# Precipitation of $Mg(OH)_2$ by the Reaction of $Mg(NO_3)_2$ with Ammonia in a Flow Reactor

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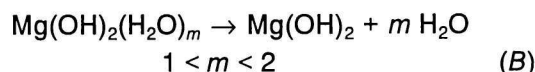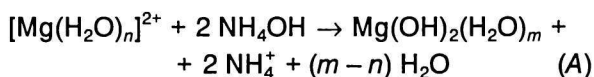Slovak Technical University, SK-812 37 Bratislava

The influence of ammonia content and of the retention time on the crystal size distribution of magnesium hydroxide prepared by the precipitation from $Mg(NO_3)_2$ solutions in a flow reactor was investigated. The temperature of the reacting mixture was 80 °C. It was found that the higher is the content of ammonia and/or its surplus with respect to the stoichiometric demand, the larger are the $Mg(OH)_2$ crystals. The longer is the retention time, the lower is the fraction of the particles smaller than 24 μm in the product. When the retention time of $Mg(OH)_2$ in the reactor is shorter than 3 min, irregular agglomerates of $Mg(OH)_2$ with sharp edges are formed while at the retention time longer than 5 min the aggregates have a round shape.

Magnesium hydroxide is used as a nontoxic flame retardant in plastic materials. In many applications the crystal size distribution (CSD) and morphology of $Mg(OH)_2$ crystals are of primary importance. $Mg(OH)_2$ is usually produced by precipitation of $MgCl_2$ that is obtained from sea water [1]. There are numerous papers in literature dealing with precipitation of $Mg(OH)_2$ [2—4]. Most of them are devoted to the precipitation of aqueous solutions of $Mg^{2+}$ ions with KOH and NaOH, respectively. $NH_4OH$ as a source of hydroxyl ions was investigated in less extent.

Phillips et al. [5] investigated the influence of pH in the range 8.7—12.5 on the size and thickness of $Mg(OH)_2$ crystals at the temperature of 60 °C. $Mg(OH)_2$ was prepared by the reaction of aqueous solution of $MgCl_2$ ($c$ = 0.75 mol dm$^{-3}$) with stoichiometric amount of $NH_4OH$ and NaOH (in the case of pH 12.5), respectively. The prepared crystals were aged for 1 h in mother liquor at 60 °C. The cited authors have found that ageing (i.e. recrystallization) proceeds with observable rate at pH > 9.5.

Precipitation of $Mg(OH)_2$ from aqueous solution of $MgCl_2$ with gaseous $NH_3$ in the presence of admixtures of citric or tartaric acid has been investigated by Shirasaky [6]. He prepared a substance of stoichiometric composition $Mg(OH)_2(H_2O)_m$. It was found that the molecules of water are placed between the layers of $Mg(OH)_2$. On the basis of these experiments the following reaction scheme for precipitation of $Mg(OH)_2$ [7] has been proposed

$$[Mg(H_2O)_n]^{2+} + 2\,NH_4OH \rightarrow Mg(OH)_2(H_2O)_m +$$
$$+ 2\,NH_4^+ + (m-n)\,H_2O \qquad (A)$$

$$Mg(OH)_2(H_2O)_m \rightarrow Mg(OH)_2 + m\,H_2O$$
$$1 < m < 2 \qquad (B)$$

Dobrescu et al. [8] investigated the influence of the retention time in a flow reactor on the nucleation and the kinetics of growth of $Mg(OH)_2$ crystals. The measurements were carried out in the system $Mg(NO_3)_2$—$NH_4NO_3$—$NH_3$(g) with the 20 % excess of ammonia in comparison to the theoretical amount at the temperature of 90 °C and the retention time ranging from 20 to 60 min. pH of the solution changed in the interval 9.25—9.55. It was found that large aggregates of diameter 20—80 μm were formed.

