Hydrolysis of MgH_2 in $MgCl_2$ solutions as an effective way for hydrogen generation

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Magnesium hydride (MgH_2) has a high hydrogen storage capacity (7.6 wt%) and the Mg element is abundant on the earth. Due to its strong reduction ability, even at room temperature it can provide the hydrogen yield reaching 15.2 wt% H (1703 mL/g) when interacting with water, which makes it very attractive for the application in supplying hydrogen for autonomous H energy systems. However, the hydrolysis reaction is rapidly inhibited by the $Mg(OH)_2$ passivation layer formed on the surface of MgH_2. In order to remove the passivation film and improve the efficiency of the MgH_2 hydrolysis process, several methods including alloying, ball milling, changing the aqueous solution, have been successfully utilized.

In this paper the process of hydrolysis of magnesium hydride in aqueous solutions of $MgCl_2$ used as a promotor of the interaction has been studied in detail. It was found that the initial hydrolysis rate, pH of the reaction mixture, and overall reaction yield are all linearly dependent of the logarithm of $MgCl_2$ concentration. It has been shown that pH of the reaction mixture in the presence of $MgCl_2$ is well described by considering a system "weak base and its salt with strong acid" type buffer solution. Reference data for this hydrolysis reaction were also carefully analyzed.

The mechanism and the kinetic model of the process of MgH_2 hydrolysis in water solutions involved passivation of the MgH_2 surface by the formed $Mg(OH)_2$ precipitate followed by its repassivation have been proposed. The obtained after the hydrolysis reactions precipitates were studied using XRD and EDS. It was found also that the final products of reaction consist of $Mg(OH)_2$ (brucsite type) and remaining MgH_2. This fact shows that the formation of solid species such as $MgCl_2 \cdot xMgO \cdot yH_2O$ at the studied conditions is unlikely and decreasing of pH the reaction mixture has a different nature.

Keywords: *Hydrolysis; Magnesium hydride; Magnesium chloride; Kinetics; Acid-base equilibrium*

Introduction

Magnesium hydride (MgH_2) has been widely investigated as a promising candidate for hydrogen generation by a hydrolysis process due to the low cost and high abundance of magnesium. MgH_2 has a high theoretical hydrogen storage capacity (7.6 wt. %) and due to its strong reducibility, even at room temperature the hydrogen yield can reach 15.2 wt. % H (1703 mL/g) when it reacts with water. The most critical issue is that hydrolysis reaction of MgH_2 can be rapidly interrupted by the formation of a $Mg(OH)_2$ passivation layer surrounding the MgH_2 particles. To address this challenge, several methods have been proposed, e.g. ball-milling, addition of catalysts, surface modification, element substitution, changing the aqueous solution, and a combined approach.

The ball-milling method can effectively increase the reaction rate and yield of hydrogen gas. This phenomenon could be ascribed to the fact that the ball milling process refines the particle and grain sizes and increases the specific surface area. In addition, the introduction of structural defects and formation of nanocrystalline structures are also beneficial for the MgH_2 hydrolysis [1]. According to [2], the highest reactivity is observed for 30 min milled MgH_2, which shows a conversion yield of 26 % as compared to 9 % for the unmilled MgH_2 powder. The specific surface area of 30 min milled powder displays a maximum of 12.2 m^2/g. Further milling reduces the specific surface area due to the particle's agglomeration. The specific surface area of 7.8 m^2/g and conversion yield of 16 % were observed for the 10 h milled MgH_2 powder. From extrapolation of the fitting curve of conversion yield of MgH_2 powders vs their specific surface area, a yield of 100 % might be reached for MgH_2 powder having a surface area of 23 m^2/g [3].

At room temperature the acids provide a remarkable increase of the MgH_2 conversion during the hydrolysis reaction. Significant amounts of hydrogen can be obtained using inorganic acids [4], organic acids, for example, acetic acid with a platinum catalyst [5], or when heating the reaction mixtures [6] in laboratory experiments. However, a commercial application of acids appears to meet the drawbacks being both expensive and not practically viable due to a significant corrosion of the reactor interior in acidic solutions. Thus, a considerable attention is recently focused on the studies of the effect of citric acid on the reaction with magnesium hydride [7, 8].It should be noted that in a dilute citric acid solution beside the hydrolysis reaction, a direct interaction between MgH_2 and $C_6H_8O_7$ or the formation of a salt due to a reaction of the acid with magnesium hydroxide occur.

