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Filip CIESIELCZYK, Andrzej KRYSZTAFKIEWICZ, Teofil JESIONOWSKI*

SEDIMENTATION AND WETTABILITY OF SYNTHETIC MAGNESIUM SILICATES

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In the paper studies were presented which aimed at obtaining synthetic magnesium silicate, which could be applied as a selective adsorbent, polymer filler or a filler of paper-coating masses. Synthetic magnesium silicate was obtained by precipitation using solutions of $MgSO_4 \cdot 7H_2O$ and Na_2SiO_3 (water glass). In view of specific application of the precipitated silicates, the process of their production was broadened by introduction to the reactive system agents which hydrophobically transform silicate surface. Non-ionic surfactants were used for this purpose. The obtained products were subjected to a comprehensive physicochemical analysis. The tested parameters included bulk density, capacities to absorb water (wettability with water), dibutyl phthalate and paraffin oil, particle size distribution, and specific surface area. A significant element of the work involved studies on sedimentation of synthetic magnesium silicates, an important variable which determines directions of their application.

Key words: synthetic magnesium silicate, non-ionic surfactants, specific surface area, sedimentation, wettability

INTRODUCTION

Sedimentation and wettability of surface with various agents belong to most significant parameters which determine application of mesopoorous silicate fillers. Due to numerous applications of both natural and synthetic magnesium silicates, their behaviour in various media has to be determined. Considering application of magnesium silicates as selective adsorbents it is necessary to determine their adsorptive properties, i.e. specific surface area and porosity.

Both natural and synthetic magnesium silicates are used as adsorbents with various effects, due to their variable specific surface areas (Kociołek-Balawejder 2006).

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* Poznan University of Technology, Institute of Chemical Technology and Engineering,
M. Sklodowskiej-Curie 2 Sq., 60-965 Poznan, Poland,
E-mail: Filip.Ciesielczyk@doctorate.put.poznan.pl, phone:+48(61)6653626, fax:+48(61)6653649.

Promising results have been obtained removing waste As(III) and As(V) ions by application of natural and modified zeolites (Elizalde-Gonzales 2001, Xu 2002), and also laterite - the mineral containing iron and aluminium oxides (Viet 2002).

Literature contains reports on the application of natural zeolites for removal of sewage Cd(II) ions (Dąbrowski 2006). A similar application involved clinoptylolite modified with hexadecyltrimethylammonium cation, which proved to be a selective ion exchanger for Cr(VI) ions in the pH range of 3 to 13 (Li 1997, Haggerty 1994). Zeolites modified with surfactants adsorb non-polar organic substances such as benzene, toluene, xylene, chlorinated aliphatic compounds, inorganic cations (e.g. Pb(II)), by ion exchange and formation of surface complexes (Dąbrowski 2006). Similar results could be expected using synthetic magnesium silicates, which manifest numerous analogies in structure and physicochemical properties with their natural analogues.

Sedimentation and wettability play a significant role, particularly when the precipitated silicates are applied as supplements to protein-coating masses or as carriers of inorganic pigments. In order to fulfil its role, the synthetic silicate should not sediment and its surface should be well wettable with the medium in which the silicate is supposed to be used. An example of such a system is provided by magnesium silicate coated with layers of TiO_2 water gels or by introduction of pure TiO_2 (in the form of a powder) into a silicate matrix (Cardona 2004). After testing, such systems can be safely used as a supplement of paints, in which they have to form a stable dispersion (Brown 1997, Kobayashi 1996).

Synthetic magnesium silicates, precipitated by reaction of inorganic salt solution and water glass solution demonstrate a pronounced sedimentation, particularly in aqueous media. In addition, modification of their surface significantly affects their behaviour in various media (Krysztafkiewicz 2004).

