Influence of admixtures and of mixing on precipitation of Mg(OH)$_2$ from nitrate solution

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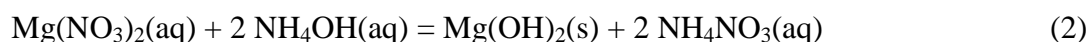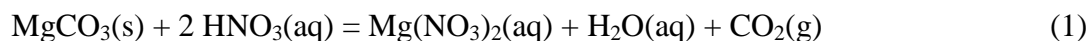**pavel.fellner@stuba.sk*

Abstract

Precipitation of Mg(OH)$_2$ from magnesium nitrate solution was studied by means of recording pH of the reacting mixture. Solution of NH$_4$OH was used as the alkalizing agent. The sequence of addition of reactants, rate and time of stirring, and the excess of NH$_4$OH with respect to stoichiometry influence change in pH, and consequently the rate of crystallization and sedimentation of the reaction product, viz. Mg(OH)$_2$. The presence of calcium nitrate up to 10 mass % does not influence remarkably the precipitation process.

Keywords: magnesium hydroxide, ammonium nitrate, calcium nitrate, rate of precipitation,

Introduction

Magnesium hydroxide is used as filling material in polymer composites. When the content of Mg(OH)$_2$ exceeds approximately 40 wt. %, the composite is inflammable. There are several literature sources dealing with the preparation and application of magnesium hydroxide (Kirk-Othmer 1981, Hsu and Nacu 2005). Most of them investigate precipitation of Mg(OH)$_2$ from chloride solutions by the addition of alkaline solution. Concentration of magnesium cations, composition of alkaline component, pH, rate of its addition, and rate of stirring influence nucleation and crystal growth of Mg(OH)$_2$. Alkalization of solution can be achieved also by electrolysis (Utamapanya et al. 1991). Literature describes preparation of Mg(OH)$_2$ fibers (Wu, Shao, Gu and Wei 2004) or preparation of nanoparticles of Mg(OH)$_2$ (Li, Sui, Ding, Zhang, Zhuang and Wang 2000). Crystals of different shape and size can be prepared (Li, Sui, Ding, Zhang, Zhuang and Wang 2000, US patent 1992, Škubla et al. 1993, Láska et al. 1993).

In this paper we will discuss some aspects of precipitation of $Mg(OH)_2$ from $Mg(NO_3)_2$ solution. This is the process which is used in Slovakia in industrial scale. Principle of the method consists in the reaction of magnesite ($MgCO_3$) with nitric acid. After purification, magnesium hydroxide is precipitated from solution of $Mg(NO_3)_2$ with ammonium hydroxide:

$$MgCO_3(s) + 2\ HNO_3(aq) = Mg(NO_3)_2(aq) + H_2O(aq) + CO_2(g) \qquad (1)$$

$$Mg(NO_3)_2(aq) + 2\ NH_4OH(aq) = Mg(OH)_2(s) + 2\ NH_4NO_3(aq) \qquad (2)$$

Ammonium nitrate is used as fertilizer. The process is described in detail in the patent literature (Škubla 1993). Improvement of the existing technology and a possibility of utilization of dolomite as a raw material for preparation of $Mg(OH)_2$ (and $CaCO_3$ or $Ca(NO_3)_2$ as by-products) is the topic of the project, first part of which is presented in this paper. Magnesium hydroxide resulting from precipitation from magnesium nitrate is not the final product of desired quality. It needs further treatment at elevated temperature in a pressure reactor and surface treatment of the product. This paper deals only with the kinetics of precipitation.

Experimental

Chemicals:

1 M solution of $Mg(NO_3)_2$ was prepared from $Mg(NO_3)_2$ of p.a. purity. pH of this solution was 5.99. 2 M solution of NH_4OH was prepared from chemical of p.a. purity. pH of the latter solution was 11.63. Also the admixtures $Ca(NO_3)_2$ and NH_4NO_3 were of purity pro analysis. Precipitation of $Mg(OH)_2$ from 100 ml solution of $Mg(NO_3)_2$ was carried out in a glass beaker under intensive stirring with submersed mixture (Braun, 300 W). 2M NH_4NO_3 was added in one shot and the intensive stirring was carried out for 30 s, 120 s or 300 s. Stirring continued with a magnetic stirrer (800 rpm). Simultaneously pH of the reaction mixture was measured and recorded by pH-meter (Metrohm, model 827 pH lab, combined electrode). Solution of NH_4OH was added in the following surplus (in %): 0, 15, 50, 100, 200, 300. These experiments were carried out at ambient temperature and pressure.

