

The impact of reagents concentration on the efficiency of obtaining high-purity magnesium hydroxide

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The work presents the impact of reagents concentration and the drying process on the efficiency of obtaining magnesium hydroxide and its specific surface area. Magnesium sulphate(VI) within the concentration range of 0.7–2.0 mol/dm³ was used in the research as magnesium feedstock and sodium hydroxide was used as a precipitating agent within the same concentration range. The process of obtaining magnesium hydroxide was carried out with a 25% excess of the precipitating agent in relation to the reaction stoichiometry. The obtained suspension was separated by way of multi-stage sedimentation with the use of acetone and freezing samples. Depending on the concentration of reagents the efficiency of obtaining magnesium hydroxide fell within the range of 88–99%, whereas the specific surface area – within 115–609 m²/g, while the high purity of samples above 99% of magnesium hydroxide was maintained.

Keywords: magnesium hydroxide, precipitation method, inorganic flame retardants.

INTRODUCTION

The use of inorganic flame retardants ensuring the appropriate effect of flame retardancy makes it necessary to introduce a significant amount of a flame retardant additive, amounting to even 60 wt%, into the polymer matrix. Such great amounts of the flame retardant introduced into the polymer matrix trigger the deterioration of mechanical properties of the material as well as disturb the process of its processing. Such disadvantages may be eliminated by using a flame retardant in the shape of nanometric additives characterized by a significantly developed specific surface area and, at the same time, reactivity^{1–3}. For example, magnesium hydroxide is used as a flame retardant additive in EVA material; however, in order to obtain a desired flame-retarding effect, it should be introduced in an amount exceeding 40% mass to obtain the oxygen index of more than 23%⁴. Modifications of magnesium hydroxide, e.g. silicone, are also used to increase the adhesion between the flame retardant and the polymer matrix⁵.

Aluminium hydroxide is the most frequently used inorganic flame retardant, however, due to the higher decomposition temperature (about 100°C) it is preferable to use magnesium hydroxide⁶. Moreover, magnesium hydroxide with a well-defined specific surface area may have a number of other applications, mainly for obtaining nanometric magnesium oxide used as a neutraliser of water pollutants and an antibacterial agent^{7–8}.

Magnesium chloride obtained mainly from marine waters, primarily in the USA and Israel^{2, 9–10}, is a convenient raw material for obtaining magnesium hydroxide for the needs of the plastics industry. An alternative magnesium feedstock for obtaining magnesium hydroxide is magnesium sulphate(VI). In Poland magnesium sulphate(VI) is obtained from dead burned magnesite with the use of secondary materials¹¹. Magnesium sulphate(VI) is also a by-product of zinc obtaining technology by electrolytic method and it may come from the processing of deposited waste such as post-chromium mud which is a by-product of obtaining sodium chromate by magnesite method.

Magnesium hydroxide is obtained by the hydration of magnesium oxide, however, this process is slow and of low-yield at a temperature of approximately 20°C. The most advantageous method of obtaining magnesium hydroxide are precipitation methods. The high yield of obtaining magnesium hydroxide and the possibility of conducting the process at low temperatures constitute advantages of these methods. During precipitation well-soluble magnesium salts as well as soluble sodium and potassium hydroxides are used. One of the disadvantages of obtaining magnesium hydroxide is the formation of conglomerates during its synthesis; the elimination of this phenomenon requires the application of additional procedures and auxiliary substances. They are often multi-stage low-yield processes^{6, 12–14}. There are known methods obtaining of magnesium hydroxide with specific surface properties in nano scale using organic or inorganic additives during Mg(OH)₂ precipitation process or using ultrasounds affecting the crystallite formation process^{5, 15}.

EXPERIMENTAL

Materials and methods

Substances used in the research: magnesium sulphate(VI), production technology of Arkop, Ltd., sodium hydroxide, p.a., produced by Avator, ammonia water containing 25% NH₃, produced by Avator and acetone technical grade, produced by Avator.