On the basis of the electrical conductivity measurements of supersaturated solutions (25 °C) Handlířová and Söhnel [9] have found that the reaction order of the crystal growth of $Mg(OH)_2$ is equal to one. The cited authors also found that the growth of crystals is controlled by surface reaction and the rate of this reaction depends on the surface area of the $Mg(OH)_2$ crystals. This conclusion is in agreement with Liu and Nancollas [4].

In this paper we will discuss the influence of ammonia concent and/or its surplus with respect to stoichiometric requirement and of the retention time of reacting mixture in a flow reactor on CSD of $Mg(OH)_2$ prepared by the reaction of magnesium nitrate with ammonia. Ammonium nitrate which results as a "waste" from this reaction can be used as fertilizer and thus this technology would produce only a small amount of wastes. The investigation was carried out at the temperature of 80 °C. This temperature was chosen on the basis of preliminary experiments. At lower temperatures the product was contaminated with $Mg(NO_3)_2$ and its purification could influence CSD of the product.

## EXPERIMENTAL

The experiments were performed in a jacketed glass flow reactor equipped with jacketed vessel. Volume of the reactor was 180 cm$^3$. Flow of the reacting solutions to the reactor was controlled by two independent peristaltic pumps. Content of the reactor was mixed by the stirrer ER-10 (VEB MLW Prüfgeräte, Medingen, Germany). Rotation of the stirrer was constant at 500 rpm. Temperature of the reacting mixture was kept constant at 80 °C using the ultrathermostat UH-16 (VEB MLW Prüfgeräte, Medingen). Arrangement of the apparatus is shown in Fig. 1.
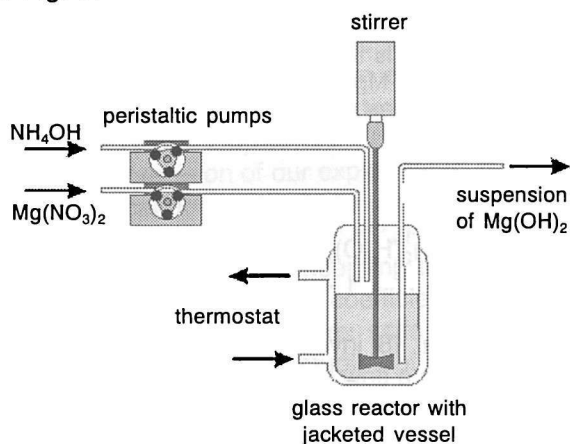


Fig. 1.  Scheme of the flow precipitation reactor.

30 mass % solution of Mg(NO$_3$)$_2$ was prepared from anal. grade magnesium nitrate (Lachema, Brno) dissolved in distilled water. Solutions of ammonia (*w* = 8.7 mass %, 18.1 mass %, and 25.0 mass %) were prepared of anal. grade ammonia (POCh Gliwice, Poland). Before the reaction, the solutions were heated up to 70 °C. Flow of the solutions into the reactor was controlled in order to assure the chosen retention time of the mixture in the reactor. The retention periods were 0.5 min, 1 min, 2 min, 5 min, and 10 min, respectively. The ratio of ammonium aqueous solution to magnesium nitrate solution is characterized by the surplus of ammonia with respect to stoichiometry of formation of Mg(OH)$_2$. The experiments with 0 %, 25 %, 50 %, and 100 % surplus of ammonium solution were carried out. The reaction mixture was continuously sampled in such a way that the volume of the reaction mixture was kept constant at 100 cm$^3$. The reaction conditions were stabilized when about 900 cm$^3$ of the suspension was taken off. After this initial period 400 cm$^3$ of suspension was sampled and analyzed. 1 h after sampling, the suspension was filtered using a sintered glass S3. The filtration cake was washed three times with 400 cm$^3$ of water and filtered again. The final product was dried at 110 °C.

Crystal size distribution (CSD) was measured using the laser apparatus SHEISHIN PRO 7000 (measuring range 1—192 μm). Shape of the Mg(OH)$_2$ crystals was determined using the scanning electron microscope. CSD measurements were carried out in ethyl alcohol suspension. Prior to the CSD measurement the aggregates were disintegrated using an ultrasonic generator.

