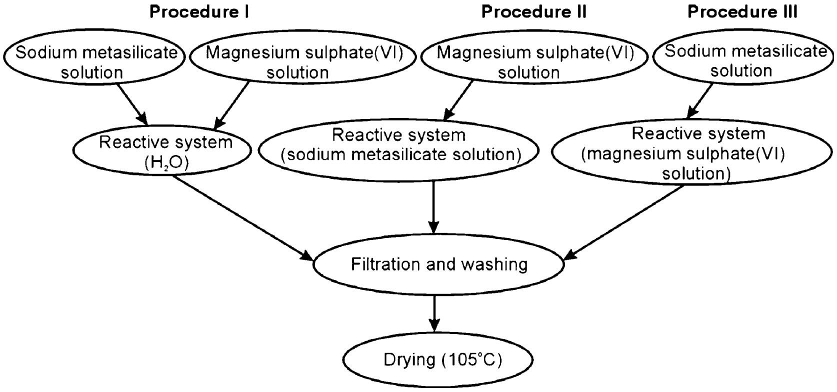


Fig. 1 Procedures for production of synthetic magnesium silicates

were determined using a WE-5 electromagnetic volumeter (Poland). The end point of water absorption capacity was noted when an excess of a single drop induced an evident liquefaction of the formed paste. The end point of dibutyl phtahalate or paraffin oil absorption capacities was registered when an excess of a single phthalate or oil drop altered abruptly the consistency of the paste which adhered to a glass plate.

In turn, crystalline structure of individual samples was estimated using X-ray diffraction. The diffractograms were recorded using the TUR–M-62 type horizontal diffractometer, equipped with HZW-3 type goniometer. In order to obtain radiation intensity distribution curve, I = f(Θ), an advantage was taken of the, so called, counting rate gauge, cooperating with the counter and electronically coupled to a graphic recorder.

Measurement of particle size distribution involved placing of an appropriately prepared sample in the cuvette of ZetaPlus apparatus (Brookhaven Instruments Co.) working on the basis of dynamic light scattering (DLS). Wavelength of the laser beam applied in the studies amounted to 670 nm. The effective particle diameter was estimated according to the following formula:

$$D_{\mathrm{eff}} = \sum Nd^6 \Big/ \sum Nd^5$$

where N is the number of particles, and d is the diameter of studied particles.

At the subsequent stage, studies on morphology and microstructure were conducted to obtain data on dispersion, grain morphology, structure of individual particles and agglomeration types in the obtained magnesium silicates. The studies were performed using Philips SEM 515 scanning electron microscope.

In order to define adsorptive properties of studied magnesium silicates, isotherms of nitrogen adsorption/desorption on their surfaces were estimated. Analysis of adsorption and desorption isotherms obtained in stationary conditions allows to estimate such parameters of studied material as size of specific surface area, pore size and pore volume distribution, etc. The measurements were conducted employing ASAP 2010 apparatus (Micromeritics Instruments Co.).

Results and discussion

Chemical composition of the obtained magnesium silicates, as affected by the way in which they were precipitated, is presented in Table 1.

Precipitation of synthetic magnesium silicates aims at obtaining samples of parameters exceeding those of natural magnesium silicates, widely used in various branches of industry (see Table 1) [27]. Data presented in Table 1 permits to conclude on domination of two oxides in the structure of synthetic magnesium silicates. Obviously, the oxides include SiO_2 and MgO. In the case of silica, its content ranged from 59.86 to 64.11% and showed a similar value independently of the way of precipitation. On the other hand, significant differences were obtained in the content of MgO. The highest amounts of the oxide were present in samples prepared according to the third procedure (14.03–14.67%), and the lowest amounts in samples precipitated according to the second procedure (7.17–8.05%). Comparing the values to contents of the same oxides in the structure of, e.g., talc (SiO_2 – 63.37% and MgO – 31.88%) it may be concluded that the highest their contents were obtained using the third procedure (mean contents of SiO_2 – 61.12%, MgO – 14.29%). The remaining oxides appearing in the structure of the obtained silicates were present in markedly lower amounts. Literature reports indicate that natural magnesium silicates may exhibit both crystalline and amorphous structure [28, 29]. In order to establish