The studies of the salt additives effects on the hydrolysis kinetics of magnesium hydride were performed as related to the content of the additives. In particular, the following solutions of salts [2, 3, 9] or acidic salts and MgH_2 [9, 10] and MgH_2/salt composites [11–13] were hydrolysed using distilled/tap/sea water. The mechanism of MgH_2 hydrolysis directly depends on the pH of the formed solution. Hydrolysis of MgH_2 with acidic salt solutions gives a maximum conversion and shows a high hydrogen release rate. Increase of the salt content (but to a certain limiting value) in solution or composite leads to the increase of hydrogen yield.

The influence of the composition of the selected ammonium salts and their concentration in aqueous solutions on the hydrolysis of magnesium hydride were studied in [9, 14]. The presence of even a small amount of NH_4Cl (0.5% solution) considerably promotes the hydrolysis: the amount of hydrogen released in 5 min exceeds the amount of hydrogen released within 24 h during the hydrolysis process in a pure water (60 and 57%, respectively). As the concentration of ammonium chloride increases from 0.5 to 7.5%, the hydrolysis rate increases and the conversion in the latter case becomes significantly higher (92 % in 5 min).

The influence of the nature of the cations contained in the chloride salts and the amount of the salts were studied in [13]. The composites MgH_2/NaCl, MgH_2/$MgCl_2$, and MgH_2/NH_4Cl were prepared with 3; 5 and 10 % salt and MgH_2 synthesized by a combustion synthesis. Hydrogen yield increased with increasing the salt content in the sequence NaCl – $MgCl_2$ – NH_4Cl. The NH_4Cl has the strongest effect on the kinetics of the hydrolysis process as compared to two other chlorides. At room temperature, MgH_2−10% NH_4Cl composite exhibited the best performance with the hydrogen generation yield of 1311 mL/g and a conversion rate of 85.69 % in 60 min.

The hydrolysis reaction of MgH_2 in aqueous solution of magnesium chloride was studied in [14, 15]. It can be noticed that in the presence of $MgCl_2$ the hydrogen yield is higher than that for pure water. According to [14, 15], the hydrogen yield was 1635 ml/g and 1137 ml/g in 0.5 M $MgCl_2$

and in 0.05 M $MgCl_2$ after 50 and 90 min, respectively. However, the effect of chlorine ions on the process of crystallization of magnesium hydroxide at the surface of MgH_2 is not completely understood even though it clearly affects the extent of the hydrolysis.

The effect of the nature of the cations on the hydrolysis of MgH_2/salt composites was studied in more detail in [12], where several chlorides including NaCl, $ZnCl_2$, $AlCl_3$, $ScCl_3$, $FeCl_3$, $TiCl_3$, $MgCl_2$, and $ZrCl_4$ were used. The effect of the anions was studied by replacing the chlorides with bromides using the salts of sodium, magnesium, and zirconium. Hydrogen yield (86% and 99% after 1 h by using $MgBr_2$ and $ZrBr_4$ as additives) was not significantly different between the two salts, but the bromides showed a faster reaction kinetics. Furthermore, it should be noted that zirconium bromide acts as the best activator of the hydrolysis reaction among all tested salts.

An increase in the rates of hydrolysis reaction is observed when using the mixtures or composites of MgH_2 with different additives. When using the milled mixture MgH_2-20.3 mol % CaH_2, the reaction yield reaches 80 % after 30 min of hydrolysis [16]. The 1 h ball-milled $Mg_{17}Al_{12}$ + 10 wt. % CaH_2 mixture produced 1389 mL H2/g at 70 ºC after 1 h of hydrolysis in pure water (hydrogen yield was 94.8%) [17]. The MgH_2/LaH_3 composites with the atomic ratio of 3:1 and 8.5:1 can generate 706.7 mL/g of H_2 in 40 min and 473.0 mL/g of H_2 in 60 min, respectively [14]. The highest observed hydrolysis yield equals to 1195 mL/g of H_2 in 80 min and belongs to the composite with the optimal mole ratio of 5:1. The $MgH_2/LaH_3/Ni$ composite obtained by hydrogenation of La_2Mg_{17}/Ni during the milling at a pressure of 7 MPa H_2 showed the best results [18]. It released 1208 L/g of hydrogen during 40 min at room temperature and showed reduced activation energy of the hydrolysis process of 52.9 kJ/mol. The air-stable $MgH_2/LiNH_2$ composites were another system investigated in the hydrolysis reaction in [19]. The composition $4MgH_2$-LiNH2 milled for 5 h generates 887.2 mL/g of hydrogen in just one minute and 1016 mL/g of hydrogen in the next 50 min. The $LiOH{\cdot}H_2O$ and NH4OH phases which are formed as hydrolysis products during the interaction of LiNH2 with water may prevent formation of the passivation layer of $Mg(OH)_2$ at the surface and supply enough channels for MgH_2 hydrolysis.

