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PRODUCTION OF MAGNESIUM OXIDE POLYHYDRATES AS FILLERS FOR ELECTRORHEOLOGICAL SUSPENSIONS

The influence of the production conditions of magnesium hydroxide on its composition, in particular the content of the non-structural “superstochiometric” water, which can be localized in the interlayer space of the layered structure. The conditions of generation and formation of the magnesium hydroxide crystal structure of brucite (nemalite) type, containing up to 8 wt % “superstochiometric” water, which is removed by heating up to 300–350ºC. Observed the formation of basic magnesium carbonate using distilled water containing dissolved carbon dioxide. When used distilled water containing dissolved carbon dioxide, magnesium basic carbonates are formed.

Introduction. Among the chemicals special attention is paid to polyhydrates of metal oxides, which are widely used for various industrial purposes. Metal oxides polyhydrates are characterized by a variety of modifications. For example, hydrated alumina, having a layered structure, as the authors note [1], may be in the form of oxyhydroxides of AlOOH − pseudoboehmite, boehmite, hydroxide $Al(OH)_3$ − bayerite, gibbsite, gidrargilit. The layered structure is typical for other hydrated oxides.

It is known [2] that polyhydrates of magnesium oxide as well as nickel and iron oxides have a layered structure of brucite type. It is noted [3] that the interplanar spacing between the layers in the structure of metal oxides polyhydrates depending on the receipt may change somewhat as a result of the localization in the interlayer space of H_2O molecules, which can be held there by the formation of strong hydrogen bonds with the oxygen of OH^--groups, coordinated by cation. Author [4] proposed to call water of this type as “superstochiometric” and refer it with regard to metal hydroxide to the non-structural H_2O.

As it is noted in [5−7], the availability of “superstochiometric” water in hydrated metal oxides predeterminates the appearance of the charge carriers in the electric field due to the protolytic dissociation of H_2O, because of what it is possible emergence of electrorheological effect (ERE) in the electrorheological suspensions (ERS). According to [8], ERE arises in the electric field due to the increase of the yield strength and the effective viscosity of the suspension.

Based on the above, the aim of this work was to study the influence of the conditions for obtaining magnesium oxide polyhydrates on the content of “superstochiometric” water, which can trigger the emergence of ERE in electrorheological suspensions.

Samples of hydrated magnesium were prepared by periodic precipitation method with the following order of reagent mixing: magnesium salt solution is injected into the precipitator, since, as it is noted in [9], precipitation of magnesium oxide polyhydrates obtained in this order of mixing, are hydrophilic due to the availability of excess OH^--groups that are adsorbing on the surface, make it hydrophilizated.

When producing precipitation of hydrated magnesium oxide concentration of solutions was modified and prepared from chloride or magnesium nitrate, temperature, flow rate (ml/min) of a solution of a magnesium salt. Aqueous ammonia solution containing 25 wt % NH_3 was used as an alkaline reagent. Deposition was carried out at 20 and 70ºC and vigorous stirring until pH of the medium 9.5−10.0. Precipitated deposits obtained at 20ºC, were aged for 48 h at 70ºC in the liquid phase, which was formed as a result of the deposition process. After aging, the deposition was separated from the liquid phase by vacuum filter, the deposition was washed until a negative reaction to the chloride or nitrate ions in the rinsing water, then was dried at (25 ± 5) ºC to constant mass.

Water, chloride, nitrate ions contents were determined by the gravimetric method, the content of MgO by the chelatometry, phase composition − with 08 Advance diffractometer Bruker AXS Company(Germany). Curve dryings were constructed on the basis of data obtained by MA (moisture analyzer) 30 Sartorius. Thermal analysis of the synthesized products was performed using derivatograph Paulik-Paulik-Erdey Q-1500.

Main part. The basis of the deposition of hydrated magnesium oxide is the reaction of hydrolysis of magnesium salts, meanwhile forming precipitation, characterized by different composition and properties. Conditions for obtaining precipitation of hydrated magnesium oxide and the results of their studies are presented in Table 1. As the table shows, sample N 1 contains 8.8 wt % of carbonate ions, due to the presence of dissolved carbon dioxide in distilled water, resulting in possible formation of basic magnesium carbonate.

