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Obtaining magnesium hydroxide of micro- or nanostructure on the basis of technical raw materials

Introduction

Magnesium hydroxide of high purity and grindability can be used as a flame retardant additive for lowering plastic's flammability. It belongs to a group of additives which is not built in polymer chains and acts as a filler (Żuchowska 2000). The principle of operation of fillers made from magnesium hydroxide is similar to aluminum hydroxide, which is used as a filler in industrial practice. During thermal decomposition, water is formed that behaves as a cooling medium, taking heat from the surroundings of vaporization and the diluted fuel gases, and blocking the access of air to the burning zone.

In the case of magnesium hydroxide, the amount of water released during degradation is lower than in the case of aluminum hydroxide because of its construction (number of hydroxyl groups attached to both metals). Further, the formed oxide impedes the transport of oxygen to the surface of the deeper layers of the plastic material and distributes heat across the surface. For these reasons, the process of plastic burning is slowed down or even stopped completely (Sain et al. 2004; Gao et al. 2008; Zaitz et al. 2010; Anderson and Horlock 1968).

The smaller amount of water emitted by the magnesium hydroxide is compensated for by the higher decomposition temperature, providing higher efficiency of the fire-fighting

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operation in comparison with the aluminum hydroxide. The use of magnesium hydroxide as a flame retardant is described in many works such as those in references (Camino et al. 2001; Howell et al. 2000; Chiu and Wang 1998). It is important that the magnesium hydroxide is characterized by a highly developed surface, which affects the uniformity of distribution in the polymer matrix. The presence of impurities may affect the combustibility of the material (Rothon et al. 1996; Zhang et al. 2004). Therefore, the flame retardant should possess high purity. The most common method of obtaining magnesium hydroxide is the precipitation method, introducing a solution of a strong base into the aqueous magnesium salt solution. The quality of the obtained magnesium hydroxide is mainly dependent on the concentration of reagents used, temperature, and precipitation conditions. The presence of impurities in the initial materials is the cause of impurities in the final product, and as a result they must be removed (Ding et al. 2001; Qiu et al. 2003). The efficiency of impurities removal from solutions is dependent on the kind and amount of impurities. Most impurities in the form of metallic ions can be removed by precipitation of insoluble hydroxides or other compounds – for example, the hydroxides Fe (III), Zn, etc. (Łętowski 1975). Considering the high purity of magnesium hydroxide, it was crucial to concentrate on purification procedures such as the techniques used for the elimination of heavy metals. To that end, the primary focus of several publications (Pawłowski 2011) is purification methods that conform to the principles of sustainable development.

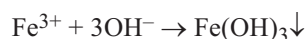
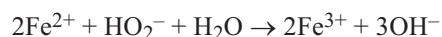
In general, the raw material for the preparation of magnesium salts under industrial conditions are magnesite, bishofite, carnallite, and water from saline seas and lakes. Increasingly used for the manufacture of salt and other compounds of this element are secondary materials, e.g. spent solution from the zinc electrolysis process. The works in references (Jarosiński and Madejska 2007; Jarosiński et al. 2012; 2013) present the extraction of high quality zinc concentrates recovered simultaneously with magnesium hydroxide from solutions deriving from the process of removing magnesium and other compounds from sphalerite concentrates. These examples also provide an assessment of the usability of $Mg(OH)_2$ obtained from such a solution after sphalerite leaching for the winning of a polyethylene composition.

The objective of this work is to obtain high cleanness of magnesium hydroxide with a solution prepared from technical magnesium sulphate, characterized by a high purity of product and a developed surface and micro or nanostructure.

