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INFLUENCE OF PRECIPITATION PARAMETERS ON PHYSICOCHEMICAL PROPERTIES OF MAGNESIUM SILICATES

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Studies were presented on optimisation of the technique of precipitating magnesium silicate of high dispersion extent so that the obtained product would exhibit possibly best physicochemical parameters. Magnesium silicate was obtained by precipitation reaction using solutions of magnesium sulphate and sodium metasilicate. The variables included temperature, the ways in which the reagents were dosed and addition of modifying substances. Physicochemical parameters of the product were estimated, including bulk density, capacities to absorb water, dibutyl phthalate and paraffin oil, particle diameters, specific surface area and electrokinetic potential.

Key words: magnesium silicate, precipitation process, surface modification, zeta potential

INTRODUCTION

In recent years, synthetic silicates gained increasing importance in several branches of industry. This reflects difficult access to natural deposits of some silicates and problems arising during technological processing of natural silicates. Moreover, synthetic silicates exhibit more pronounced dispersion than the natural materials, which is also an advantageous property. Their increasingly frequent use reflects their broad application potential in various branches (Görlich 1957).

Similarly to natural silicates, synthetic silicates may exhibit crystalline or amorphous structure. In several cases silicates exhibit a similar chemical composition but show distinct physical properties, which is critical for the direction of their application.

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In numerous papers (Krysztafkiewicz 1984, 1986, 1987, 1988) methods were presented of obtaining synthetic silicates of aluminium, zinc and calcium. Principal physicochemical data, decisive for such applications, were also collected.

Basing on the studies, the precipitation process and physicochemical parameters of synthetic magnesium silicate have been analysed in greater detail.

Magnesium silicate surface is partially hydrophobic and partially hydrophilic. The hydrophobic part includes siloxane ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) groups and the hydrophilic portion contains isolated hydroxy groups ($-\text{Mg}-\text{OH}$), individual silanol groups ($\equiv\text{Si}-\text{OH}$) and hydrogen bonds formed due to close vicinity of hydroxy groups linked to neighbouring silicon atoms (Iler 1979). Surface modification is performed to augment hydrophobicity of silicate surface and, thus, to promote binding of several compounds. The modification takes place by introduction of new organofunctional groups to silicate surface (Krysztafkiewicz 1996, Jesionowski 2001).

Apart from calcium silicate, aluminium silicate and zinc silicate, magnesium silicate is used as adsorbent for purification and decolouring of sugar, products of fermentation industry, mineral oils. Moreover, it is used as an insoluble component of rubber mixtures and similar organic polymers and as a filler of polyurethanes and vinyl polychloride (Domka 1997). The advantages of employing silicates as fillers include not only improved physicochemical properties of the filled plastics but also the fact that silicates belong to the so called light fillers which do not change colour of the material. Several applications of magnesium silicate include also its use as a carrier of drugs or plant protection agents, pesticides and of an inorganic pigment (Krysztafkiewicz 1998) or filler of varnishes (Kotowski 1994).

The so broad applications of magnesium silicate argue for a more detailed analysis of the process of obtaining it and for determination of its basic physicochemical properties. This was the aim of present study.

EXPERIMENTAL

MATERIALS

For production of magnesium silicate, the following substrates were used: 5% solution of magnesium sulphate and sodium metasilicate (5% aqueous solution in respect to SiO_2 content). The sodium metasilicate solution exhibited the following parameters: Na_2O 8.8 %; SiO_2 28.5 %, density 1.38 g/dm^3 and module of 3.33. Surface modification of magnesium silicate was performed using Rokanol K7- oxyethylenated unsaturated fatty alcohol $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ (where $\text{R}=\text{C}_{16-22}$, $n_{\text{av}}=7$) and Rokafenol N9 - nonylphenylpolyoxyethyleneglycol ether $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ (where $n_{\text{av}}=9.7$), produced by Chemical Works „Rokita”.

METHODS OF STUDIES

At the first stage of the studies magnesium silicate was precipitated using 5% solutions of magnesium sulphate and sodium metasilicate. The reaction was conducted

in a three-necked flask of 250 cm³ capacity, equipped with a rapidly revolving stirrer. The reaction system was kept in thermostat-stabilised chamber. In the flask 100 cm³ sodium metasilicate solution was placed and the same amount of magnesium sulphate was dosed to it. The process was conducted at 20, 40, 60 or 80°C.