A detailed physicochemical analysis of various $MgO\text{-}SiO_2$ systems has been described in detail in various studies (Wentzcovitch 1995, Karki 1997, Chaplot 2000, Belonoshko 1996). In turn, Temuujin (1998) and co-authors have described studies on the role of water in mechanic-chemical reactions of $MgO\text{-}SiO_2$ systems.

EXPERIMENTAL

MATERIALS

Synthetic magnesium silicate was obtained by precipitation reaction, using 5% $MgSO_4 \cdot 7H_2O$ solution (5% in respect to $MgSO_4$) and 5% aqueous solution of Na_2SiO_3 (5% in respect to SiO_2). The sodium metasilicate solution manifested the following parameters: contents of Na_2O - 8.8 %; SiO_2 - 28.5 %, density - 1.38 g/dm^3 and modulus 3.33. Surface hydrophobization was conducted using appropriate non-ionic surfactants produced by the PPC „Rokita" S.A. Compounds applied for this purpose included nonylphenylpolyoxyethyleneglycol ethers, Rokafenols N3, N6, N9, of the general formula $C_9H_{19}C_6H_4O(CH_2CH_2O)_nH$ (where $n_{av}=3$; $n_{av}=6$; $n_{av}=9.7$ for respective Rokafenol) and oxyethylated unsaturated fatty alcohols, Rokanols K3 and K7, of the general formula $RO(CH_2CH_2O)_nH$ $R=C_{16-22}$, where $n_{av}=3$; $n_{av}=7$ for respective Rokanol).

METHODS OF STUDIES

In the earlier performed studies (Ciesielczyk 2004) the process of obtaining synthetic magnesium silicates by chemical reaction was optimised, using 5% waste solutions of magnesium sulphate(VI) and sodium metasilicate. The reaction was conducted in a reactor of 500 cm^3 capacity, equipped with top stirrer. Into a reactor containing appropriate amount of magnesium(VI) sulphate, the same amount of water glass solution was dosed. The process was conducted at room temperature.

After obtaining synthetic magnesium silicates, the precipitation process was broadened by introduction to the reactive system of hydrophobicity-inducing agents in the form of non-ionic surfactants: Rokafenols N3, N6 and N9 and Rokanols K3 and K7. Respective surfactants were introduced in the amount of 1; 3; of 5 weight parts, implementing the so called “wet” modification process.

In order to obtain images of the obtained modified and unmodified magnesium silicates, their selected samples were examined in a scanning electron microscope (Philips SEM 515).

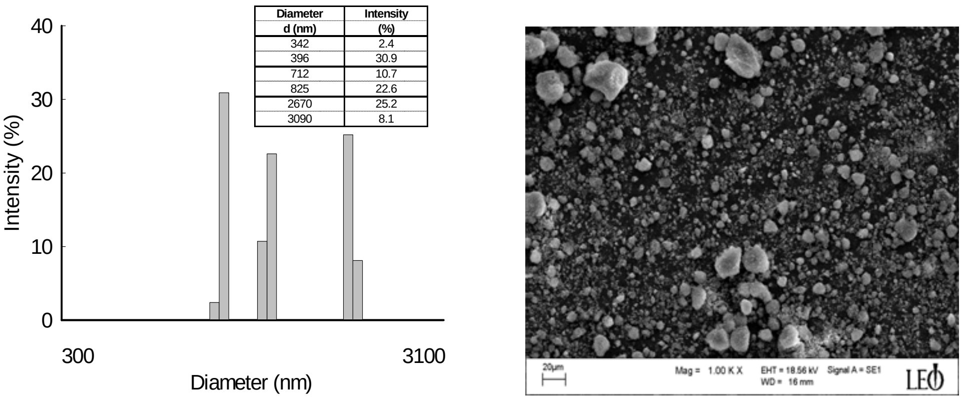
For all the samples particle size distributions were established, basing on dynamic light scattering (DLS) technique and using for the purpose ZetaSizer Nano ZS apparatus (Malvern Instruments Co).