## RESULTS AND DISCUSSION

### The Influence of the Excess and Content of Ammonia

In Fig. 2, CSD of Mg(OH)$_2$ prepared by precipitation of 30 mass % Mg(NO$_3$)$_2$ solution with 8.7 mass % aqueous solution of ammonia is plotted as a function of the excess of ammonia. It can be seen that the distribution curves of the product prepared with surplus of 25 %, 50 %, and 75 % are almost
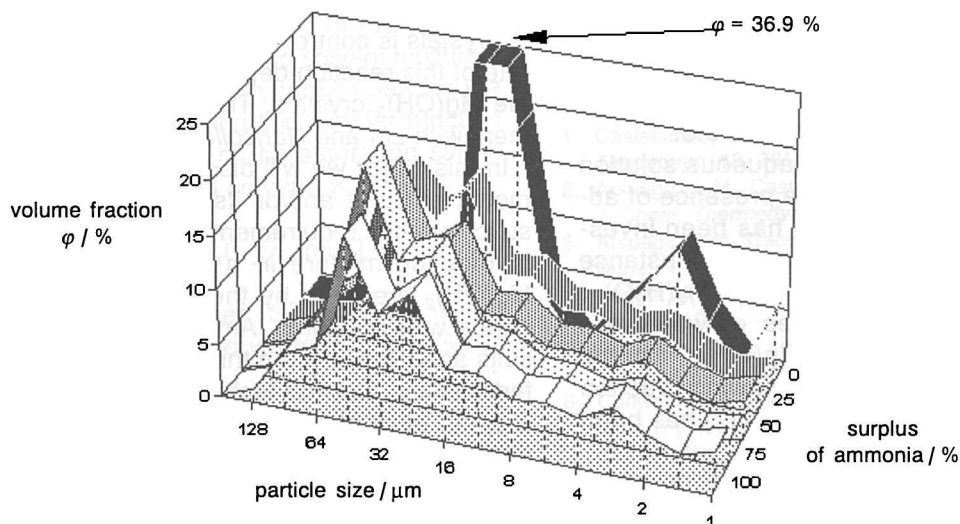


Fig. 2.  Samples prepared with different surplus of ammonia at the temperature of 80 °C and retention time of 1.0 min. Content of ammonia 8.7 mass %.
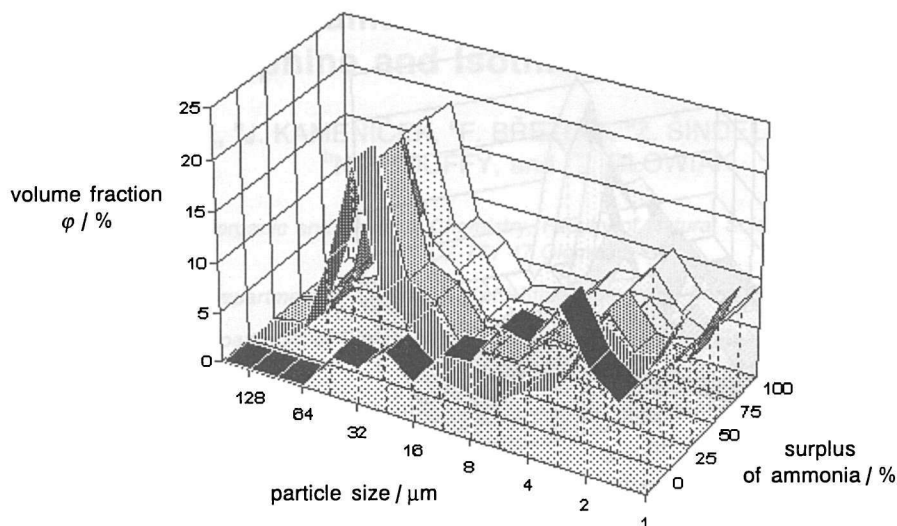
**Fig. 3.** The same as in Fig. 2. Content of ammonia 18.1 mass %.

the same. It can be also seen that in comparison with Mg(OH)₂ prepared at zero excess of ammonia the aggregates larger than 20 μm are formed at a greater extent.