At the second stage of studies the procedure was repeated but 70 cm³ water was placed in the flask, to which magnesium sulphate and sodium metasilicate solutions were dosed (100 cm³ of each).

Moreover, the second reaction system was modified by addition adequately of 0.5; 1; 3; 5; or 10 weight parts of the Rokanol K7 or Rokafenol N9.

For each sample(s) bulk density as well as capacities to absorb water, dibutyl phthalate and paraffin oil were estimated. Moreover, particle size distribution was tested in the samples. ZetaPlus (Brookhaven Instruments Inc., USA) permitted to establish particle size using the potential of the dynamic light scattering method.

Using the apparatus, the electrokinetic potential (zeta potential) was also estimated, providing a measure of stability of the dispersion systems such as magnesium silicate.

In order to examine images of the obtained magnesium silicate surface, the selected samples were examined in the scanning electron microscope, Philips SEM 515.

For selected samples of the precipitated silicates specific surface area was estimated using BET technique as well as diameter and volume of pores were determined. The measurements took advantage of ASAP 2010 apparatus (Micrometrics Instruments Co., USA).

RESULTS AND DISCUSSION

Principal physicochemical properties of magnesium silicate obtained at the first and the second stage of the studies are listed in Table 1.

Magnesium silicate obtained at the first stage manifested relatively low physicochemical parameters. At any temperature, bulk density of the product was high, while capacities to absorb water, dibutyl phthalate and paraffin oil exhibited similar values. Surface of such a silicate should be more hydrophobic or capacities to absorb the organic compounds should be decisively higher.

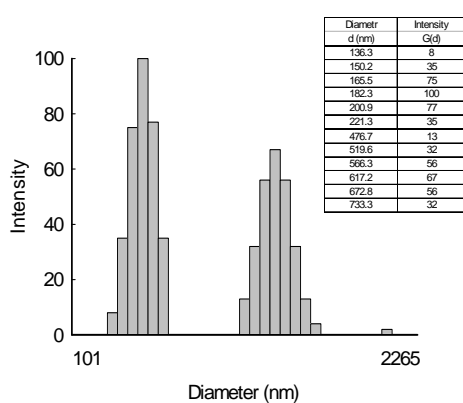
The method of precipitation implemented at the second stage of the studies permitted to obtain definitely better parameters of the precipitated magnesium silicate. Bulk densities obtained at any temperature were lower than those obtained at the first stage of the studies. In the case of absorptive capacities, an evident difference appeared between the capacity to absorb water and the capacities to absorb dibutyl phthalate and paraffin oil. The surface of magnesium silicate obtained at the second stage of the studies demonstrated a markedly higher hydrophobic character.

The best parameters were obtained for the sample precipitated at the temperature of 20°C (bulk density 205 g/dm³; capacity to absorb water 300 cm³/100g; capacity to absorb dibutyl phthalate 400 cm³/100g; capacity to absorb paraffin oil 625 cm³/100g).

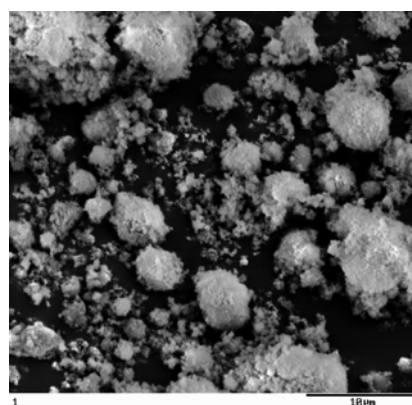
The results seemed to be corroborated by the data presented in Fig.1, including particle size distribution and SEM microphotograph of magnesium silicate obtained at the second stage of studies, at 20°C.

Table 1. Principal physicochemical properties of obtained magnesium silicate

Bulk density (g/dm ³)	Water absorbing capacity (cm ³ /100g)	Dibutyl phthalate absorbing capacity (cm ³ /100g)	Paraffin oil absorbing capacity (cm ³ /100g)
I stage (magnesium sulphate dosed to sodium metasilicate placed in the flask)			
20°C			
370	200	225	200
40°C			
422	150	200	200
60°C			
370	150	150	200
80°C			
280	150	150	200
II stage (both reagents dosed to water placed in the flask)			
20°C			
205	300	400	625
40°C			
249	225	400	600
60°C			
261	200	425	625
80°C			
245	250	350	550



a)



b)

Fig.1. a) Particle size distribution and b) SEM microphotograph of magnesium silicate