1. Experimental work

Studies on the preparation of magnesium hydroxide included the removal of Fe (III) prepared from the technical solutions of magnesium sulfate, magnesium hydroxide precipitation from the purified solution by means of precipitating agents such as 0.1 mol NaOH/dm³, milk of lime (5% Ca(OH)₂) or solid magnesium oxide, and specific surface area determination for the magnesium hydroxide obtained. The process of purification of the

solutions was preceded by oxidation of Fe (II) to Fe (III) with hydrogen peroxide. The oxidation of these ions and their precipitation process describe the following reactions:



The amount of precipitation agent was limited by the final pH value of the solution, and so for the sodium hydroxide and for lime milk amounted to 9.5, and for the precipitation by means of magnesium oxide was carried out to pH 9.0. The process of precipitation is carried out at 60°C with vigorous stirring. After completion of the precipitation, the solution was filtered and the filtrate was concentrated for the purpose of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystallization. The obtained salt was used to prepare solutions of magnesium sulphate. The content of iron and magnesium in the initial and final solution, as well as in the obtained deposit, were analyzed. Loss of magnesium in the course of the purification process of the solution was determined depending on the initial concentration of the magnesium sulfate (VI). The content of iron and magnesium was determined using colorimetric methods.

The procedure for preparing the magnesium hydroxide is illustrated in Figure 1. The initial material for obtaining magnesium sulphate solutions was solid $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The precipitation of magnesium hydroxide was carried out by means of magnesium sulfate (VI)

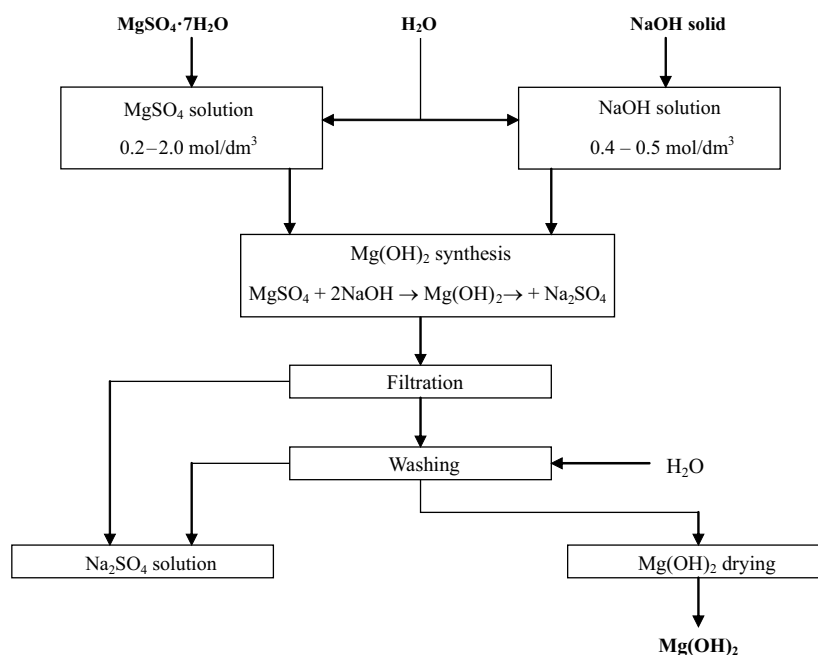
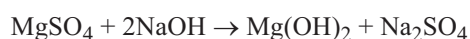


Fig. 1. Diagram of obtaining $\text{Mg}(\text{OH})_2$ by means of precipitation from magnesium sulfate solution

Rys. 1. Schemat otrzymywania $\text{Mg}(\text{OH})_2$ poprzez wytrącanie się z roztworu siarczanu magnezu

solutions at concentrations 0.2, 0.6, 0.8, and 2.0 mol MgSO₄/dm³, while the concentrations of sodium hydroxide amounted to 0.4 or 0.5 mol NaOH/dm³. The precipitation process proceeded according to the following summarized reaction:



2. Description of results

The initial solutions were prepared from technical magnesium sulfate containing 13.98% Mg, 0.0092% Fe, and 28.46% H₂O (total water).

As a result of the first stage studies, the purification of magnesium sulfate solution was achieved depending upon the precipitation agent as shown in Table 1.