In Fig. 3, the results of CSD obtained with 18.1 mass % content of ammonia are shown. It can be seen that the amount of fines smaller than 8 μm decreased in comparison with the former case. Crystals with diameter in the interval 32—64 μm prevail.

In Fig. 4, the CSD of Mg(OH)₂ obtained with 25 mass % ammonia solution is plotted. It follows that the mean particle size diameter increased again, the largest part of the crystals being in the range 48—96 μm.

In all three cases the results of CSD obtained with zero surplus of ammonia are different from the results obtained with the excess of ammonia. This may be caused by a nonstability of pH of the reaction mixture and no definite conclusions can be drawn from this series of measurements.

It follows from the obtained results that the excess of ammonia and its content influence the CSD of Mg(OH)₂ prepared by precipitation from nitrate solutions. This effect is most pronounced at the content of 25 mass % of ammonia.

**The Influence of the Retention Time**

The influence of the retention time on CSD of Mg(OH)₂ can be seen from the data plotted in Fig. 5 and from the electron micrographs (Figs. 6 and 7). On the basis of these results it can be concluded that the longer is the retention time of reacting suspension in the reactor, the larger are the obtained particles. This is an expected result which is in agreement with literature [8]. It can be also seen that at longer retention times the aggregates with rounder shape were obtained.

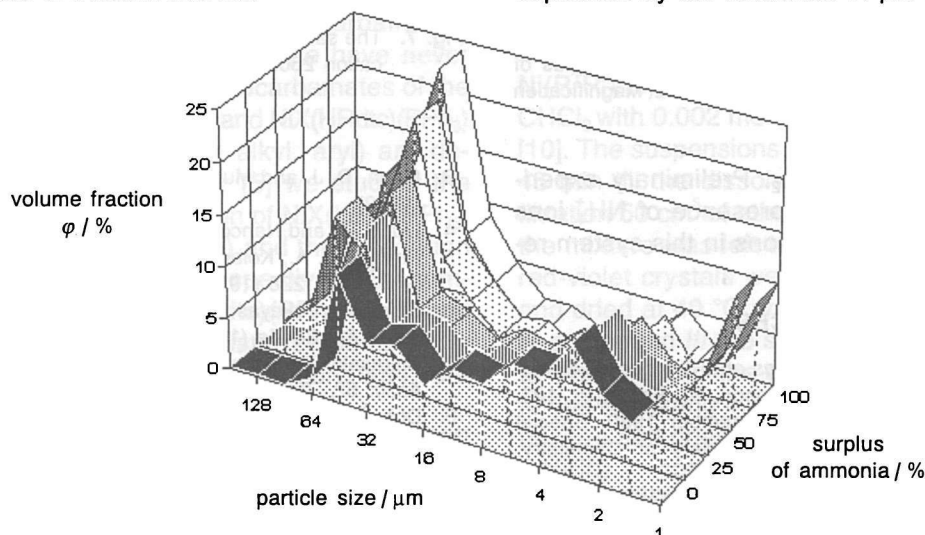The influence of ammonia content can be partly explained by the influence of pH and NH₄NO₃ con-