The aim of the research was to determine the impact of the concentration of sodium hydroxide and magnesium sulphate(VI) on the specific surface area of the obtained magnesium hydroxide and the process yield. Obtaining of magnesium hydroxide was carried out by dosing the solution of sodium hydroxide to a previously measured volume of magnesium sulphate(VI) solution. It was assumed that 10 g of the substance would be obtained once, with the application of a 25% excess of the precipitating agent in relation to the reaction stoichiometry in order to obtain the highest process efficiency possible. The synthesis of magnesium hydroxide was conducted

by dosing the sodium hydroxide solution to the solution of magnesium sulphate(VI) every minute in the amount of 10 cm³ until a calculated volume including the 25% excess in relation to the reaction stoichiometry was introduced. Obtaining of Mg(OH)₂ was carried out in a reactor equipped with a mechanical stirrer operating at a rotational speed of 800 rpm. The process was conducted at ambient temperature.

When the process of precipitating magnesium hydroxide was completed, ammonia water containing 25% mass NH₃ in the amount of 1cm³/1g Mg(OH)₂ was added to samples. Next the mixture was left for 24 h for the obtained precipitate to undergo sedimentation. When the sediment settled a clear supernatant liquid was separated. The remaining suspension was refilled again with deionized water with the addition of ammonia water calculated as before. The process of washing with water with the addition of ammonia was performed twice. The sedimentation process lasted approximately 12 h. The suspension obtained after sedimentation was separated from the clear liquid and refilled with acetone to the volume of 1 dm³ and then cooled until a temperature of -25°C was reached.

The process was conducted for 12 h. Then the mixture was separated and the process was repeated. After the second freezing the sample was separated by vacuum filtration. Such obtained sediment was gently dried at a temperature of 50°C, and then at 130°C. Two-stage drying aimed at slow removal of acetone and the ammonia residue contained in the sediment. Drying at a higher temperature was carried out in order to remove the remaining moisture as well as the residual ammonia and acetone. The procedure chart is shown in Tab. 1.

The solution from above the surface of the condensed sediment of magnesium hydroxide was periodically siphoned out of the measuring system and subjected to regeneration. Sulphate salts (Na₂SO₄) – as a by-product of obtaining magnesium hydroxide – were recovered from these solutions by polythermal crystallization; ammonia was recovered as well. The ammonia absorbed in water was reused in the process of washing magnesium hydroxide sediment. On the other hand, the solutions containing acetone were regenerated by passing the air through the solution in order to remove the residual ammonia and by distilling the acetone which was recycled for sediment washing.

The dried sediment of magnesium hydroxide was analyzed as far as the size of specific surface area and density were concerned, the latter being determined by the pycnometer method with the use of acetone as a substance of known density. Moreover, purity of the obtained magnesium hydroxide was determined by the analysis of magnesium content in the sample (using calorimetric methods). An additional thermal analysis

of the selected samples of the obtained substance was performed (TA Instruments SDT 2960). The specific surface area of magnesium hydroxide samples was determined using Micrometrics ASAP 2020 sorptiometer and the apparatus of Blaine. For the microscopic observations of selected magnesium hydroxide samples was used high-resolution scanning electron microscope Jeol JSM-5400 with EDS adapter.

Moreover, tests on obtaining magnesium hydroxide under similar conditions excluding the process of multi-stage drying were conducted. The obtained sediment was washed with deionized water until sulphate(VI) ions were not present, and then it was dried and weighed. These tests were performed in order to determine the efficiency of the process of obtaining magnesium hydroxide.

In order to eliminate ammonia water from the drying process tests were conducted in which ammonia water was used as a precipitating agent. The synthesis of magnesium hydroxide was carried out with the concentration of magnesium sulphate(VI) solution similar to the previous ones and with a constant concentration of ammonium hydroxide in the form of ammonia water containing 25 wt% NH₃ (1.34 mol/dm³). The process of obtaining magnesium hydroxide was conducted under similar conditions using a 25% excess of the precipitating agent. When the synthesis of magnesium hydroxide was completed, the sample was subjected to washing with water and 12h sedimentation, similarly to previous tests; however, ammonia water was not introduced additionally to the process. The remaining steps in dealing with the suspension of magnesium hydroxide were analogous to those from Fig. 1.