Table 1. Comparison of the results of magnesium sulfate purification depending on the precipitation agent used

Tabela 1. Porównywanie wyników oczyszczania siarczanu magnezu w zależności od stosowanego czynnika wytrącającego

Concentration of initial solution of MgSO ₄ [mol/dm ³]	Degree of Fe removal from initial solution [%]	Loss of magnesium [%]	Degree of Fe removal from initial solution [%]	Degree of Fe removal from initial solution [%]	Loss of magnesium [%]
	precipitation way by means of NaOH		precipitation way by means of MgO	precipitation way by means of Ca(OH) ₂	
2.2	98.8	39.6	71.71	99.40	14.14
2.0	95.7	18.2	66.56	99.11	9.78
1.8	94.1	19.4	62.32	98.69	5.42
1.6	91.9	10.5	61.01	97.80	4.41
1.4	94.3	8.97	54.38	97.51	3.60

The data presented show that the highest degree of removal of iron from the initial solution was obtained in the case where calcium hydroxide was used as a precipitating agent. With the increase in the concentration of the initial solution, increased efficiency of removal of the iron ions was observed. The least effective agent for precipitating iron ions from the initial solution of magnesium sulfate was magnesium oxide. For the lower concentration of the initial solution, loss of magnesium was less. For example, for a solution of 2.2 mol/dm³ magnesium, losses reached a value of almost 40%. The lowest levels of iron removal were obtained in the case of using MgO as the precipitating agent. The degree of removal of iron ions for these conditions varied from 71.71 to 54.38%.

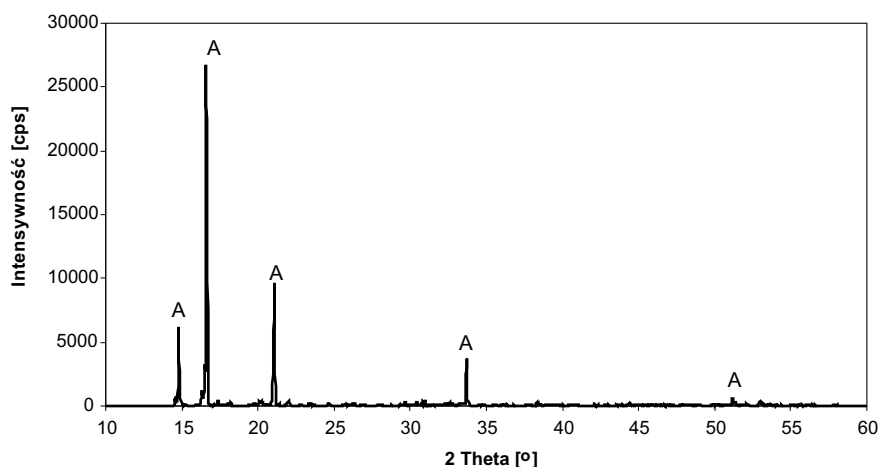


Fig. 2. X-ray diffraction pattern of obtained magnesium salt: A – $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Rys. 2. Dyfraktogram rentgenowski otrzymanej soli magnezowej: A – $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

From the tested solutions, magnesium sulphate was isolated by crystallization. For example, Figure 2 shows the diffraction pattern of crystallized magnesium sulfate from a tested solution in which sodium hydroxide was used as precipitating agent.

Then, from the obtained salt, the solutions for further examination were prepared at the following concentrations: 0.2, 0.6, 0.8, and 2.0 mol $\text{MgSO}_4/\text{dm}^3$. From these solutions magnesium hydroxide was obtained. As a preparation agent, solutions of sodium hydroxide were used, followed by determination of the specific area of the obtained products. The results from this series of analyses are given in Table 2.

Table 2. Conditions of obtaining magnesium hydroxide and their effects on the size of the specific area

Tabela 2. Warunki otrzymywania wodorotlenku magnezu i ich wpływ na powierzchnię właściwą

No.	Concentration [mol/dm ³]		Yield [%]	Specific area [m ² /g]
	Salt	Alkali		
1.	2.0	0.5	97.52	X
2.	0.8	0.5	94.83	64.42
3.	0.6	0.4	87.15	X
4.	0.2	0.4	84.22	115.20

X – lack of proper surface analysis, sample was agglomerated

The yield of the magnesium hydroxide obtaining process was connected with both the concentration of the magnesium sulfate and sodium hydroxide solutions. The yield of magnesium hydroxide was 84% at the initial concentration of magnesium sulfate solution,

0.2 mol/dm³, and 97% for 2.0 mol/dm³ MgSO₄. The results obtained show that the higher the concentration of the magnesium sulfate solution and sodium hydroxide, the higher the efficiency of the process.