Table 1 Elemental composition of precipitated magnesium silicates

Procedure	Temperature (°C)	Content (%)					Humidity (%)
		SiO_2	MgO	CaO	Na_2O	K_2O	
I	20	62.50	10.69	0.21	0.93	0.02	25.40
	40	64.11	13.30	0.52	0.30	0.01	23.41
	60	63.73	13.09	0.35	1.08	0.05	24.19
	80	62.51	12.47	0.51	2.07	0.01	24.01
II	20	62.98	7.32	0.32	1.83	0.11	27.42
	40	61.44	8.05	0.47	1.51	0.16	28.31
	60	62.95	7.17	0.29	1.70	0.10	27.66
	80	63.27	7.56	0.38	2.07	0.08	26.58
III	20	61.64	14.17	0.22	0.05	0.01	23.95
	40	62.30	14.67	0.12	0.02	0.01	22.88
	60	59.86	14.03	0.25	0.04	0.01	25.87
	80	60.71	14.32	0.32	0.03	0.01	24.62
Talc	–	46.40–63.41	24.32–31.90	0.43–13.00	–	–	0.10–0.60

crystallographic structure of the precipitated in a laboratory synthetic magnesium silicates, their X-ray diffractograms were prepared. An example of a diffractogram, prepared for magnesium silicate sample precipitated according to the third procedure at the temperature of 40 °C is presented in Fig. 2.

The conducted X-ray diffractographic studies demonstrated that the performed precipitation processes yielded synthetic magnesium silicates of an amorphous form (the X-ray diffractograms demonstrated no typical peaks, pointing to their crystalline character). The amorphous form of studied magnesium silicates appeared independently of the precipitation temperature (20, 40, 60 or 80 °C) and in every procedure of producing synthetic magnesium silicates.

A more detailed physicochemical analysis of precipitated magnesium silicates required that particle size distributions and SEM micrographs were obtained (the particle size distributions and SEM micrographs of synthetic magnesium silicates obtained at 40 °C using any of the three procedures are presented in Figs. 3 to 5).

Particle size distribution of magnesium silicate precipitated at the temperature of 40 °C is presented in Fig. 3(a). The distribution manifested two bands. The first of them represented particles of the 231–388 nm range of diameters (maximum intensity of 100 corresponded to particles of 335.3 nm in diameter). The other band represented markedly larger particles—agglomerates of 1498–2081 nm in diameter. Maximum intensity of 47 corresponded to the particle diameter of 1766.2 nm. The presence of two bands in the particle size distribution and the polydispersity value of 0.238 indicated that a non-uniform sample was obtained. This was corroborated by the SEM micrograph (Fig. 3b).

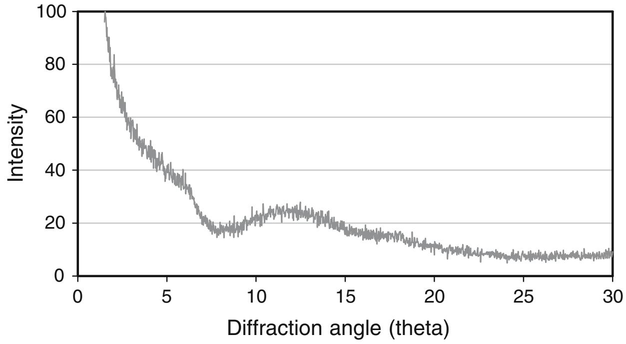


Fig. 2 X-ray diffractogram of magnesium silicate sample precipitated according to the third procedure at 40°C

In turn, particle size distribution and respective SEM electron microgram of the silicate obtained according to the second procedure also at the temperature of 40 °C are presented in Fig. 4(a, b).

The particle size distribution demonstrated four bands. The first of them represented particles of 168–328 nm in diameter, with maximum intensity of 100 for particles of 251.5 nm in diameter, while the second, third and fourth band represented particle diameter ranges of 727–1083 nm, 2403–2744 nm and 3579–4668 nm, respectively. In the samples obtained at this stage particles of low diameter dominated. Nevertheless, particles of diameters exceeding 2000 nm could also be encountered. They represented agglomerates of magnesium silicate particles, unfavorably affecting physicochemical properties of the entire sample. Manifestation of particles in the above mentioned ranges of diameters were corroborated by the respective SEM micrograph of the silicate (Fig. 4b).