A significant element of the studies involved determination for the samples of sedimentation tendency in aqueous media and wettability with water. The studies were performed using K100 tensometer (Krüss).

RESULTS AND DISCUSSION

Particle size distribution and SEM microphotograph of synthetic magnesium silicate obtained with no supplementation of the hydrophobicity-inducing agent are presented in Fig.1.

In the particle size distribution (Fig.1) three bands could be noted. The first occupied the diameter range of 342-396 nm with maximum intensity of 30.9 for particles of 396 nm in diameter. The other band corresponded to particles of diameters in the range of 712-825 nm (maximum intensity of 22.6 corresponded to agglomerates of 825 nm in diameter). The third band, in turn, fitted the range of 2670-3090 nm, with maximum intensity of 25.2 for particles of 2670 nm in diameter. The unmodified sample contained both particles of high diameters (representing agglomerates of magnesium silicate particles, which unfavourably affected physicochemical parameters of the entire sample), and particles of lower diameter.

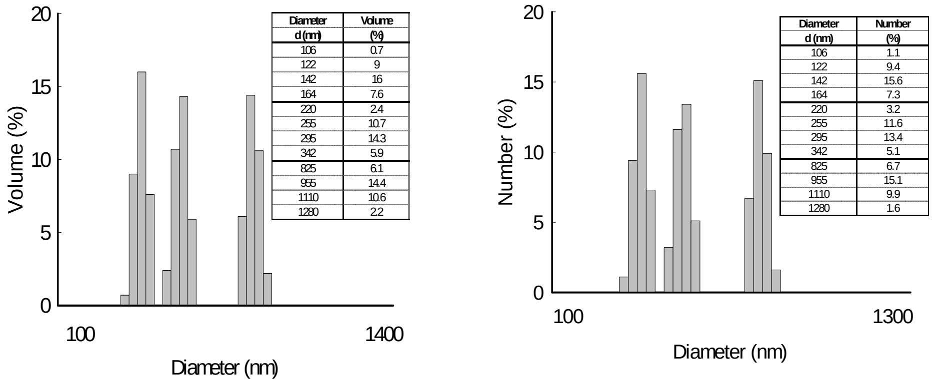


Diameter d (nm)	Intensity (%)
342	2.4
396	30.9
712	10.7
825	22.6
2670	25.2
3090	8.1

(a) (b)

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

The distribution was confirmed by graphs illustrating input of particles of a given diameter into volume and number of particles in the sample (Fig. 2). The graph illustrating volume input of particles of a given diameter showed that particles of the lowest diameters comprised 37% of sample volume, while particles of the second band and agglomerates comprised each 33% of the volume. Numerical input of the particles in the examined sample was similar: particles of individual bands comprised 36%, 30% and 34% samples particles for the first, second and third band, respectively. The distribution of particle diameters was confirmed by SEM microphotograph of the unmodified sample (Fig. 1b).

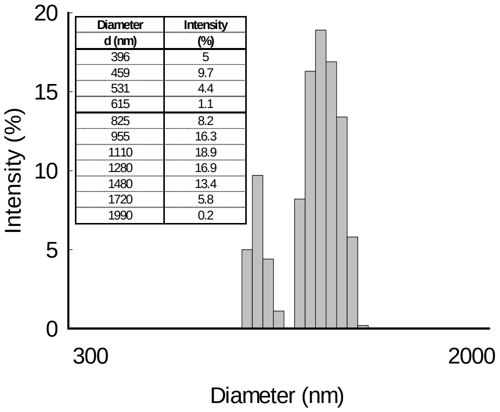


Diameter d (nm)	Volume (%)
106	0.7
122	9
142	16
164	7.6
220	2.4
255	10.7
295	14.3
342	5.9
825	6.1
955	14.4
1110	10.6
1280	2.2