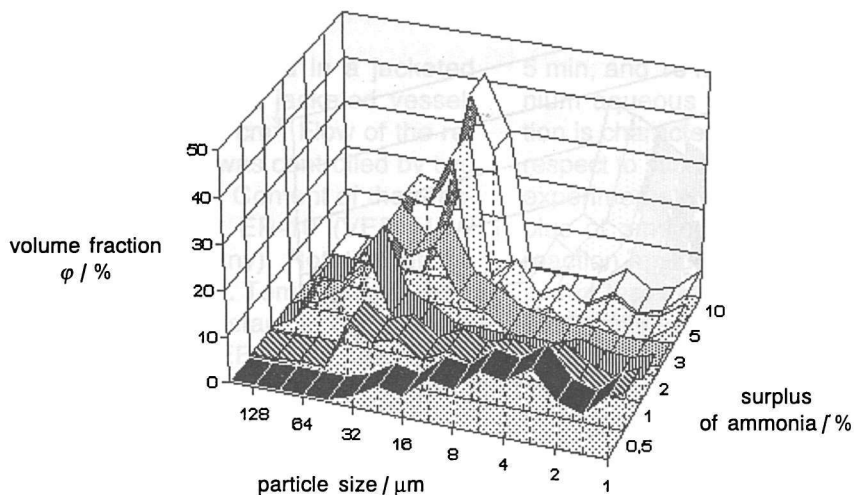**Fig. 4.** The same as in Fig. 2. Content of ammonia 25.0 mass %.

**Fig. 5.** Comparison of CSD curves of $Mg(OH)_2$. $\theta = 80\ °C$, content of ammonia 18.7 mass %, surplus of ammonia 50 %.



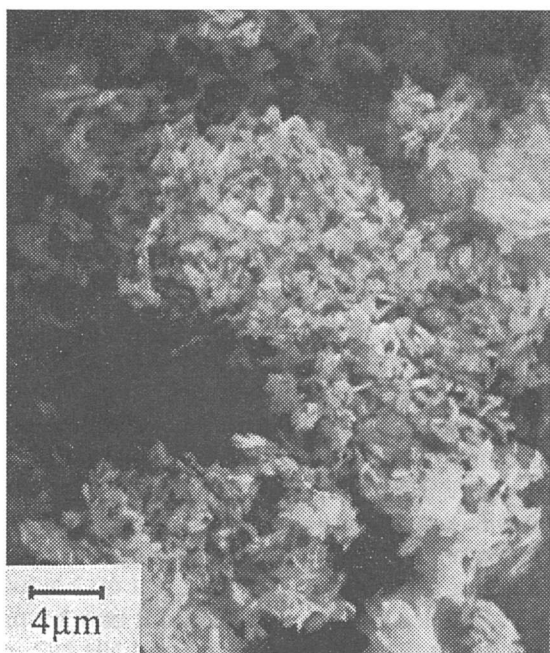**Fig. 6.** Electron micrograph of $Mg(OH)_2$ agglomerates. $\theta = 80\ °C$, content of ammonia 18.7 mass %, surplus of ammonia 50 %, retention time 1.0 min. Magnification 2500×.
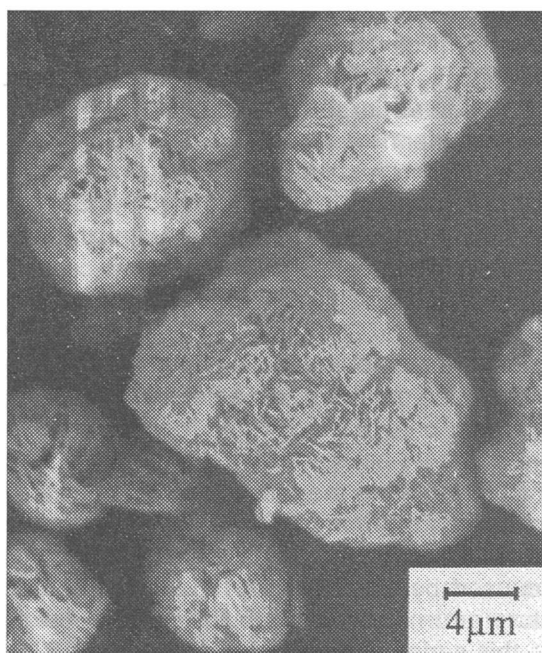


**Fig. 7.** The same as in Fig. 6. Retention time 5.0 min. Magnification 2500×.

tent on solubility of $Mg(OH)_2$. Preliminary experiments have shown that the presence of $NH_4^+$ ions increases solubility of Mg(II) ions in this system remarkably.

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