According to [10], the transition from the hydroxide structure to the basic salt structure is made by the chemically responsive intermediate layers by substitution of the hydroxyl groups of the layers to other anions. In the formation of basic salts in the hydroxide structure the symmetry of location of ions of metal retains, typical for the corresponding hydroxide lattice.

Table 1

Conditions for obtaining precipitation of hydrated magnesium oxide and the results of their research and the results of their research

Sample, N	Conditions for obtaining				Results of research			
	Chemistry and concentration of the salt solution	Consumption of magnesium salt solution, ml/min	*T*, ºC	Value pH	Content, wt %		Mass loss while burning, wt %	Hydrolysis degree
					MgO	CO_2		
1	$MgCl_2$, 0.05 n.	50	20	10.0	60.7	8.8	37.4	0.98
2	$MgCl_2$, 0.05 n.	50	20	10.0	66.3	0.9	32.6	0.98
3	$MgCl_2$, 1.0 n.	3	20	10.0	59.3	0.4	39.1	0.98
4	$Mg(NO_3)_2$, 1.0 n.	3	20	9.9	68.3	0.5	31.7	1.0
5	$MgCl_2$, 1.0 n.	3	70	9.7	62.6	0.8	37.1	0.99

Note. Sample N 1 was precipitated from solution by distilled water. Samples N 2–5 were deposited from solution on basis of double-distilled water. Sample N 5 was obtained without the stage of the precipitate aging in liquid phase.

At the same time, there is an increase in distances between the cations, depending subject to the type of substituting foreign anion, so it may be as static distribution of anions with a continuous transition of the composition of the hydroxide to the composition of the basic salt, and limited replacement of the hydroxyl ions.

Due to the localization of the carbonate ions in the structure of magnesium hydroxide, in the deposition of sample 1its X-ray is characterized by slightly blurry intense peaks, which correspond to the peaks of the X-ray brucite (Fig. 1).

Sample N 2, obtained from solutions based on double-distilled water under the same conditions as sample N 1, contains 0.9 wt % of carbonate ions, the amount of CO_2 in sample N 5 is on the same level. The amount of carbonates is within 0.5 wt % for samples N 3, 4 (Table 1).