The particle size distribution demonstrated three bands. The first band corresponded to silicate particles of the lowest diameters and encompassed the range of 136.3 to 221.3 nm (maximum intensity of 100 corresponded to the particle diameter of 182.3 nm). The second band of lower intensity covered the range of 476.7 to 871.1 nm and represented particles of higher diameters, including aggregates (maximum intensity of 67 corresponded to particles of 617.2 nm in diameter). The third band of a very low intensity corresponded to particles of 1865.8 nm in diameter. The band reflected presence of secondary agglomerates in the studied sample. In the sample, the mean particle diameter was 273.5 nm, and polydispersity amounted to 0.235. SEM microphotograph (Fig.1a) confirmed the presence of particles of low diameter, which bound to each other forming larger clumps of particles (aggregates and agglomerates).

In order to improve chemical parameters and dispersion of the precipitated magnesium sulphate, it was subjected to surface modification using various amounts of Rokanol K7 or Rokafenol N9. Basic physicochemical properties of the modified silicate are shown in Table 2.

Table 2. Principal physicochemical properties of magnesium silicate following modification with Rokanol K7 or Rokafenol N9

Temp. (°C)	Modifying agent	Amount of modifying agent (w/w)	Bulk density (g/dm ³)	Water absorbing capacity (cm ³ /100g)	Dibutyl phthalate absorbing capacity (cm ³ /100g)	Paraffin oil absorbing capacity (cm ³ /100g)
20°C	Rokanol K7	0,5	148	300	475	725
		1	151	275	475	625
		3	134	300	500	700
		5	180	300	425	475
		10	156	325	425	575
20°C	Rokafenol N9	0,5	218	225	425	550
		1	197	275	350	600
		3	178	300	375	625
		5	206	275	375	525
		10	200	275	375	525

Again, the best parameters were obtained at the temperature of 20°C. When 3 weight parts of Rokanol K7 were used, bulk density reached 134 g/dm³, capacity to absorb water was 300 cm³/100g, capacity to absorb dibutyl phthalate 500 cm³/100g, and the capacity to absorb paraffin oil reached 700 cm³/100g. Similar absorptive capacities were obtained for the same amount of Rokafenol N9 used to modification. However, the sample exhibited higher bulk density, of 178 g/dm³.

Particle size distributions and electron micrographs of magnesium silicate modified with 3 weight parts of Rokanol K7 and Rokafenol N9 respectively are presented in Figs.2 and 3. In both cases the graphs demonstrated presence of two bands. In the case

of Rokanol K7, the first band corresponded to particles of small diameters. It fitted the diameter range of 160.9 to 209.0 nm (maximum intensity of 57 corresponded to the particle diameter of 183.4 nm). The other band of higher intensity reflected the presence of silicate aggregates (594.9 to 825.0 nm). Maximum intensity of 100 corresponded to the aggregates diameter of 678 nm. Polydispersity, similarly to the unmodified sample, was relatively high and amounted to 0.274 while the mean particle diameter was 374.1 nm.

For silicate modified with Rokafenol N9 the mean particle diameter was somewhat lower and amounted to 281.3 nm, and polydispersity reached 0.226. The first band fitted the diameter range of 145.3 to 191.9 nm (maximum intensity of 80 corresponded to the particle diameter of 171.7 nm). The other band reflected the presence of aggregates of 441.7 to 583.2 nm in diameter (maximum intensity of 100 corresponded to the aggregates diameter of 493.6 nm).

In each case the results were corroborated by SEM microphotographs, in which clumps of particles of higher diameters (aggregates) prevailed.