RESULTS AND DISCUSSION

Table 1 shows the efficiency of obtaining samples of magnesium hydroxide; they are average values from three identical samples. Out of the obtained magnesium hydroxide preparations the highest efficiency was achieved for the solution of 2 mol/dm³ magnesium sulphate(VI) with the use of a 2.0 mol/dm³ sodium hydroxide solution. Together with an increase in the concentration of the magnesium sulphate(VI) solution the efficiency increases, similarly with an assumed concentration of the MgSO₄ solution an increase in the efficiency together with an increase in the concentration of the precipitating agent is observed.

Table 2 collates the size of specific surface area of the obtained magnesium hydroxide. The size of specific surface area was determined with the BET method for the samples of magnesium hydroxide obtained at the concentration of magnesium sulphate(VI) equal to 0.75 mol/dm³. These samples served as standards while determining the specific surface area with the use of

Table 1. Efficiency [%] of obtaining magnesium hydroxide

NaOH concentration [mol/dm ³]	MgSO ₄ concentration [mol/dm ³]					
	0.75	1.00	1.25	1.50	1.75	2.00
0.75	88.2	91.2	93.6	96.4	97.3	98.4
1.00	88.9	91.7	93.9	96.4	97.5	98.5
1.25	89.3	92.4	94.1	96.8	97.8	98.7
1.50	89.9	92.6	94.4	97.0	97.9	98.9
1.75	90.4	92.9	95.0	97.1	98.0	99.0
2.00	91.2	93.4	95.7	97.5	98.2	99.1