In a similar way, magnesium silicate precipitated according to the third procedure was characterized by the presence of two typical bands in the particle size distribution (Fig. 5a). The first of them represented particles of lower diameters, fitting the range of 113–143 nm (maximum intensity of 19 corresponded to the

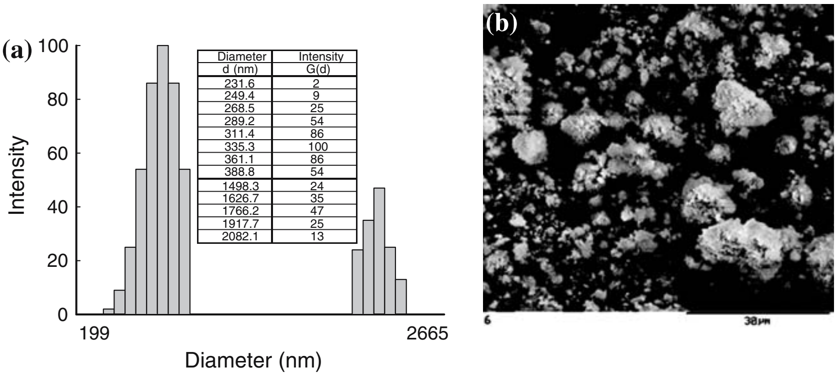


Fig. 3 (**a**) Particle size distribution and (**b**) SEM micrograph of magnesium silicate precipitated according to the first procedure, at the temperature of 40 °C

Diameter d (nm)	Intensity G(d)
231.6	2
249.4	9
268.5	25
289.2	54
311.4	86
335.3	100
361.1	86
388.8	54
1498.3	24
1626.7	35
1766.2	47
1917.7	25
2082.1	13

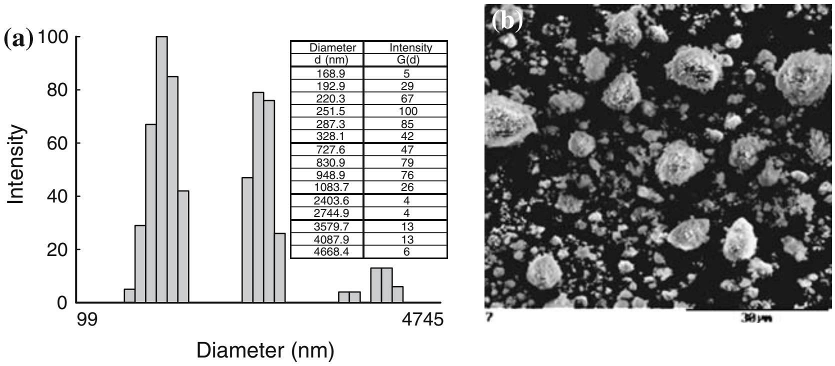


Fig. 4 (**a**) Particle size distribution and (**b**) SEM micrograph of magnesium silicate precipitated according to the second procedure, at the temperature of 40 °C

Diameter d (nm)	Intensity G(d)
168.9	5
192.9	29
220.3	67
251.5	100
287.3	85
328.1	42
727.6	47
830.9	79
948.9	76
1083.7	26
2403.6	4
2744.9	4
3579.7	13
4087.9	13
4668.4	6

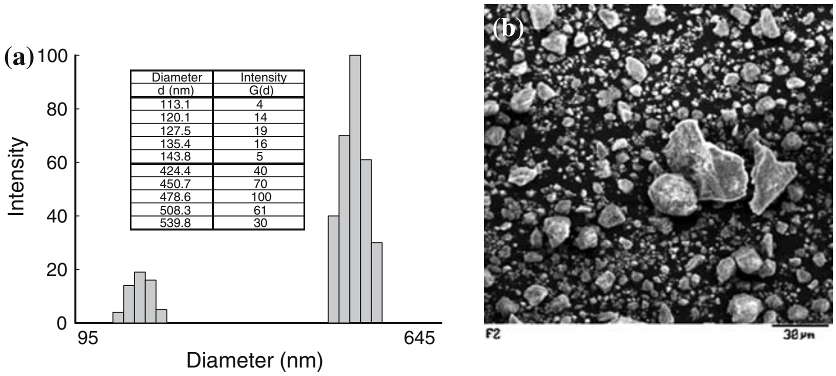


Fig. 5 (**a**) Particle size distribution and (**b**) SEM micrograph of magnesium silicate precipitated according to the third procedure, at the temperature of 40 °C