For samples 1 and 3, the resulting precipitate was not suitable for the analysis because of the drying step of the deposit; its solid particles were agglomerated, which is disadvantageous when using magnesium hydroxide as a flame retardant additive. For samples 2 and 4, the resulting product was free-flowing. The specific surface area as opposed to the yield was higher at lower concentrations of the reagents (Table 2).

In all the described samples, magnesium content ranged from 41.67% at a level which practically corresponds to the hypothetical content of magnesium hydroxide.

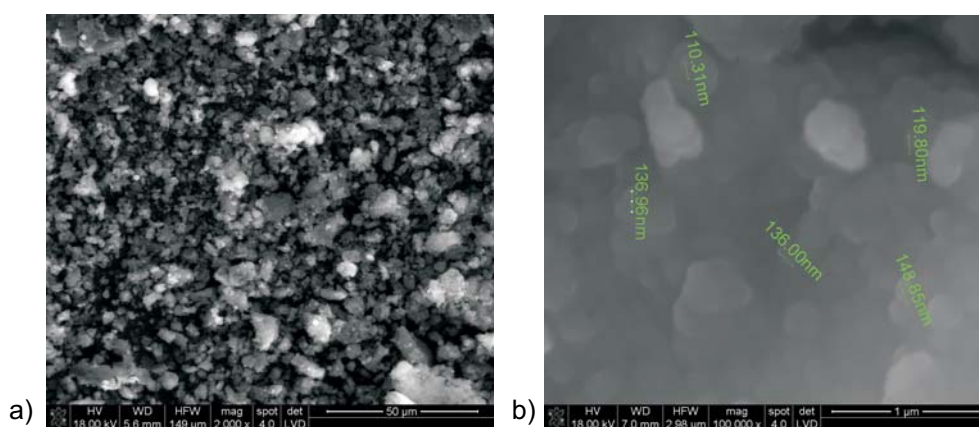


Fig. 3. SEM images of magnesium hydroxide – sample 4

Rys. 3. Mikrofotografia SEM wodorotlenku magnezu – próba 4

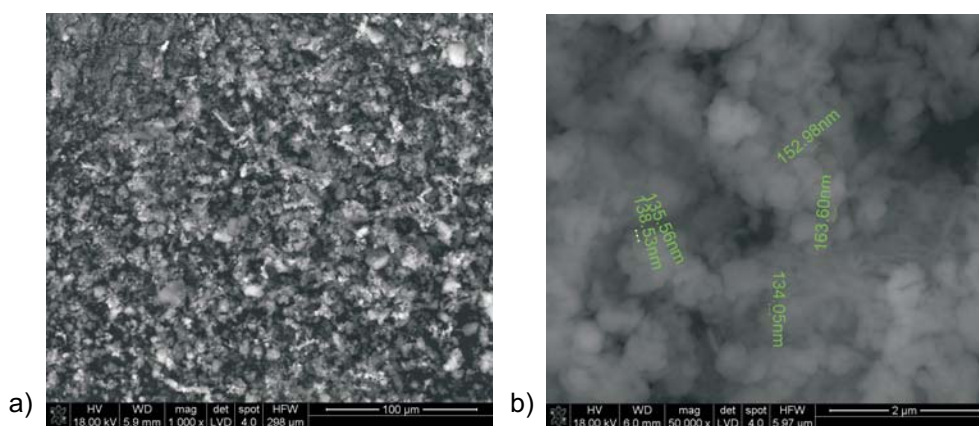


Fig. 4. SEM images of magnesium hydroxide – sample 2

Rys. 4. Mikrofotografia SEM wodorotlenku magnezu – próba 2

Observations of the structure of samples 2 and 4 were performed using a scanning electron microscope (SEM). The resulting images are shown on Figure 3 (sample 4) and Figure 4 (sample 2).