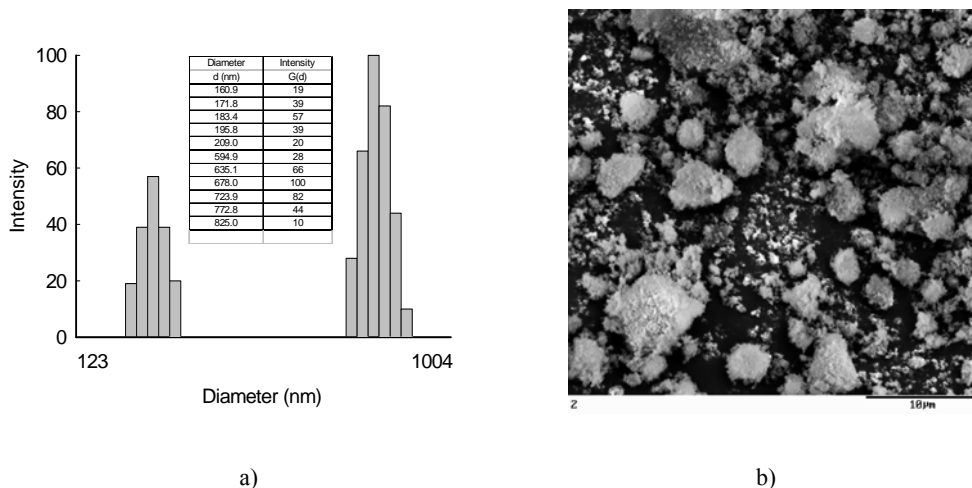


Fig.2. a) Particle size distribution and b) electron micrograph of magnesium silicate following modification with 3 weight parts of Rokanol K7

Electrokinetic potential (zeta potential) represents a significant variable in characteristics of dispersion systems. It serves as a measure of stability of dispersion systems. Its high positive or negative value characterises stable systems, its low value is typical for unstable systems. The relation between zeta potential and pH for the modified and unmodified magnesium silicate (precipitated at 20°C) is presented in Fig.4.

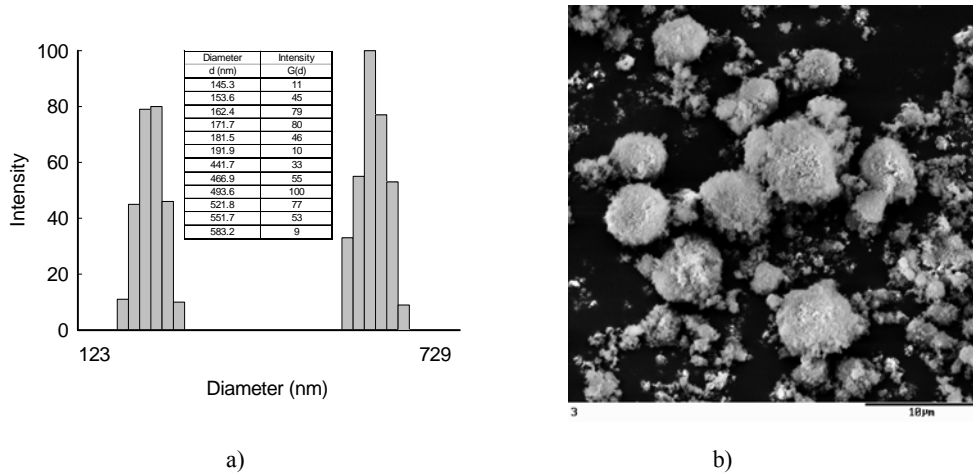


Fig.3. a) Particle size distribution and b) electron micrograph of magnesium silicate following modification with 3 weight parts of Rokafenol N9

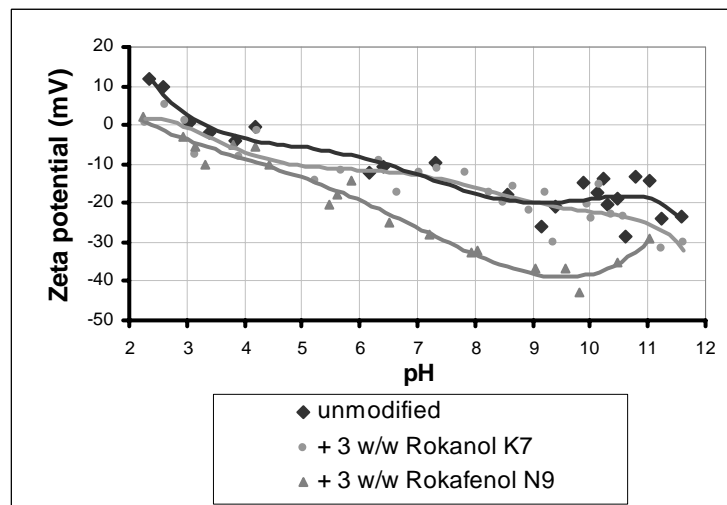


Fig.4. Relation between zeta potential and pH for modified and unmodified magnesium silicate (silicate was precipitated at 20°C)

Eletrokinetic curves for the modified magnesium silicates exhibited a similar course to that for the unmodified silicate. Values of the isoelectric point (or pH at which zeta potential acquires zero value) were as follows: unmodified magnesium silicate 2.29; magnesium silicate modified with 3 weight parts of Rokanol K7 - 2.97;

magnesium silicate modified with 3 weight parts of Rokafenol N9 - 3.16. All the samples in the range of pH from 4 to 12 exhibited negative values of zeta potential.