Diameter d (nm)	Intensity G(d)
113.1	4
120.1	14
127.5	19
135.4	16
143.8	5
424.4	40
450.7	70
478.6	100
508.3	61
539.8	30

particles of 127.5 nm in diameter). In turn, the other band was formed by particles of 424–539 nm in diameter (maximum intensity of 100 corresponded to the particles of 478.6 nm in diameter). Also in this case a non-uniform sample was obtained (although in this case polydispersity was lower, amounting to 0.189).

Comparison of the particle size distribution indicated that again the best sample in respect to particle diameter was obtained employing the third procedure (the same conclusion was reached following analysis of elemental composition).

Considering the fact that precipitated synthetic silicates can be used interchangebly with their natural equivalents, proper attention should be devoted to their surface. The surface character is defined, first of all, by the surface groups (siloxane $\equiv$Si–O–Si$\equiv$, magnesil –Mg–OH and silanol $\equiv$Si–OH groups). They provide the surface with a hydrophilic (silanol and magnesil groups) or hydrophobic (siloxane groups) character, a determine reactivity of the synthetic silicate surface with other materials.

Silicates obtained according to the first and third procedures at the temperature of 40°C manifested relatively high hydrophobicity (defined by the capacities to absorb dibutyl phthalate: 400 cm^3/100 g for products obtained according to the first procedure and 325 cm^3/100 g for the third procedure and by capacities to absorb paraffin oil: 600 cm^3/100 g for the first and

400 cm^3/100 g for the third procedure). Samples obtained according to the second procedure showed a relatively more hydrophilic character (low capacities to absorb organic agents, at the level of 200 cm^3/100 g). In order to examine surface activity of synthetic magnesium silicates and, indirectly, to augment their hydrophobicity, modification was conducted of the samples obtained by the third procedure, using non-ionic surfactants and silane pro-adhesive compounds.

The first measurable effect of the modification involved augmented capacity to absorb organic agents (depending on the applied modifying agent, the capacity to absorb dibutyl phthalate increased by 100–150 cm^3/100 g and the capacity to absorb paraffin oil by 175–225 cm^3/100 g). Similarly to samples of unmodified silicates, also the modified samples were subjected to a detailed physicochemical analysis.

The examples of particle size distributions for magnesium silicate samples modified with 3 weight parts of Rokafenol N9 or Rokanol K3 are presented in Fig. 6(a, b).

As compared to unmodified samples, no significant changes were observed following application of 3 weight parts of Rokafenol N9 or Rokanol K3, Particle size distributions for the samples resembled those for the discussed earlier silicate samples. The silicate modified with 3 weight parts of Rokafenol N9 (Fig. 6a) demonstrated the presence in its structure of particles ranging in diameter from 155 to 189 nm and from 424 to 593 nm (maximum intensity of 100 corresponded to the particle diameter of 499.7 nm). The silicate modified with 3 weight parts of Rokanol K3 (Fig. 6b) contained particles ranging in diameter from 120 to 151 nm and from 378 to 504 nm. The dominating particles (for the intensity of 100) showed the diameters of 424 and 450 nm, respectively.