Diameter d (nm)	Number (%)
106	1.1
122	9.4
142	15.6
164	7.3
220	3.2
255	11.6
295	13.4
342	5.1
825	6.7
955	15.1
1110	9.9
1280	1.6

a) (b)

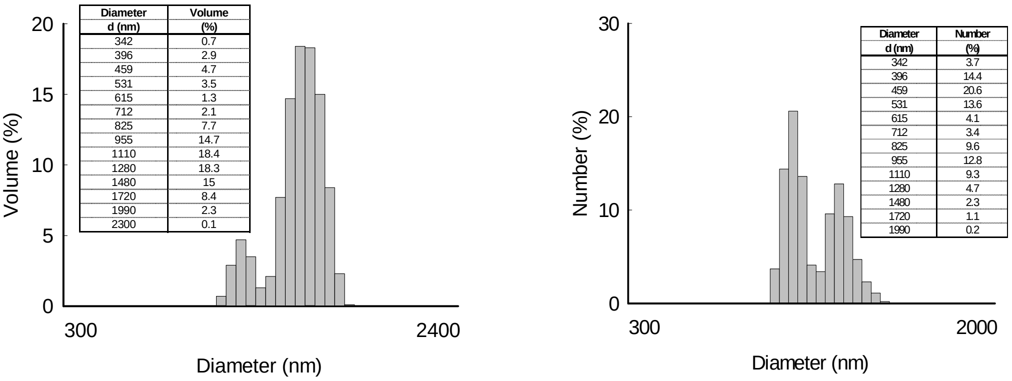
Fig. 2. (a) Volume and (b) numerical input of individual particles of unmodified magnesium silicate



Diameter d (nm)	Intensity (%)
396	5
459	9.7
531	4.4
615	1.1
825	8.2
955	16.3
1110	18.9
1280	16.9
1480	13.4
1720	5.8
1990	0.2

Fig. 3. Particle size distribution of magnesium silicate modified with 3 w/w of Rokanol K7

Application for the modification of 3 weight parts of Rokanol K7 (Fig. 3) insignificantly improved quality of the sample. In the particle size distribution two bands were noted. The most intense band corresponded to particles of 825-1990 nm in diameter (maximum intensity of 18.9 corresponded to the particles of 1110 nm in diameter), while the other band representing the particle diameter range of 396-615 nm was characterized by maximum intensity of 9.7 for the particles of 459 nm in diameter.



Diameter d (nm)	Volume (%)
342	0.7
396	2.9
459	4.7
531	3.5
615	1.3
712	2.1
825	7.7
955	14.7
1110	18.4
1280	18.3
1480	15
1720	8.4
1990	2.3
2300	0.1

Diameter d (nm)	Number (%)
342	3.7
396	14.4
459	20.6
531	13.6
615	4.1
712	3.4
825	9.6
955	12.8
1110	9.3
1280	4.7
1480	2.3
1720	1.1
1990	0.2

(a) (b)

Fig. 4. (a) Volume and (b) numerical input of individual particles of magnesium silicate modified with 3 w/w of Rokanol K7

In analysis of volume input of particles of a given diameter (Fig. 4a) it could be noted, in comparison with the unmodified sample, that the number of agglomerates (the band of particles in the range of 1110-2300 nm) markedly increased. Particles of lower diameters, i.e. in the range of 300 to 825 nm, comprised only 20% volume of all the particles. In turn, considering numerical input of particles of a given diameter in the sample (Fig. 4b) the difference in numbers of large and small particles could be noted to be much less pronounced: the particles corresponding to the first band comprised 60% and those corresponding to the second band included 40% of all particles. This, however, reflected the applied measuring technique since the larger particles (agglomerates) yielded a definitely stronger signal even if they might be present in lower numbers in the sample. Therefore, to corroborate the presence of particles of a specific diameter in the sample, analysis of particle size distribution had to be performed in respect to band intensity and input into sample volume/numerical force particles. Sedimentation of magnesium silicates unmodified or modified using non-ionic surfactants is presented in Fig. 5.