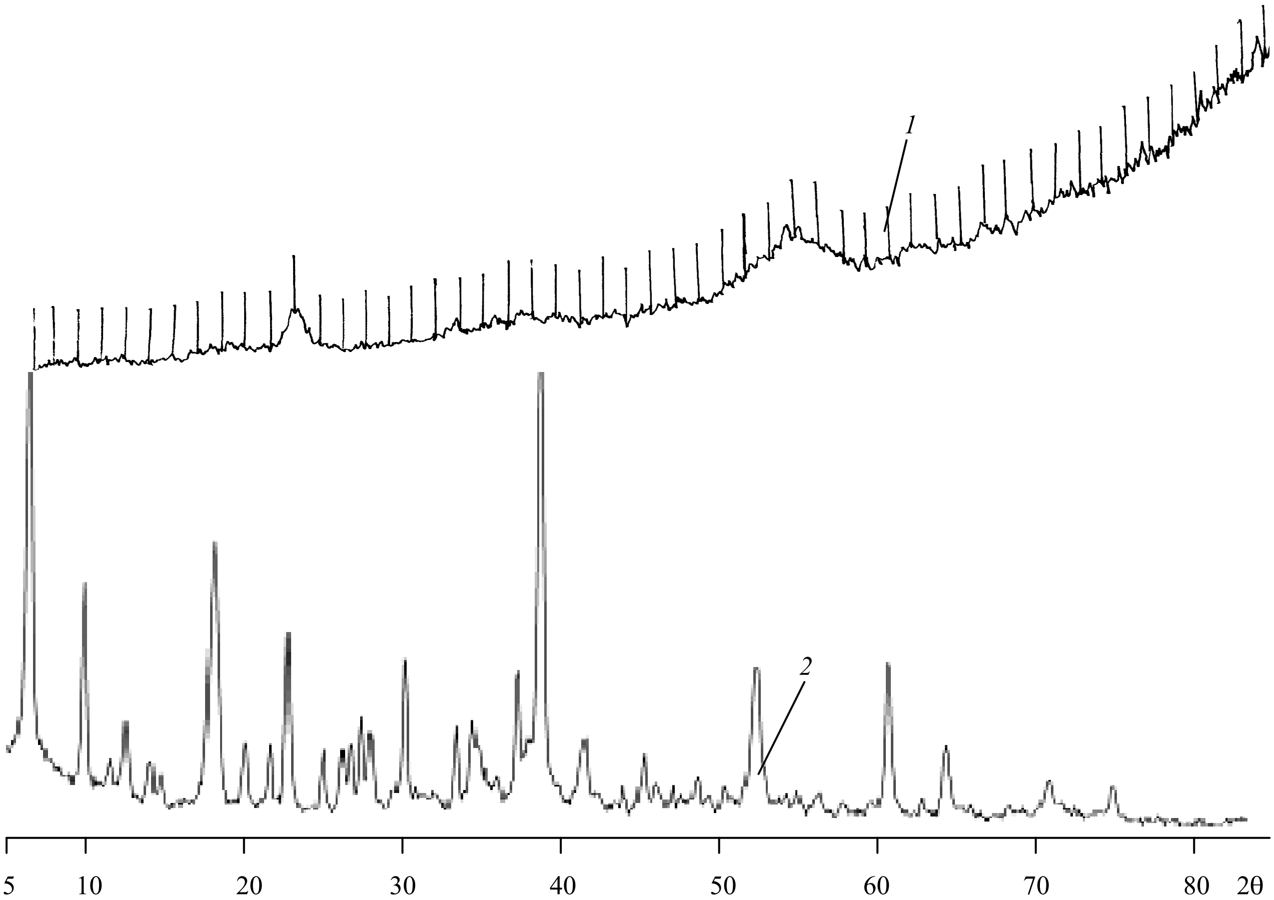

Fig. 1. X-ray pictures of magnesium oxide polyhydrates:
1 – X-ray of sample N 1; *2* – X-ray of the sample N 3 (Table 2)

Estimating the degree of hydrolysis showed that complete conversion of magnesium salts in hydrated oxide was reached only in case of magnesium nitrate application, which is conditioned by, as it was noted in [11], its higher ability to hydrolyze, in case of magnesium chloride using, the hydrolysis degree is 0.98–0.99.

According to the stochiometric composition of magnesium hydroxide $Mg(OH)_2$, it containes 68.96 and 31.04 wt % MgO and H_2O respectively. According to experimental data, the composition of sample N 4 practically corresponds to the stochiometric composition (Table 1), while other samples are somewhat different in content of MgO, and H_2O. From the data on mass loss by samples of hydrated magnesium oxide, dried under the same conditions and heated to 850ºC, it follows that the maximum water content is observed in sample N 3 (Table 1).

This indicates to the presence of molecules of "stochiometric" water in the sample, the amount of which in other samples below and is 1.9, 0.5, 6.5 wt % for samples N 2, 4, 5 respectively. Based on experimental data, the gross composition of the samples was calculated; it is presented in Table 2.

Table 2

Gross composition of magnesium oxide polyhydrates

Sample, N	Gross composition samples
1	$MgO \cdot H_2O \cdot \{0.05H_2O\} \cdot 0.17CO_2 \cdot 0.01Cl_2$
2	$MgO \cdot H_2O \cdot \{0.06H_2O\} \cdot 0.02CO_2 \cdot 0.01Cl_2$
3	$MgO \cdot H_2O \cdot \{0.45H_2O\} \cdot 0.003CO_2 \cdot 0.01Cl_2$
4	$MgO \cdot H_2O \cdot \{0.015H_2O\} \cdot 0.015CO_2$
5	$MgO \cdot H_2O \cdot \{0.23H_2O\} \cdot 0.004CO_2 \cdot 0.01Cl_2$

Note. { } – amount "superstoichiometric" water.

According to the gross composition, 1 mol of MgO has 1 mol of chemically bound water in the form of OH^--groups and a different number of "stochiometric" unstructured water as adsorbed and is likely to localize in the interlayer space of the layer structure.