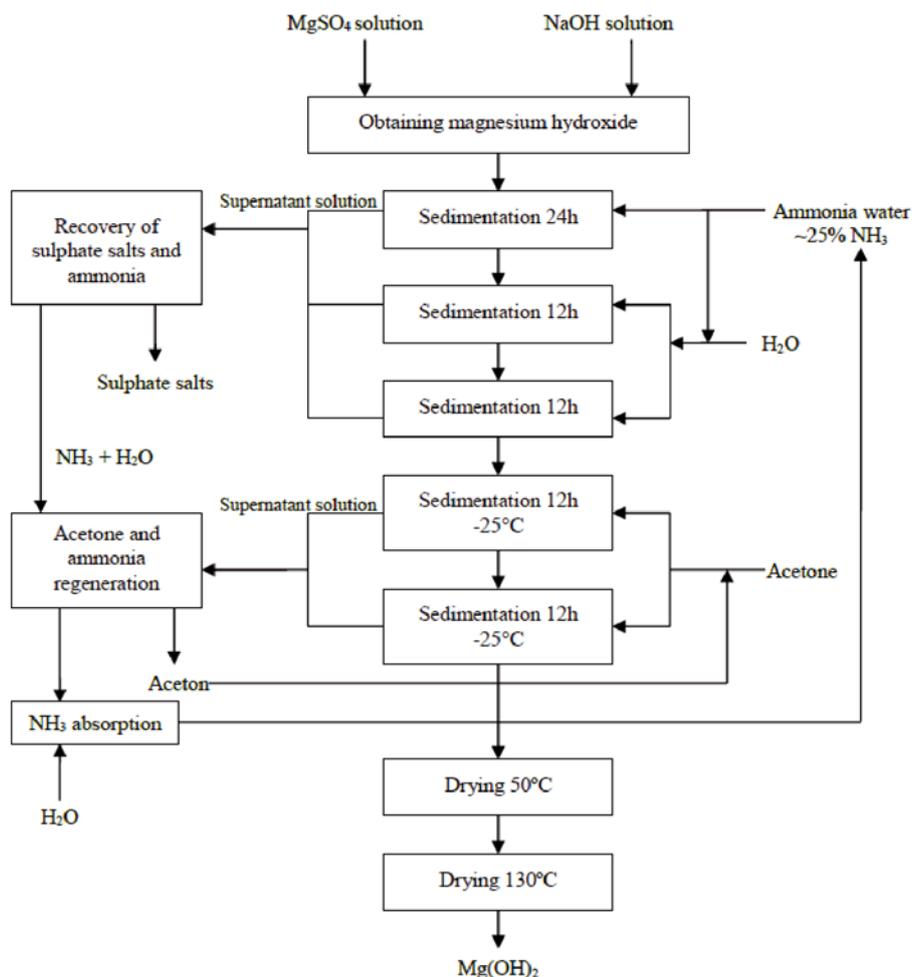


Figure 1. Scheme of drying magnesium hydroxide with the use of sedimentation, ammonia and acetone

Table 2. Collation of the obtained specific surface areas of $Mg(OH)_2$

NaOH concentration [mol/dm ³]	MgSO ₄ concentration [mol/dm ³]					
	0.75	1.00	1.25	1.50	1.75	2.00
0.75	115*	198	246	265	285	304
1.00	145*	244	270	299	317	356
1.25	199*	271	322	341	371	390
1.50	247*	311	362	392	431	444
1.75	299*	355	398	421	485	529
2.00	342*	402	446	473	541	609

*in these samples the specific surface area was determined with the BET method

Blaine apparatus (comparative method). The included values are the arithmetic mean of three identical samples.

Table 3 presents results of determining density of the selected samples of the obtained magnesium hydroxide and the average magnesium content. The values are the average of three measurements.

Table 4 shows values for specific surface area of magnesium hydroxide obtained with the application of ammonia water as a precipitating agent. For a sample obtained from a 1.25 mol/dm³ solution of magnesium sulphate(VI) the specific surface area was determined with the use of the BET method; with other samples the Blaine method was used.

Table 3. Magnesium content and density of the selected samples of magnesium hydroxide

MgSO ₄ concentration [mol/dm ³]	NaOH concentration [mol/dm ³]	Density g/cm ³	Mg ²⁺ content [% mass]
0.75	0.75	2.37	41.63
0.75	1.00	2.37	41.67
1.50	1.00	2.38	41.67
0.75	1.25	2.37	41.67
1.50	1.25	2.37	41.67
0.75	1.50	2.38	41.67
1.50	1.50	2.37	41.67
0.75	1.75	2.37	41.67
1.50	1.75	2.37	41.67
0.75	2.00	2.37	41.67

Table 4. Specific surface area of magnesium hydroxide obtained with the use of ammonia water

MgSO ₄ solution [mol/dm ³]	0.75	1.00	1.25	1.50	1.75	2.00	2.25
Specific surface area [m ² /g]	58.75	51.39	41.21*	34.12	22.98	14.21	8.74