An increase of the hydrolysis temperature, as expected, leads to an increase in both reaction rates and hydrogen yields [8, 18–22]. Evaluation of the apparent activation energy of the hydrolysis reactions calculated using the Arrhenius equation and based on the analysis of the kinetic curves of hydrogen generation at different temperatures showed that different additives were able to significantly decrease the activation energy.

Importantly, magnesium chloride may be considered as a perspective material to improve the efficiency of the hydrolysis of magnesium hydride as it is an ecofriendly material, has an affordable price and a low molecular mass (this defines overall hydrogen generation efficiency of the mixtures MgH_2+$MgCl_2$). Unfortunately, the mechanisms of chemical interactions in the systems MgH_2–MCl_n–H_2O in general and in the system MgH_2–$MgCl_2$–H_2O in particular, are studied insufficiently. One can however assume that facilitation of the hydrolysis of magnesium hydride in the presence of metal chlorides is caused by their hydrolysis resulting in the formation of hydrochloric acid. Nevertheless, many aspects relevant for describing the catalytic or promoting behaviors of the metal chlorides remain unclear, including the fact that typically used amounts of metal chlorides are significantly smaller as compared to the amount of magnesium hydride involved into the process. Thus, the amount of hydrochloric acid formed via the hydrolysis of chloride is insufficient to allow a complete conversion of MgH_2.

Thus, in presented work we studied the dependence of the kinetics of H_2 evolution via the hydrolysis of constant masses of MgH_2 on the concentration of constant volumes of solutions of $MgCl_2$ with the aim to eliminate the impact of the process of dissolution of dry magnesium chloride on the chemical equilibria.

Experimental Details

MgH_2 was prepared by a reactive ball milling of magnesium (Fluka, grit, 50-150 mesh, 99.8%) in hydrogen gas using a planetary ball mill Fritsch Pulverisette-6. Milling was carried out in a custom-made SS vial with a volume of 550 mL. The vial was equipped with two Swagelok needle valves for hydrogen inlet and outlet. As grinding bodies, the stainless steel balls (50 with a diameter of 16 mm; m_{balls}=817 g) were used. The weight ratio of the grinding bodies to the weight of the sample was

40:1. The grinding was performed at a rotational speed of 400 rpm and an initial hydrogen pressure of 2.5 MPa.

Kinetics of MgH_2 hydrolysis was investigated at 20° C in pseudo-isothermal conditions in a setup consisting of a two-neck glass vessel immersed into a water bath equipped with a magnetic stirrer and injectors of the solutions of $MgCl_2$ and citric acid. Typically, 0.2 g of MgH_2 was introduced into the reactor. After that, 20 mL of an aqueous solution prepared using deionized water (pH=7.00) was quickly added. The generated hydrogen was released through Allihn-type fluid-cooled condenser connected to a bottle filled with water at room temperature. Then, H_2 was collected by replacing the water in a beaker. To evaluate an extent of the MgH_2 conversion, the solution of citric acid (2 mol/L; 20 mL) was introduced after the hydrolysis reaction slowed down in order to measure the amount of the unreacted MgH_2.

The pH of the reaction mixtures was monitored after 100 min from the start of the hydrolysis experiment using a carefully calibrated prior to the measurements pH electrode. The pH electrode was calibrated using the standard buffer solutions having pH = 7.00, pH = 9.21, and pH = 11.00.

The XRD patterns were measured at a diffractometer DRON-3.0 using Cu-Kα radiation. Elemental analysis of the precipitates was performed using an EVO-40 XVP (Carl Zeiss) scanning electron microscope equipped with Inca Energy 350 (Oxford Instruments) microprobe analysis system.