X-ray analysis showed that samples N 2–5 have the same X-gram picture shown in Fig. 1, which, according to a set of values of interplanar spacing is identical to X-ray picture of magnesium hydroxide having a layered structure of brucite. Derivatogram of sample N 3 is shown in Fig. 2, in which there are two endothermic effect in the temperature range of 30–360 and 360–560°C, with minima at 130 and 430°C respectively.

The first endothermic effect may be specified by elimination of "superstochiometric" water, which is localized in the interlayer space and adsorbed on the surface of the particles, and the endothermic effect with minimum at 430ºC is associated with the removal of chemically bound water in the form of OH^--groups coordinated by cation.

According to thermogravimetric TG curve (Fig. 2), in the temperature range at 30–360°C, the mass loss is 7.7 wt %, and at 360–560°C – 31.0 wt %, which practically corresponds to 1 mol of chemically bound H_2O by 1 mol of MgO in the sample involved.

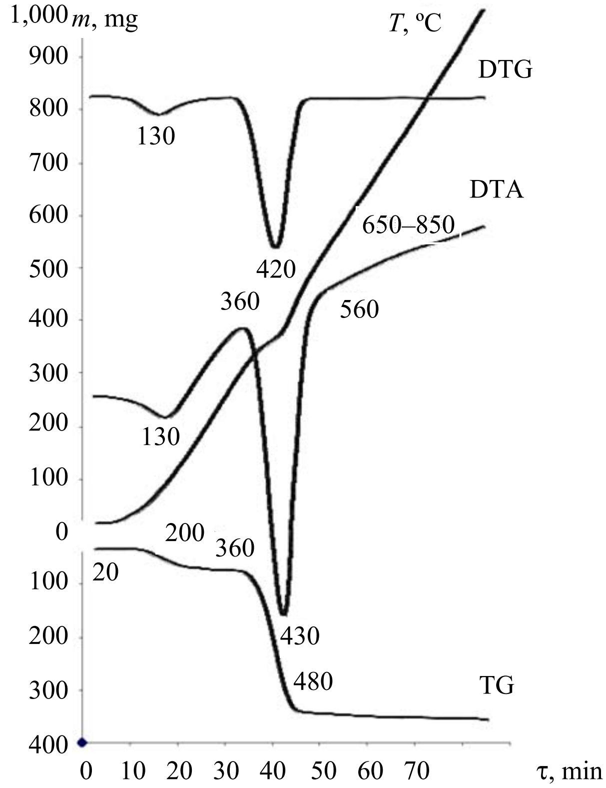

Fig. 2. Thermogravimetric magnesium oxide polyhydrates

The experimental data of mass loss by samples N 1–5 in polythermal mode in the temperature range 30–850ºC (Fig. 3) were obtained for studying the thermal dehydration of magnesium hydroxide samples. As it can be seen from the figure, the trend of curves for samples N 2–5 is identical, there are two inflection points – the first point at 300ºC, the second point at 550ºC. As it was recorded, chemically bound water begins slivering at 300–350ºC. At temperatures from 30 to 350ºC mass loss of the samples comes up to 3.7, 7.7, 4.65, 8.29 wt % for samples N 2–5 respectively. Under the circumstances, for samples N 2 and 4 mass of receding H_2O in the temperature range 100–300ºC does not exceed 2.5 wt %, for samples N 3 and 5 it is much higher and it comes up to 5.6 and 5.0 wt % respectively.