Results and Discussion

Influence of surplus of NH₄OH on pH of reacting mixture during precipitation of Mg(OH)₂

Rate of reaction (2) can be estimated from the change of pH of the reacting mixture. Zero time determines the moment of addition of NH₄OH. In Fig. 1, the change of pH is plotted as function of time for the stoichiometric amount of NH₄OH (0 % surplus), and for the addition of NH₄OH in 15 % and 50 % surplus, respectively. In the beginning of experiment, pH increases with surplus of NH₄OH. However, the decrease of pH with time reflects kinetics of precipitation of $Mg(OH)_2$. As mentioned earlier, pH of 1 M $Mg(NO_3)_2$ solution is 5.99, while pH of 2 M solution of NH₄OH is 11.63. pH of water suspension of $Mg(OH)_2$ is 10.30 and pH of 0.5 M solution of NH_4NO_3 is 6.64. It is obvious that shape of the curves for 0 % surplus of NH₄OH is rather different from those with surplus of the alkaline component.
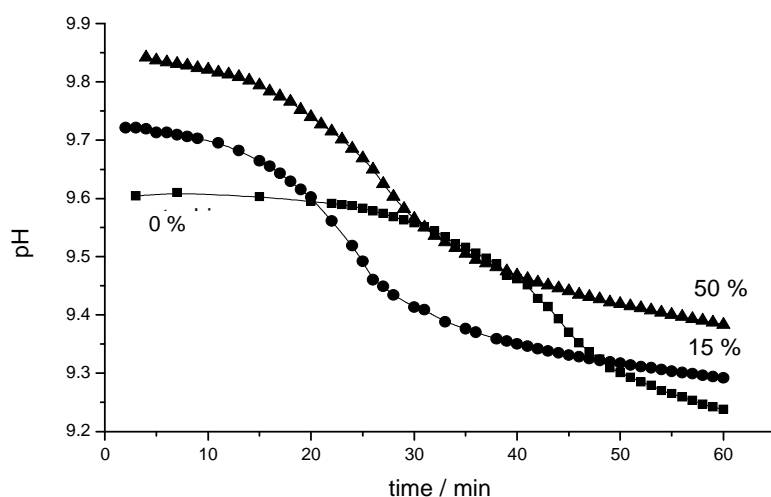

Fig. 1. Dependence of pH of reacting mixture $Mg(NO_3)_2 \leftarrow NH_4OH$ as function of time at different surplus of NH₄OH. (Intense stirring was carried out for 30 s.)

Influence of duration of intense stirring on pH of reacting mixture during precipitation of Mg(OH)₂

In these series of experiments, the influence of duration of intense stirring, viz. 0 s, 30s, and 300 s, respectively, on pH of reacting mixture was investigated. As in the previous case, surplus of NH₄OH was 0, 15 and 50 %. The results are plotted in Figs. 2 and 3. It can be seen that the intensive mixing causes sharp decrease of pH in the beginning of experiment. This corresponds to the increasing rate of formation of $Mg(OH)_2$. This effect is especially

remarkable in Fig. 3 where the change of pH with time is plotted for mixtures without stirring and after 300 s of intensive stirring. In this case the surplus of NH_4OH with respect to stoichiometry was 50 %.
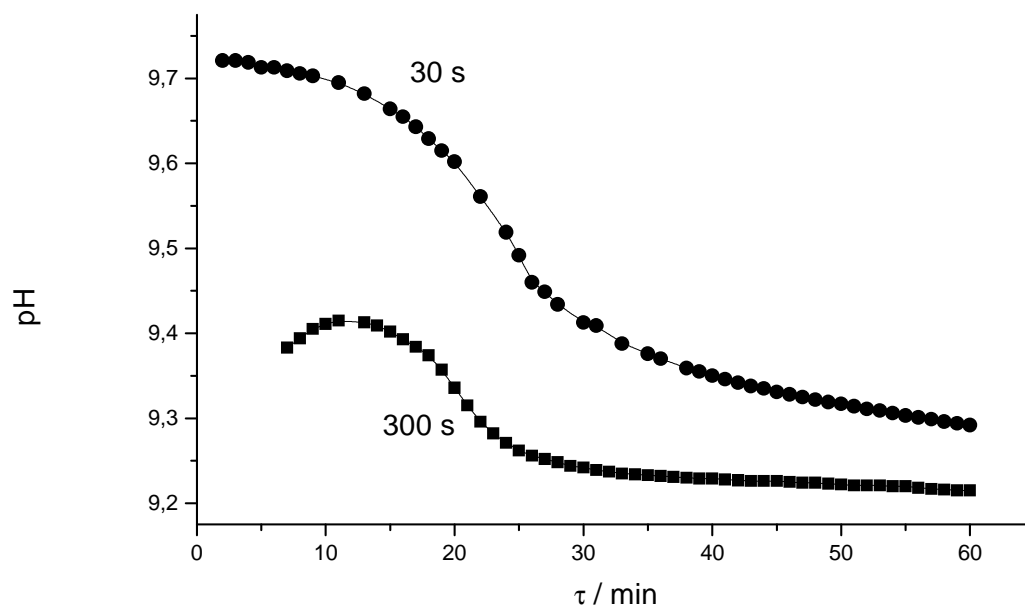