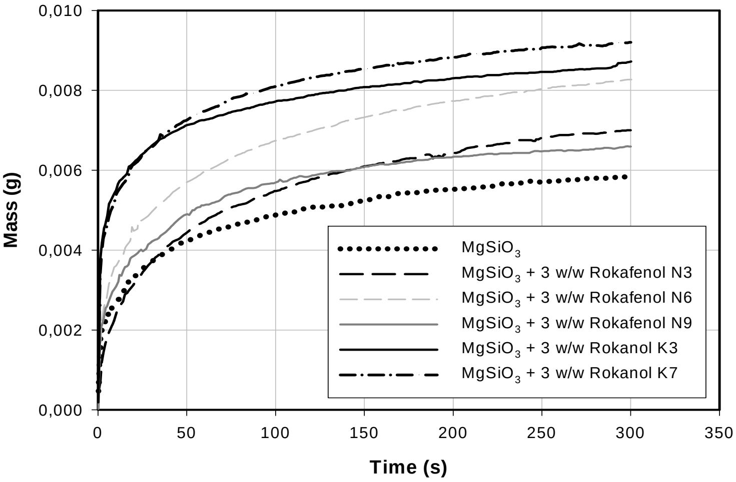


Fig. 5. Curves of sedimentation of magnesium silicate particles, unmodified or modified using non-ionic surfactants

The graph allowed to determine effect of the applied modifying agent on agglomeration tendency of precipitated silicate particles and, thus, on their sedimentation in water solutions. The most pronounced mass increments were recorded in the first 50 s of measurement, which might point to a very good sedimentation of the samples. After subsequent seconds the mass became stable, as shown by the course of the curves. In analysis of the total mass of the sedimented samples at a given time, it could be found to be radically different for the modified and unmodified samples. For the unmodified sample the mass amounted to 0.0059 g being the lowest among all samples tested. For the samples modified with non-ionic surfactants the value amounted, for samples modified with 3 weight parts of Rokafenol N3 to 0.0070 g, for samples modified with 3 weight parts of Rokafenol N6 to 0.0082 g, for samples modified with 3 weight parts of Rokafenol N9 to 0.0065 g, for samples modified with 3 weight parts of Rokanol K3 to 0.0089 g and for samples modified with 3 weight parts of Rokanol K7 to 0.0092 g. This might indicate that supplementation with appropriate non-ionic surfactant induced agglomeration of silicate particles, which was confirmed by the increased volume of the sedimented sample (as compared to the unmodified one) at the same time point. Surface wettability with water of modified and unmodified synthetic magnesium silicates is illustrated in Fig. 6.

Synthetic magnesium silicates belong to substances, which manifest high wettability with water. In view of numerous applications, silicate surface is subjected to surface modifications to increase hydrophobic character of the surface. In the cases of samples modified with non-ionic surfactants every sample manifested a distinct wettability. All the modifiers increased wetting time, as indicated by the character of wetting curves in the course of the first 1000 s. The magnesium silicate sample modified with 3 weight parts of Rokafenol N6 proved to be slowest in wetting, followed by samples modified with 3 weight parts of Rokafenol N3, Rokanol K7, Rokanol K3 and Rokafenol N9. The most rapidly wetted sample was found to be unmodified magnesium silicate. The total amount of adsorbed water for all the samples ranged between 1.5 and 1.8 g. In the same period of time the highest amount of water was adsorbed by the sample modified with 3 weight parts of Rokafenol N3, the lowest amount of water – by the sample modified with 3 weight parts of Rokafenol N6 and by the unmodified sample.