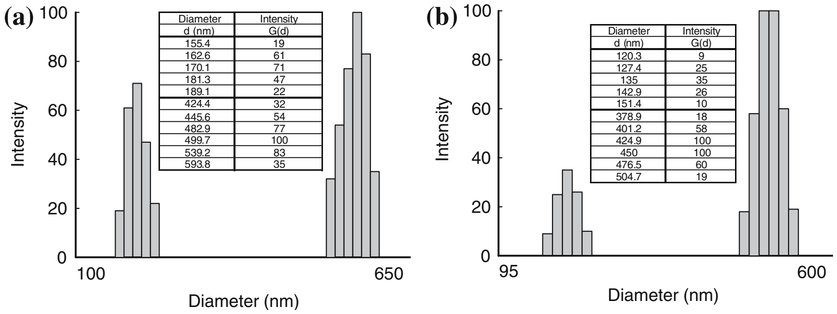
Application of non-ionic surfactants in low quantities, i.e., in 1 or 3 weight parts, failed to induce significant alterations in the particle size distribution. On the other hand, their higher amounts resulted in a marked agglomeration of the samples and, thus, domination of particles of higher diameters.

Modification with silane pro-adhesive compounds resulted in a distinct situation. Application of even the lowest amounts of such modifiers resulted in agglomeration of the precipitated silicate sample. The silicate modified with 3 weight parts of U-15 silane (Fig. 7a) contained particles ranging in diameter from 300 to 439 nm (maximum intensity of 100 corresponded to particles of 398.7 nm in diameter) and from 948 to 1102 nm, with maximum intensity of 78 for the particles of 1012.4 nm in diameter. Application of 1, 3 or 5 weight parts of U-15 silane was followed by a decisive increase in particle diameter, as compared to that for the unmodified magnesium silicate. This may indicate a significant effect of the modifier on agglomeration of particles in the precipitated silicate, a significantly more pronounced effect than that of non-ionic surfactants.

Particle size distribution for the silicate modified with 3 weight parts of U-511 silane resembled that of the earlier discussed silicate modified with U-15 aminosilane. The silicate modified with 3 weight parts of U-511 silane (Fig. 7b) manifested in its structure the presence of particles ranging from 340 to 483 nm and from 899 to 1044 nm in diameter (maximum intensity of 100 corresponded to the particle diameter of 994.2 nm).

The obtained distribution unequivocally indicated that modification with silane proadhesive compounds resulted in augmentation of silicate particle sizes. The more modifier was applied in the modification process, the more pronounced was its promotion of magnesium silicate sample agglomeration.

One of the more recent and promising applications of magnesium silicates involves their application as adsorbents to remove certain toxic ions, such as Nd^{3+} or Ce^{3+} (model studies are being performed using clinoptylolite) [13]. Therefore, it is important to recognize adsorptive properties of also the synthetic magnesium silicates. The properties may be defined by estimation of nitrogen adsorption/desorption isotherms on the surface of precipitated silicates. This will permit to qualify the laboratory-obtained



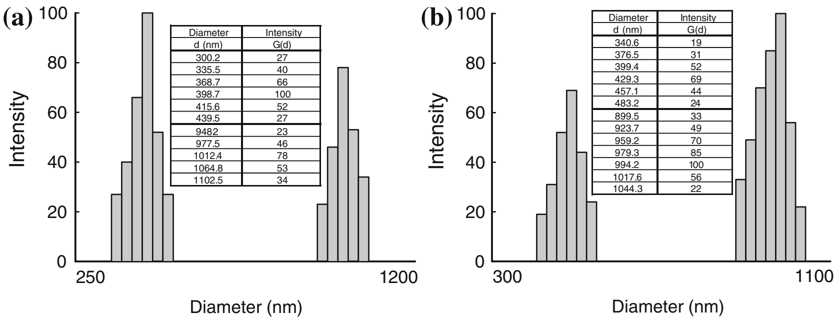
(a)

Diameter d (nm)	Intensity G(d)
155.4	19
162.6	61
170.1	71
181.3	47
189.1	22
424.4	32
445.6	54
482.9	77
499.7	100
539.2	83
593.8	35

(b)

Diameter d (nm)	Intensity G(d)
120.3	9
127.4	25
135	35
142.9	26
151.4	10
378.9	18
401.2	58
424.9	100
450	100
476.5	60
504.7	19

Fig. 6 Particle size distribution of magnesium silicate precipitated according to the third procedure, at the temperature of 40 °C modified with: (**a**) 3 weight parts of Rokafenol N9 and (**b**) 3 weight parts of Rokanol K3



(a)