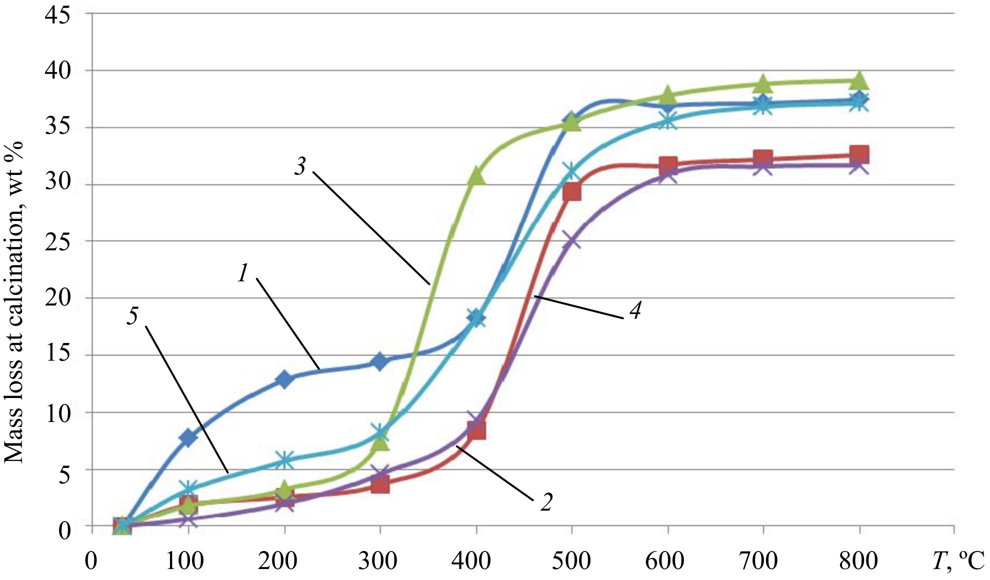

Fig. 3. Mass loss curves by hydrated magnesium oxides:
1–*5* – mass loss curves by samples N 1–5 respectively

These results led to the assumption that, first, in the samples there is "superstochiometric" water, which is localized in the interlayer space of the layered structure of brucite and is held firmly by the formation of hydrogen bonds with the oxygen chemically bound OH^--groups, and secondly, its amount is determined by the synthesis conditions, i.e. the concentration of reagent solutions and deposition rate. Adsorbed H_2O is likely to be removed at temperatures not higher than 100ºC, and its content is at 2–4 wt %, which follows from the drying curves (Fig. 4). With increasing temperature up to 130ºC cleavable mass of water increases and reaches 3.1 and 5.7 wt % for samples N 3 and 5 respectively.

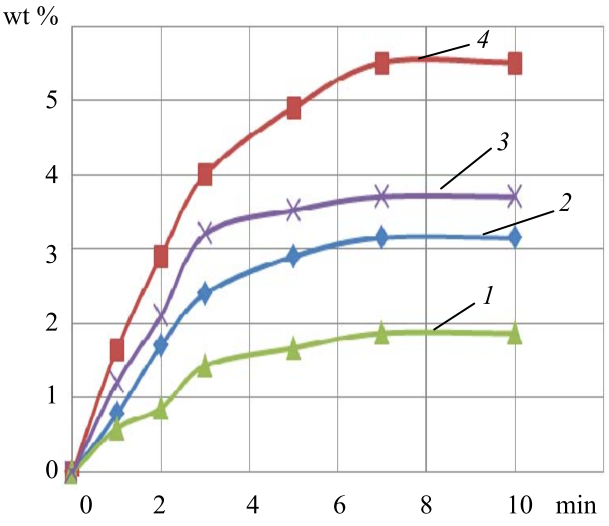

Fig. 4. Drying curves for polyhydrates
of magnesium oxide:
1, *3* – at 100ºC; *2*, *4* – at 130ºC
for samples N 3, 5 respectively

However, mass of water remaining in the samples, endured at 130ºC in isothermal conditions, exceeds the calculated H_2O content in $Mg(OH)_2$.

The presence of unstructured "superstoichiometric" water in polyhydrates of magnesium oxide which can be an activator of electrorheological effect, suggests that the compound obtained under given conditions, can be used as fillers of ERS.

Conclusion. It is shown the influence of the conditions for obtaining magnesium hydroxide on its composition, in particular the content of the non-structural "superstochiometric" water, and CO_3^{2-}.

The conditions of deposition of hydrated magnesium oxide (reagent consumption, concentration, temperature) are established, which produce the precipitation comprising up to 8 wt % of "superstochiometric" water, which is removed by heating at 300–350ºC and can be an activator of electrorheological effect in ERS.

It is registered the formation of basic magnesium carbonate using distilled water containing dissolved carbon dioxide.

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