Isotherms of nitrogen adsorption/desorption for the three precipitated silicates are presented in Fig.3. The isotherms corresponding to silicates modified with three weight parts of Rokanol K7 and Rokafenol N9 exhibited a shape very similar to that of the isotherm for the unmodified silicate. The amount of nitrogen adsorbed by the silicates increased with rising relative pressure and a rapid increase was observed at the pressure range of 0.7 do 1.0. Such course of the curves provided proof for a high activity of the silicates. Observed amount of the adsorbed nitrogen at $p/p_0=1$ reached $400 \text{ cm}^3/\text{g}$ for the unmodified silicate and exceeded $450 \text{ cm}^3/\text{g}$ for magnesium silicate modified with 3 weight parts of Rokanol K7 and Rokafenol N9. The obtained effect provided a significant proof for augmented activity of the silicate precipitated in the presence of non-ionic surfactant. Such a course of the isotherms proved also that the silicates belonged to mesoporous substances (volume of the adsorbed nitrogen did not increase until high relative pressures, exceeding the value of 0.7).

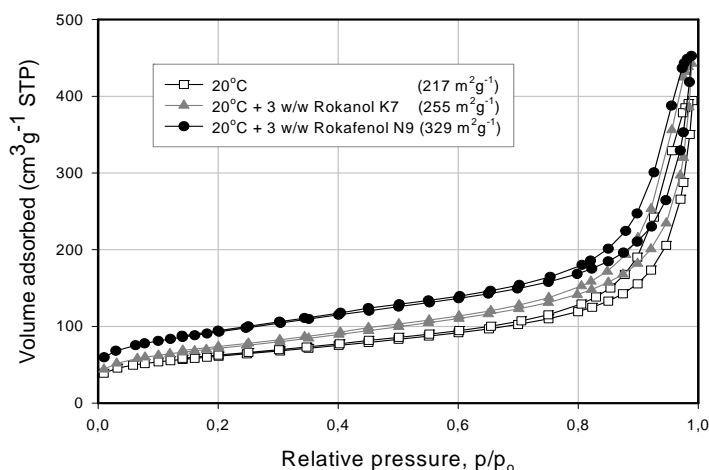


Fig.5. N_2 adsorption/desorption isotherms of the examined magnesium silicates

CONCLUSIONS

The suggested technique of precipitating magnesium silicate according to the second stage procedure yielded better results than the first technique. Introduction of modifying agents additionally improved physicochemical properties of the precipitated silicate. This was particularly evident in cases of bulk density and

capacities to absorb water, dibutyl phthalate and paraffin oil. The shape of electrokinetic curves pointed to a slight effect of modification of the silica surface with Rokanol K7 and Rokafenol N9. The modification did not alter density or charge distribution on the surface of the silicate. On the other hand, effect of the modifiers was evident in isotherms of nitrogen adsorption/desorption. Thus, it could be concluded that they significantly affected activity of the precipitated silicate (best results were obtained for magnesium silicate precipitated in the presence of 3 weight parts of Rokafenol N9 – its specific surface area amounted to 329 m²/g).

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Ciesielczyk F., Krysztafkiewicz A., Jesionowski T., *Wpływ parametrów strącania na właściwości fizykochemiczne krzemianów magnezu*, Physicochemical Problems of Mineral Processing, 38, (2004) 197-205 (w jęz. ang.).

Przedstawiono badania nad zoptymalizowaniem metody strącania krzemianu magnezu o dużym stopniu dyspersji, tak by uzyskać produkt o jak najlepszych parametrach fizykochemicznych. Krzemian magnezu otrzymywano w reakcji strącania z użyciem roztworów siarczanu magnezu i metakrzemianu sodu. Zmieniającymi się parametrami były: temperatura, sposób dozowania reagentów oraz dodatek substancji modyfikujących. Wyznaczono parametry fizykochemiczne takie jak: gęstość nasypowa, chłonności wody, ftalanu dibutyli i oleju parafinowego, średnice cząstek, powierzchnię właściwą oraz potencjał elektrokinetyczny.