Results and Discussion

The influence of $MgCl_2$ on the kinetics of MgH_2 hydrolysis has been studied in a broad range of concentrations of $MgCl_2$ (Table 1). It was found that in all the cases $MgCl_2$ solutions have increased the rate of hydrolysis (Fig. 1) as well as the conversion of reaction (Table 1). It was observed that the kinetics curves are characterized by exponential shape and contain two parts: initial fast release of hydrogen lasting for approximately 10 minutes and a slow H_2-generation part lasting for up to 150 minutes (Fig. 1). One of the assumptions explaining a high promotive activity of $MgCl_2$ is the formation of complex solid precipitates similar to Sorel cement which are less soluble than $Mg(OH)_2$ leading to a decreasing of pH [12]. Therefore, the obtained after the hydrolysis reactions precipitates were studied using

XRD and EDS. However, it was found that the final products of reaction consist of $Mg(OH)_2$ (brucsite type) and remaining unreacted MgH_2. This fact shows that the formation of solid species such as $MgCl_2 \cdot xMgO \cdot yH_2O$ [12] at the studied conditions is unlikely and decreasing of pH of the reaction mixture has a different nature.

Table 1. The dependence of conversion of MgH_2 hydrolysis and pH of reaction mixture on $MgCl_2$ concentration.

$C(MgCl_2)$, mol/L	Conversion after 150 min, %	pH(exp)	pH(calc)	Equation used for pH calculation
0	18	10.89	11.07	(1.4)
0.0046	43	–	10.48	(2.7)
0.0092	57	10.22	10.18	(2.7)
0.0138	67	–	10.00	(2.7)
0.0184	70	10.10	9.88	(2.7)
0.0368	79	9.89	9.58	(2.7)
0.0738	89	9.63	9.28	(2.7)

Hence with the aim of evaluation of the mechanism of MgH_2 hydrolysis in the presence of $MgCl_2$ the values of pH of reaction mixtures at high degrees of conversion of reaction when the acidity of solutions is stationary were measured. It was found that pH of reaction mixtures decreases with increasing $MgCl_2$ concentration (Table 1).

For evaluation of the mechanism of hydrolysis, the reaction system MgH_2–H_2O–$MgCl_2$ must be considered in details. The sets of all possible chemical transformations can be written as follows.

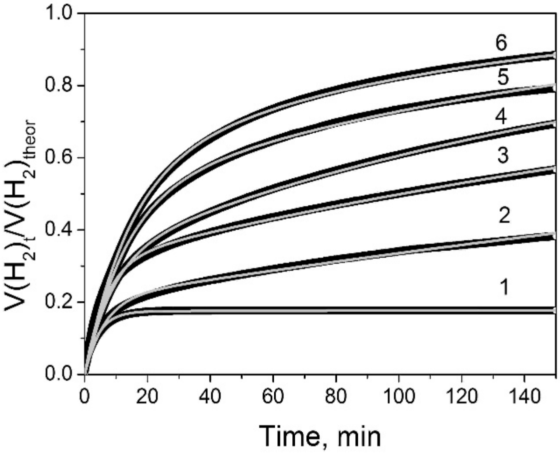

Fig. 1. Kinetic curves of H_2 evolution during MgH_2 hydrolysis at different initial concentrations of $MgCl_2$: 1 – 0; 2 – 0.0046; 3 – 0.0092; 4 – 0.0184; 5 – 0.0368; 6 – 0.0738 mol/L. Points are the experimental data and lines are the fitted by eqs. (3.4) – (3.6) curves.

Hydrolysis of MgH_2 in pure water:

$$MgH_2 + 2H_2O = Mg(OH)_2 + 2H_2\uparrow \quad (1.1)$$

$$Mg(OH)_2 \Leftrightarrow Mg(OH)_2\downarrow \quad (1.2)$$

$$Mg(OH)_2 \Leftrightarrow Mg(OH)^+ + OH^- \quad (1.3)$$

$Mg(OH)_2$ is a weak alkali with a low solubility in water. The basicity constant (pK_1) and the value of the solubility product (pSP) of a freshly precipitated $Mg(OH)_2$ are equal to 2.58 and 9.22, respectively. Please note that $Mg(OH)_2$ dissociates only partially (eq. 1.3). With the progressing conversion reaction, when the $Mg(OH)_2$ precipitate is formed, the calculated concentrations of Mg^{2+} and OH^- become equal to $5.3\cdot10^{-4}$ and $10.6\cdot10^{-4}$ mol/L, respectively. Then, pH of the solution can be calculated as follows:

$$pH = 14 - ½\, pK_1 + ½\, \log(C_B) \quad (1.4)$$

Here C_B is the $Mg(OH)_2$ concentration and can be considered as equal to the concentration of the dissolved hydroxide, i.e. to $5.3\cdot10^{-4}$ mol/L. The calculated pH of the solution of 11.07 is in a good agreement with the experimentally measured one (see Table 1) validating the evaluation.