Diameter d (nm)	Intensity G(d)
300.2	27
335.5	40
368.7	66
398.7	100
415.6	52
439.5	27
9482	23
977.5	46
1012.4	78
1064.8	53
1102.5	34

(b)

Diameter d (nm)	Intensity G(d)
340.6	19
376.5	31
399.4	52
429.3	69
457.1	44
483.2	24
899.5	33
923.7	49
959.2	70
979.3	85
994.2	100
1017.6	56
1044.3	22

Fig. 7 Particle size distribution of magnesium silicate precipitated according to the third procedure, at the temperature of 40 °C modified with: (**a**) 3 weight parts of U-15 aminosilane and (**b**) 3 weight parts of U-511 silane

synthetic magnesium silicates to specific groups of adsorbents as well as allow to determine the size of their specific surface area, diameter and size distribution of pores.

Isotherms of nitrogen adsorption/desorption on surfaces of the unmodified silicates and magnesium silicates modified using non-ionic surfactants are presented in Figs. 8 and 9.

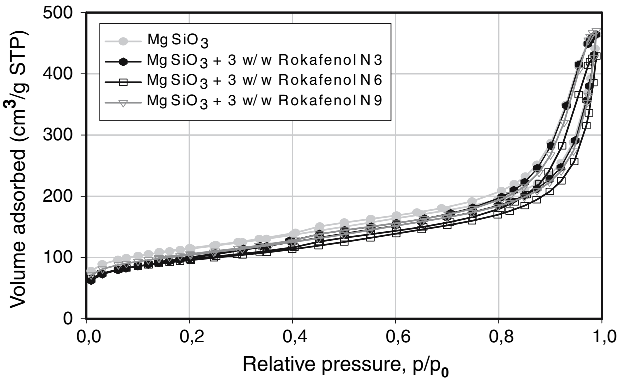


Fig. 8 Isotherms of nitrogen adsorption/desorption for unmodified magnesium silicate and for magnesium silicates modified with 3 weight parts of Rokafenol N3, N6 or N9 (third procedure, precipitation temperature of 40 °C)

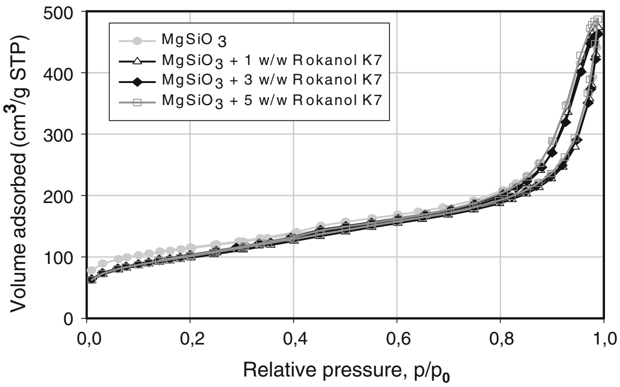


Fig. 9 Isotherms of nitrogen adsorption/desorption for unmodified magnesium silicate and for magnesium silicates modified with 1, 3 and 5 weight parts of Rokanol K7 (third procedure, precipitation temperature of 40 °C)

In the graph (Fig. 8), a very similar character could be noted of distributions obtained for individual modifiers. The distribution pointed to a mesoporous structure of the samples. The amount of adsorbed nitrogen smoothly grew until the partial pressure of 0.8 was obtained. After exceeding the value, the amounts of adsorbed nitrogen abruptly increased for samples modified with 3 weight parts of Rokafenol N3 or N9 as well as for the unmodified silicate, reaching the highest levels of 460–470 cm^3/g (at $p/p_0 = 1$). In the case of magnesium silicate modified with 3 weight parts of Rokafenol N6 the amounts of adsorbed nitrogen showed the lowest values, which at $p/p_0 = 1$ amounted to 425 cm^3/g.

For the modified silicates, the character of adsorption isotherms resembled those obtained for the unmodified silicate. Within the relative pressures of 0–0.8, the modified samples demonstrated a slight decrease in the amounts of adsorbed nitrogen, as compared to the unmodified silicate. This pointed to a restricted access of nitrogen to the sample surface due to the presence on the surface of the modifier molecules. It could also be noted that the amount of the applied modifier failed to significantly affect the shape of adsorption isotherms. At the pressure of $p/p_0 = 1$, the highest amounts of adsorbed nitrogen were noted for magnesium silicate modified with 5 weight parts of Rokanol K7 (it amounted accurately to 490 cm^3/g). Amounts of nitrogen adsorbed on the remaining samples ranged from 460 to 470 cm^3/g.