Fig. 2. Dependence of pH of reacting mixture $Mg(NO_3)_2 \leftarrow NH_4OH$ as function of time of intensive mixing (30 s and 300 s, respectively.) (Stoichiometric ratio $Mg(NO_3)_2$ and NH_4OH.)
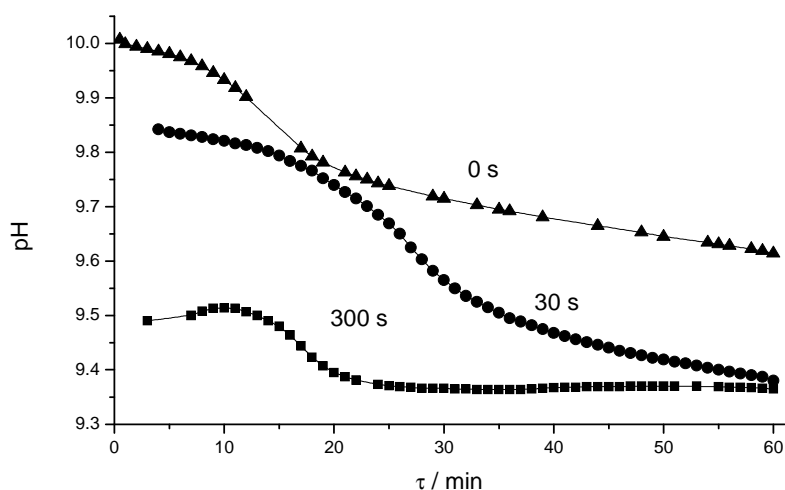

Fig. 3. Dependence of pH of reacting mixture $Mg(NO_3)_2 \leftarrow NH_4OH$ as function of time of intensive mixing (0 s, 30 s, and 300 s, respectively.) (50 % surplus of NH_4OH with respect to stoichiometry.)

Streaming Mg(NO₃)₂ solution into NH₄OH

In this paragraph we will show what happens when we add solution of magnesium nitrate into the solution of ammonium hydroxide. This is an opposite procedure to that discussed in preceding paragraphs. In this case the excess of ammonium hydroxide is actually infinite in the beginning and it decreases to a chosen value. In this experiment, duration of intensive mixing was 120 s. Final excess of ammonium hydroxide with respect to stoichiometry was 0 %, 50 %, and 100 %, respectively. The change of pH with time after intense stirring is plotted in Fig. 4. As in the previous cases, the solution was mixed with the magnetic stirrer. It is interesting to observe that after the intense stirring, pH of the reacting mixture drops down (not shown in the Fig. 4). This decrease in pH is a result of the addition of Mg(NO₃)₂ solution (pH = 6.91) in one shot. When Mg(NO₃)₂ is consumed due to its reaction with NH₄OH, pH increases and it reaches maximum after 10 min to 15 min. Formation of Mg(OH)₂ causes slow decrease of pH because its pH is lower than that of ammonia.
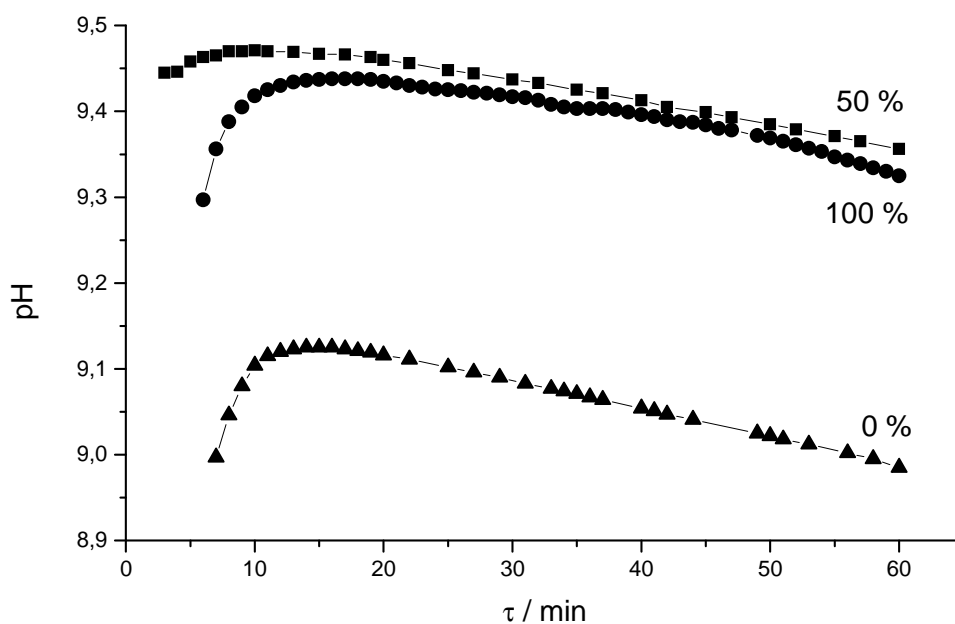