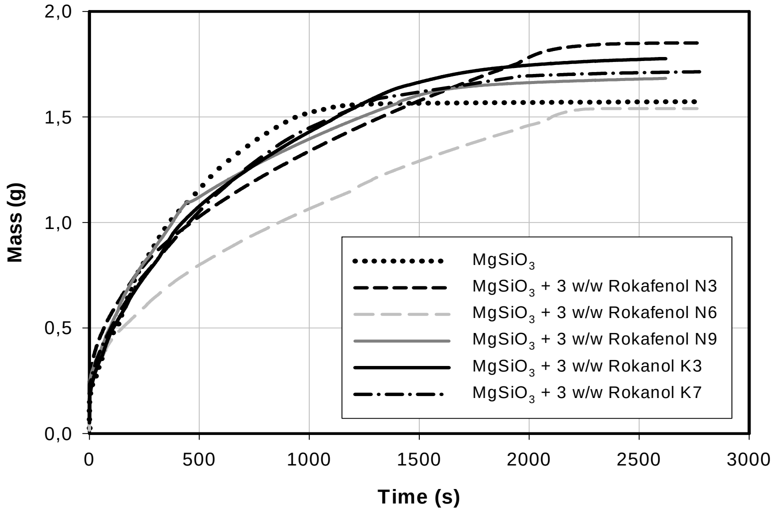


Fig. 6. Curves of wetting with water of the surface of magnesium silicate, unmodified and modified using non-ionic surfactants

CONCLUSIONS

As the result of performed studies synthetic unmodified and modified magnesium silicates were obtained which could successfully be used as selective adsorbents, fillers of polymers and of paper-coating masses. This was indicated first of all by the potential for modification of physicochemical properties of the precipitated silicates using appropriate compounds (in this case this involved hydrophobization of the surface using non-ionic surfactants).

Addition of small amounts of non-ionic surfactants was found to induce no pronounced changes in diameters of magnesium silicate particles. Higher amounts of the agents induced extensive agglomeration of the obtained sample (confirmed by the particle size distribution). In turn, more pronounced agglomeration of the sample intensified sedimentation of synthetic magnesium silicate particles (in particular the modified ones) in water solutions. In the solutions within a defined time period a decisively higher sample mass sedimented as compared to the unmodified silicate. In addition, the samples precipitated in the presence of respective modifying agents manifested lower rate of wetting with water as compared to the unmodified sample. This resulted from the accentuated hydrophobic character of the synthetic magnesium silicate surface, particularly following the modification with higher amounts of non-ionic surfactants.

The simple method for production of synthetic magnesium silicates and for modification of their physicochemical properties causes that the products may successfully compete with their natural equivalents, both in their physicochemical properties and in direction of their application.

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Ciesielczyk F., Krysztafkiewicz A., Jesionowski T., *Sedymentacja i zwilżalność syntetycznych krzemianów magnezu,* Physicochemical Problems of Mineral Processing, 40 255-263, (2006) (w jęz.. ang.).

W pracy przedstawiono badania prowadzone w celu otrzymania syntetycznego krzemianu magnezu, mogącego posłużyć jako selektywny adsorbent, napełniacz polimerów lub wypełniacz do mas powlekających papier. Syntetyczny krzemian magnezu otrzymano w reakcji strącania z użyciem roztworów $MgSO_4 \cdot 7H_2O$ i Na_2SiO_3 (tzw. szkła wodnego). Ze względu na konkretne aplikacje strącanych krzemianów proces ich otrzymywania rozszerzono o element wprowadzenia do układu reakcyjnego czynników hydrofobizujących powierzchnię. W tym celu zastosowano niejonowe związki powierzchniowo czynne. Otrzymane w ten sposób produkty poddano szerokiej analizie fizykochemicznej. Oznaczono: gęstość nasypową, chłonności wody (zwilżalność wodą), ftalanu dibutylu i oleju parafinowego, rozkłady wielkości cząstek, powierzchnię właściwą. Istotnym elementem pracy były badania nad sedymentacją syntetycznych krzemianów magnezu, ważnym parametrem decydującym o kierunkach zastosowania.