Hydrolysis of MgH_2 in a $MgCl_2$ solution

In $MgCl_2$ solutions, we can expect the following reactions to occur:

$$MgCl_2 + H_2O \Leftrightarrow Mg(OH)^+ + H^+ + 2Cl^- \qquad (2.1)$$

$$MgH_2 + 2H^+ = Mg^{2+} + 2H_2\uparrow \qquad (2.2)$$

$$MgH_2 + 2H_2O = Mg(OH)_2 + 2H_2\uparrow \qquad (2.3)$$

$$Mg(OH)_2 \Leftrightarrow Mg(OH)_2\downarrow \qquad (2.4)$$

$$Mg(OH)_2 \Leftrightarrow Mg(OH)^+ + OH^- \qquad (2.5)$$

As can see be seen, the reaction solution is acidic before the introduction of MgH_2. pH of such a solution can be calculated by using an equation

$$pH = 7 - ½\, pK_1/2 - \log([MgCl_2]) \qquad (2.6)$$

At the applied experimental conditions pH of the initial MgCl2 solutions are within 6.88 – 6.28 showing the formation of close to neutral solutions. After adding the MgH_2, the hydrolysis reaction and the formation of $Mg(OH)_2$ are taking place and after some time magnesium hydroxide precipitates are formed. As a result, the reaction system appears to contain two solid species, namely, MgH2 and Mg(OH)2 which are in equilibrium with the solution providing the stable concentrations of Mg(OH)2 and $MgCl_2$ soluble species. Such $MgCl_2$ + $Mg(OH)_2$ solution can be considered as a buffer solution "weak base and its salt with a strong acid", and pH of such a solution can be calculated by using an equation:

$$pH = 14 - pK_1 + \log([Mg(OH)_2]/[MgCl_2]) \qquad (2.7)$$

As mentioned above, magnesium hydroxide has a low solubility in water. Consequently, after its precipitation, the concentration of $Mg(OH)_2$ in the solution will be constant and it can be calculated using pSP. Therefore, pH of a reaction mixture should be linearly dependent on $\log([MgCl_2])$. The latter assumption is in a good agreement with experimental observations, see Table 1. Based on the abovementioned experimental data and modeling, the mechanism of $MgCl_2$ action in the reaction of MgH_2 hydrolysis can be described as follows. Due to a minor influence of the hydrolysis of the initial $MgCl_2$ solutions on the pH of the starting reaction mixture, the reaction of MgH_2 and water forming soluble $Mg(OH)_2$ is suggested to occur as a very fast process. Such a reaction leads to the formation of a buffer solution "$MgCl_2$ + $Mg(OH)_2$" which determines pH of the reactive solution. pH of such a solution increases with the increasing conversion up to the reaching of the solubility product of magnesium hydroxide when the precipitation of $Mg(OH)_2$ starts. After starting the precipitation of $Mg(OH)_2$, its concentration in the solution remains constant and pH will remain stable (eq. 2.7).

As it was mentioned above pH of working solution is inversely proportional to the logarithm of $MgCl_2$ concentration (see eq. 2.7). It was found that the volumes of released H_2 (or degree of conversion of reaction) are proportional to log($MgCl_2$) (Fig. 2).

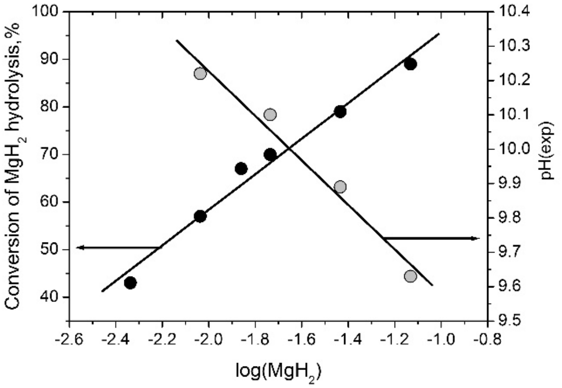

Fig. 2. The dependencies of the conversion of MgH_2 hydrolysis reaction and measured pH of the solutions on log($MgCl_2$).