Fig. 4.   Dependence of pH of reacting mixture NH₄OH ← Mg(NO₃)₂ as a function of time. The solution of Mg(NO₃)₂ was added to NH₄OH under 120 s of intense stirring. Final surplus of ammonium hydroxide was 0 %, 50 %, and 100 %.

Influence of the admixture of calcium nitrate on precipitation of Mg(OH)₂

As a row material for preparation of Mg(OH)₂ we can utilize also dolomite instead of magnesite. In this case the reacting mixture contains also calcium nitrate. Investigation of this reaction is a rather broad topic that will be discussed in elsewhere. In this paragraph we will show how the presence of calcium nitrate may influence precipitation of magnesium hydroxide. The reacting mixture contained up to 5.5 wt. % of calcium nitrate. No remarkable influence of calcium nitrate on the precipitation of Mg(OH)₂ or its sedimentation was observed. Neither shape or size of crystals of Mg(OH)₂ was observed. It can be concluded that when dolomite is used instead of magnesite, magnesium hydroxide of the same quality can be obtained.

Investigation of the influence of ammonium nitrate on the precipitation of Mg(OH)₂

Solubility product of magnesium hydroxide in water at 25 °C is 8.9×10^{-12}. This means that solubility of Mg(OH)₂ in pure water is rather low. Ammonium nitrate originates as a by-product at the precipitation of Mg(OH)₂ from solution of Mg(NO₃)₂ with ammonia or ammonium hydroxide (Eq. 2). We found out that the presence of ammonium salts remarkably (ca 100 times) increases the solubility of Mg(OH)₂ in aqueous solution. This is in agreement with literature (Kirk-Othmer 1981). There might be two reasons for this phenomenon. Firstly, dissociation of NH₄OH at ambient temperature is rather low. Ionization constant of NH₄OH is 1.8×10^{-5}. When we add NH₄NO₃ into the solution we lower the concentration of OH⁻ ions. This results in the increase in solubility of Mg(OH)₂. The second reason might be formation of complexes of Mg^{2+} with ammonia, as suggested by Fredholm (cited according to Remy 1961).

Anyway, the increase of solubility of Mg(OH)₂ in the presence of ammonium cations is a fact that fundamentally influence nucleation, crystallization and growth of crystals of Mg(OH)₂.

Conclusion

Precipitation of Mg(OH)₂ is influenced by the following factors:

Surplus of NH₄OH lowers the rate of precipitation of Mg(OH)₂. However, it speeds up sedimentation. Similar, but less noticeable is the influence of NH₄NO₃.

Presence of Ca(NO₃)₂ up to 10 mass % influences precipitation only in a negligible way.

It is important whether we add magnesium nitrate to ammonium hydroxide or ammonium hydroxide to magnesium nitrate. The process and properties of the product, viz. $Mg(OH)_2$, are rather different.

Nucleation and crystal growth of $Mg(OH)_2$ is remarkably influenced by the presence of ammonium salts that increase solubility of $Mg(OH)_2$.

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