The obtained results documented an insignificant effect of both the type and the amount of the applied modifier on adsorptive capacity of synthetic magnesium silicates.

Isotherms of nitrogen adsorption/desorption on magnesium silicate modified with 3 weight parts of various silanes (U-311, U-511 and U-611) are presented in Fig. 10. The isotherm shape was similar for various modifiers. The amount of adsorbed nitrogen delicately grew until relative pressure of 0.8 was obtained. After exceeding the pressure, the amount

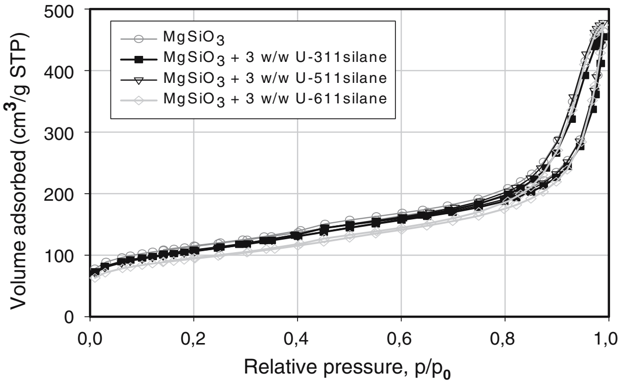


Fig. 10 Isotherms of nitrogen adsorption/desorption for unmodified magnesium silicate and for magnesium silicates modified with 3 weight parts U-311, U-511 and U-611 silane (third procedure, precipitation temperature of 40 °C)

of adsorbed nitrogen abruptly increased to reach the peak value of 480 cm^3/g in the sample modified with 3 weight parts of U-511 or U-611 silane (at $p/p_0 = 1$). In the case of magnesium silicate modified with 3 weight parts of U-311 silane the amount of adsorbed nitrogen was the lowest, amounting to 450 cm^3/g at the maximum partial pressure of $p/p_0 = 1$.

Isotherms of nitrogen adsorption/desorption for samples of unmodified magnesium silicate or magnesium silicate modified with 1, 3 or 5 weight parts of U-15 silane are presented in Fig. 11.

The character of the isotherms was similar for the modified magnesium silicate samples and for the unmodified silicate. In the partial pressure range of 0–0.8 the modified samples demonstrated a slight decrease in the amount of adsorbed nitrogen, as compared to the unmodified silicate. This might indicate an effect of modifier molecules on the character of magnesium silicate surface (the adsorbing nitrogen might have a restricted access to the surface of examined sample). It could also be noted that the amount of applied modifier failed to affect the shape of adsorption isotherms. At the pressure of $p/p_0 = 1$, the highest amounts of adsorbed nitrogen were noted for magnesium silicate samples modified with 1 weight part of U-15. It amounted to 480 cm^3/g. In turn, magnesium silicate modified with 3 or 5 weight parts of U-15 aminosilane manifested lower nitrogen adsorption at the relative pressure of $p/p_0 = 1$ (at the level of 450 cm^3/g).

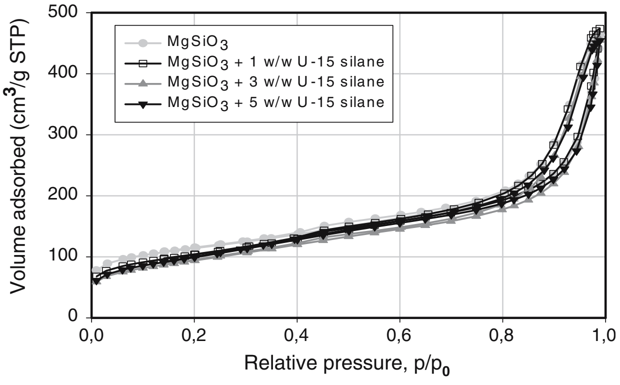


Fig. 11 Isotherms of nitrogen adsorption/desorption for unmodified magnesium silicate and for magnesium silicates modified with 1, 3 and 5 weight parts of U-15 aminosilane (third procedure, precipitation temperature of 40 °C)

The nitrogen adsorption/desorption isotherms obtained for unmodified silicates and for silicates modified using non-ionic surfactants or silane pro-adhesive compounds permit to include the synthetic magnesium silicates to the group of mesoporous adsorbents. Moreover, both the type and the amount of applied modifying compounds can be concluded to exert no significant effect on adsorptive properties of the precipitated silicates.