These magnesium hydroxide samples differ in their surface development. Figure 3 shows a sample of an area of 115 m²/g, and Figure 4 an area of 64 m²/g.

In the drawings, it can be seen that the magnesium hydroxide is obtained despite how the strong grinding tends toward cluster-conglomerates during drying. The collected conglomerates have a variable size depending on the conditions of the precipitation of magnesium hydroxide.

Conclusions

The hydrolytic method used to remove iron compounds from technical magnesium sulfate led to satisfying results. The method's efficiency depends on solution concentration and the kind of precipitating agent. The best results were achieved for calcium hydroxide, although problems arose connected with the filtration of the suspension. Independently from the purification methods, the magnesium sulfate heptahydrate was crystallized from the solution after concentration. On the basis of the semi-product, magnesium hydroxide was obtained when sodium hydroxide was used for precipitation. The surface area of the deposits was within the interval of 65–115 m²/g, but some samples were aggregated. This last factor adversely influences magnesium hydroxide's utilization as a flame retardant additive. Observations of SEM images of deposits show that the deposits are characterized by high susceptibility to aggregation. It can be concluded that high purity magnesium hydroxide winning by precipitation is a relatively difficult process.

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OTRZYMYWANIE WODOROTLENKU MAGNEZU O MIKRO- I NANOSTRUKTURZE NA BAZIE TECHNICZNYCH ZWIĄZKÓW MAGNEZU

Słowa kluczowe

wodorotlenek magnezu, micro-, nanostruktura, uniepalniacz

Streszczenie

W pracy przedstawiono wstępne wyniki otrzymywania wodorotlenku magnezu o wysokiej czystości i mikro- lub nanostrukturze na bazie surowców technicznych. Wodorotlenek magnezu może znaleźć potencjalne zastosowanie w przemyśle tworzyw sztucznych jako dodatek opóźniający zapłon. Musi cechować się wysoką powierzchnią właściwą (powyżej 100 m²/g), silnym rozdrobnieniem oraz wysoką czystością. W badaniach stosowano techniczny siarczan magnezu, który przed procesem otrzymywania wodorotlenku magnezu oczyszczano z zastosowaniem metod hydrolytycznych. Z oczyszczonych roztworów krystalizowano sól siedmiowodną, która była surowcem do otrzymywania wodorotlenku magnezu. Badania prowadzono dla różnych stężeń siarczanu magnezu 0,2–2,0 mol/dm³, jako czynnik strącający stosowano wodorotlenek sodu w przedziale stężeń 0,4–0,5 mol/dm³. Otrzymany osad analizowano przy użyciu technik SEM oraz BET, czystość określano technikami kolorymetrycznymi.

**OBTAINING MAGNESIUM HYDROXIDE OF MICRO OR NANOSTRUCTURE
ON THE BASIS OF TECHNICAL RAW MATERIALS**

Key words

magnesium hydroxide, micro, nanostructure, flame retardants

Abstract

This paper presents the initial results of efforts to obtain high-purity magnesium hydroxide with micro or nano-structure from technical raw materials. Magnesium hydroxide can be used in the plastic industry as a flame retardant additive. $\text{Mg}(\text{OH})_2$ should be characterized by high surface area (above $100 \text{ m}^2/\text{g}$), high disintegration, and high purity. In the research, technical magnesium sulfate was used which was purified by hydrolytic methods before obtaining the magnesium hydroxide. Heptahydrate, the specific raw material for magnesium hydroxide synthesis, was crystallized from purified solutions. The study was conducted for magnesium sulfate concentration in an interval of $0.2\text{--}2.0 \text{ mol}/\text{dm}^3$ and a sodium hydroxide interval of $0.4\text{--}0.5 \text{ mol}/\text{dm}^3$. The precipitate was analyzed by the SEM method and BET, and its purity was tested using the colorimetric technique.