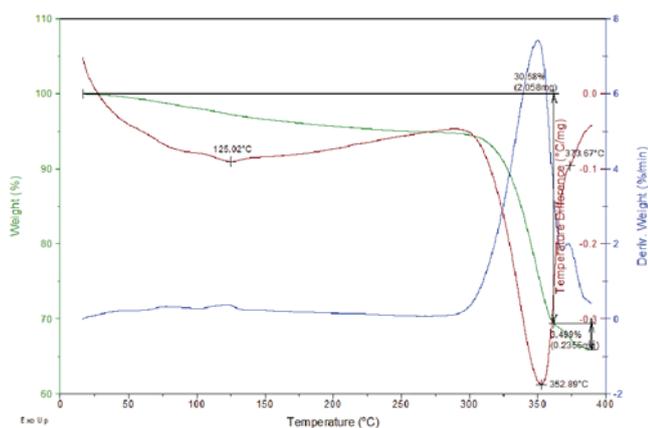
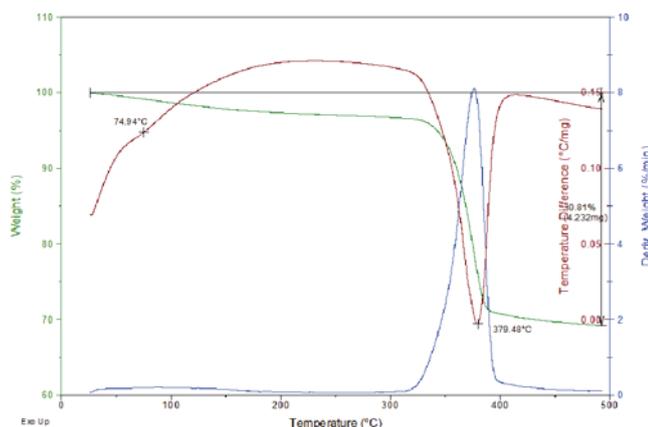
*the value of specific surface area determined with the application of the BET method

Table 5. The efficiency of obtaining Mg(OH)₂ depending on the baseline concentration of MgSO₄ solution

MgSO ₄ concentration [mol/dm ³]	0.75	1.00	1.25	1.50	1.75	2.00	2.25
Efficiency [%]	51.79	53.21	54.64	56.08	57.44	58.61	59.41

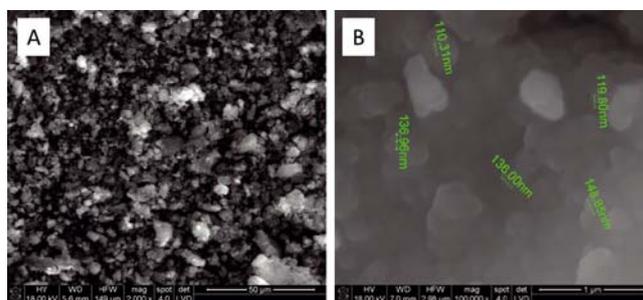
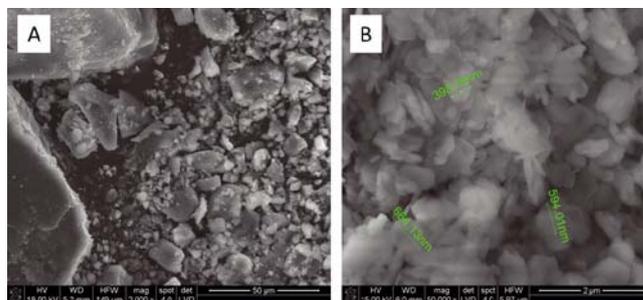
Table 5 shows the efficiency of obtaining magnesium hydroxide with the use of ammonia water as a precipitating agent.

The selected samples of magnesium hydroxide were subjected to thermal analysis in order to determine the calcination temperature. The result of thermal analysis of preparations with specific surface area equal to 244 and 529 m²/g is shown in Fig. 2 and 3. The analysis conditions: temperature ranges: 25–400°C and 25–500°C, heating rate: 20°C/min.

**Figure 2.** Thermal analysis of a magnesium hydroxide sample with a specific surface area of 244 m²/g**Figure 3.** Thermal analysis of a magnesium hydroxide sample with a specific surface area of 529 m²/g

The dispersion degree of magnesium hydroxide influences both an initial temperature of the calcination process and its maximum value. Together with an increase in the specific surface area the maximum temperature was changing from around 320°C to around 380°C. The temperature shift into higher temperature ranges is advantageous and makes magnesium hydroxide more applicable as a potential flame retardant additive for polymer materials.

Fig. 4 and 5 show the surface observations of magnesium hydroxide samples with a specific surface area – 244 m²/g (Fig. 4 – concentration of magnesium sulfate and sodium hydroxide – 1.00 mol/dm³) and 51.39 m²/g (Fig. 5 – concentration of magnesium sulfate 1.00 mol/dm³, 25 wt% ammonia water).