To describe the kinetics of hydrolysis of MgH_2 in the $MgCl_2$ solutions we propose to use a simplified kinetics scheme, which is based on the following simplifying assumptions.

It appears that only initial stages of the process show rapid changes (quick increase of the pH of the reaction mixture). Thus, the values of pH needed to initiate $Mg(OH)_2$ sedimentation are reached at early stages of the hydrolysis, when the conversion level is just 0.04 – 1 %. As after the start of $Mg(OH)_2$ sedimentation the value of pH of the solution becomes stable and concentration of H^+ will be accounted when determining the rate constants of various contributing reactions. Thus, an overall kinetics scheme includes three pseudo-elementary reactions (3.1) – (3.3):

$$MgH_2 \rightarrow 2H_2\uparrow \qquad (3.1)$$

$$MgH_2 \rightarrow P \qquad (3.2)$$

$$P \rightarrow 2H_2\uparrow \qquad (3.3)$$

(3.1) Fast interaction of solid MgH_2 with water releasing H_2; k_1 is the rate constant of the process.

(3.2) $Mg(OH)_2$ is formed during the hydrolysis process and blocks the surface of the remaining MgH_2 and forms low-active product P. k_2 is the rate constant of the process.

(3.3) Despite blocking the MgH_2 surface by $Mg(OH)_2$, water molecules can still slowly diffuse through its layer reaching MgH_2 and reacting with MgH_2. k_3 is the rate constant of the process.

Fitting of the kinetics curves of MgH_2 hydrolysis yielding the values of the rate constants of the reactions were performed using COPASI software [23]. By using the described kinetic model, we were able to satisfactory describe experimental curves, as can be evidenced from the Fig. 1. At the same time, the rate constants of the studied reactions exhibit a dependence on the concentration of $MgCl_2$, as show the data in Table 2.

Table 2. Dependences of the refined from the model rate constants of MgH_2 hydrolysis on the $MgCl_2$ concentration.

$[MgCl_2]$, mol/L	Rate constants, min^{-1}		
	k_1	k_2	k_3
0	0.031±0,004	0.19±0.02	0.000015±0.0000003
0.0046	0.034±0.003	0.12±0.01	0.0017±0.0004
0.0092	0.036±0.004	0.10±0.02	0.0031±0.0004
0.0138	0.038±0.002	0.07±0.02	0.0048±0.0007
0.0184	0.040±0.002	0.07±0.03	0.0054±0.0008
0.0368	0.041±0.002	0.037±0.006	0.0064±0.0009
0.0738	0.043±0.002	0.021±0.004	0.009±0.001

Such observed dependencies can be summarized as follows:

(1) A slight increase in the rate constant k_1 takes place with increasing concentration of $MgCl_2$ and can be related to the changes in the acidity of the solution;

(2) A decrease in the values of k_2 is observed with an increase of the $MgCl_2$ concentration which can be related to a decreased number of the blocking $Mg(OH)_2$ particles at an interface between the solution and the surface of MgH_2 thus resulting in reduced passivation of MgH_2;

(3) A more distinct increase of k_3 as compared to k_1 observed with increasing $MgCl_2$ concentration is associated not only with the changes of pH of the solution, but is mainly caused by the growth of the size of $Mg(OH)_2$ crystallites and, correspondingly, with a higher rate of the diffusion of water through the inhomogeneous passivation film.

Such an explanation of the promoting action of the metal chlorides of different nature during the reaction of MgH_2 hydrolysis, in spite of its simplicity, well describes the observed experimental dependencies and is expected to be further developed in the future.

Conclusions

The hydrolysis reaction of MgH_2 in the $MgCl_2$ solutions was investigated at pseudo-isothermal conditions. Based on the analysis of the process kinetics, changes of the pH of the solutions and the phase-structural composition of the reaction products it can be concluded:

– pH of a working solution linearly depends on the logarithm of $MgCl_2$ concentration;

– pH of the reaction mixture in the presence of $MgCl_2$ is well described by considering a system “weak base and its salt with strong acid” type buffer solution.

The mechanism of hydrolysis of MgH_2 in $MgCl_2$ solutions includes formation of the buffer solution controlling the pH of the reaction mixture leading to the formation of inhomogeneous passivation film on the surface of MgH_2. The kinetic model of the hydrolysis of MgH_2 in $MgCl_2$ solutions involved passivation of the MgH_2 surface by the formed $Mg(OH)_2$ precipitate followed by its repassivation has been proposed.

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