The obtained isotherms of nitrogen adsorption/desorption permitted to estimate the size of specific surface area, diameter and size distribution of pores in studied samples of magnesium silicate. The results are listed in Table 2.

In the unmodified sample, its specific surface area amounted to 399 m^2/g and was markedly higher than in the modified samples. Only the magnesium silicate modified with 3 weight parts of Rokanol K3 manifested specific surface area higher than that for the unmodified sample (421 m^2/g). Modification with either non-ionic surfactants or organofunctional silanes promoted a decrease in specific surface area in the studied samples. This reflected blocking by the modifiers of active silanol groups, decisive for the surface activity of magnesium silicates. Accumulation of any compounds on the surface of synthetic magnesium silicates results in a steric hindrance, hampering migration of nitrogen to the surface.

The slight increase in mean pore diameter in the modified as compared to unmodified magnesium silicates might result from migration of surfactants and organofunctional silanes to the pore interior which might result in their swelling. Modification of synthetic magnesium silicate surface did not exert any pronounced effect on pore volume.

Conclusions

In the conducted studies three procedures were suggested for production of synthetic highly dispersed magnesium silicates. Samples of the best physicochem-

Table 2 Adsorptive properties of unmodified magnesium silicate and of magnesium silicate modified with non-ionic surfactants or organofunctional silanes

Temperature (°C)	Modifying agent	Amount of modifying agent (w/w)	Specific surface area BET (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (nm)
40	–	–	399	0.57	5.7
	Rokafenol N3	3	350	0.55	6.3
	Rokafenol N6	3	334	0.48	5.8
	Rokafenol N9	3	364	0.54	6.0
	Rokanol K3	3	421	0.53	7.0
	Rokanol K7	3	361	0.54	6.0
	U-15 Silane	3	333	0.56	6.7
	U-222 Silane	3	363	0.55	6.1
	U-311 Silane	3	374	0.52	5.8
	U-511 Silane	3	372	0.56	6.1
	U-611 Silane	3	331	0.54	6.5

ical parameters were obtained using the third procedure while the second procedure yielded the least advantageous parameters of the magnesium silicate. The samples precipitated according to the third procedure manifested a relatively highly hydrophobic character and low bulk density. Following any of the procedures non-uniform silicate samples were obtained but the samples obtained according to the third procedure manifested the lowest diameters (304 nm). It was worth mentioning that temperature of precipitation did not affect chemical composition of the precipitated magnesium silicate. Magnesium silicate precipitated at any temperature demonstrated an amorphous form.

Modification of magnesium silicate surface using either non-ionic surfactants or silanes promoted agglomeration of its particles (noted in the particle size distributions). Supplementation of small amounts of non-ionic surfactants did not induce marked alterations in diameters of magnesium silicate particles. Higher amounts of the surfactants resulted in marked agglomeration of the obtained sample. Supplementation with even the lowest amounts of silane pro-adhesive compounds resulted in markedly augmented diameters of the obtained magnesium silicate particles.

Determination of nitrogen adsorption/desorption isotherms on the surface of precipitated magnesium silicates permitted to define adsorptive properties of studied samples as well as to define their alterations following the modification. The amount and type of the applied modifiers were found to remain without effects on shape of the isotherms and affected only slightly the amounts of adsorbed nitrogen. It seemed significant that addition of the modifiers promoted reduction in BET specific surface area of the precipitated magnesium silicates. The highest specific surface area (421 m^2/g) was demonstrated by magnesium silicate samples precipitated according to the third procedure, at the temperature of 40°C in presence of 3 weight parts of Rokanol K3.

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