**Figure 4.** SEM images of (A, B) magnesium hydroxide surface analysis (magnesium sulfate and sodium hydroxide – 1.00 mol/dm³)**Figure 5.** SEM images (A, B) of magnesium hydroxide surface analysis (magnesium sulfate 1.00 mol/dm³, 25 wt% ammonia water)

In the case of magnesium hydroxide obtained using a solution of magnesium sulfate (1.00 mol/dm³ and ammonia water (25 wt%) the crystallites are comparatively large (400–660 nm) in comparison to a sample of magnesium hydroxide obtained using magnesium sulfate and sodium hydroxide (1.00 mol/dm³), where crystallites are several times smaller (110–150 nm). In Fig. 4A and 5B at identical increase show that in the sample with a larger specific Surface area (244 m²/g) and obtained with the use of multi-stage drying there are conglomerates with smaller dimensions as opposed to the sample with a lower specific surface area (51.39 m²/g).

CONCLUSIONS

On the basis of the sulphate(VI), magnesium hydroxide with a specific surface area of 115–610 m²/g was obtained, depending on the concentration of magnesium salts and sodium hydroxide. An increase in the specific surface

area together with an increase in the concentration of both reagents is observed. The yield for the obtained magnesium hydroxide amounted to 88% for the lowest concentrations of magnesium sulphate(VI) and sodium hydroxide, and 99% for the highest concentrations of both reagents. The applied method for obtaining the hydroxide with the use of a multi-stage process allows to eliminate the formation of conglomerates at the stage of precipitating magnesium hydroxide in an aqueous medium.

The obtained product was characterized by a magnesium content at the level of 41.63–41.67% mass. at a hypothetical magnesium content in $\text{Mg}(\text{OH})_2$ amounting to 41.68% mass., which accounts for the minimum purity of the obtained magnesium hydroxide equal to 99%; a preparation with the above parameters may have a more widespread application than as a potential flame retardant additive for plastics.

The calcination (dehydration) temperature of magnesium hydroxide depends on the size of specific surface area and it shifts into a higher temperatures range together with an increase in the specific surface area. This tendency is favourable as far as applications of magnesium hydroxide are concerned. The dehydration of magnesium hydroxide occurs when the temperature exceeds 300°C; in preparations which have a high specific surface area and which, at the same time, are highly dispersed, dehydration temperature exceeds 320°C.

Additional studies relying on the application of ammonia water as a precipitating agent with further elimination of the water from a multi-stage process of washing magnesium hydroxide sediment showed an expectedly low yield for the magnesium hydroxide synthesis not exceeding 59% for the highest concentration of the magnesium sulphate(VI) solution. This results from the fact that ammonium hydroxide does not precipitate magnesium compounds completely due to the fact that the solubility equilibrium of magnesium hydroxide is not exceeded and the balance occurs between ammonium ions derived from ammonium hydroxide and ammonium sulphate(VI) being formed¹⁰. Moreover, the specific surface area of the obtained product is lower (9–59 m²/g) than with similar conditions for obtaining magnesium hydroxide with the use of sodium hydroxide as a precipitating agent, which – together with a low yield of the synthesis process itself – limits its applications.

The use of a multi-stage drying process leads to obtaining magnesium hydroxide with high fragmentation and crystallites in the range of 110–150 nm.

Choosing appropriately the concentrations of sodium hydroxide and magnesium sulphate(VI), a material with a postulated value of the specific surface area may be obtained. What is more, the application of a developed technique of drying sediment makes the obtained magnesium hydroxide sediment well-dispersed and the obtained values – repeatable. The obtained magnesium hydroxide, apart from a diversified specific surface area, is characterized by high purity, which significantly expands the range of its potential applications. Density of the obtained magnesium hydroxide is virtually equal to the density of a reagent, which also confirms purity of the obtained product.

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