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E. V. Makhrova, assistant lecturer (BSTU); **L. S. Eshchenko**, D.Sc. (Engineering), professor (BTSU)**FEATURES OF THE PROCESS FOR PRODUCING HYDRATED ALUMINA WITH A LAYERED STRUCTURE**

The influence of conditions for obtaining a hydrated aluminium oxide on its chemical and phase composition namely the pH of reaction medium is established. The pH of the reaction medium in which aluminium tri-hydroxides and oxy-hydroxides with various crystal structures can be formed is determined. Features of formation of the crystal structure of hydrated aluminium oxides on the mechanism of „oriented building” are pointed.

Introduction. Due to the variety of chemical and physical properties some chemical compounds are "universal" for a variety of industries. A bright representative of such compounds considered to be hydrated alumina. It is used for water purification, in medicine, and as an adjuvant in the manufacture of vaccines, the flame retardant (suppressor combustion) in plastics and other materials. The use of this compound in the catalysts of the absorption technique, as well as a filler of electro-rheological suspensions is also known. Recently, hydrated aluminas are of interest as a template to produce a complex compounds with a set of properties by intercalation. There are several different versions of hydrated aluminum oxides. In literature [1] there is some information on three models of aluminum tri-hydroxide $\text{Al}(\text{OH})_3$ – gibbsite (gibbsite), bayerite and nordstrandite and two versions aluminum oxy-hydroxide AlOOH – and pseudo-boehmite.

In spite of identical chemical composition, these modifications differ in their structure and consequently have different properties. The formation of certain types of structure depends on on the preparation conditions. Many ways to get hydrated aluminum oxides and various modifications of their formation and the formation of chemical vapor on stages of residue, aging and drying are described in the literature [2–4]. However, these data are fragmented in some cases and are contradictory, that is likely to be connected with a variable composition of the hydrated aluminum oxide formed by chemical sedimentation deposition. At the same time, the composition and structure of the hydrated aluminas determine practical use of these compounds. In this regard, the aim of this work was to obtain hydrated aluminum oxides of given composition and structure as a basis for obtaining intercalation compounds.

Hydrated aluminas were obtained by a continuous deposition method. The solutions of sodium aluminate with a ratio of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$, equal to 1.93, and solutions of aluminum salts, as precipitating agent – solutions of nitric acid or alkali were used as the source of aluminum-containing reagents. Variable parameters during the deposition were the pH of the reaction medium, the concentration of reactants and temperature. The obtained

pellets were subjected to aging at both room and elevated temperature, and then were filtered off on a vacuum filter, washed and dried to constant weight at a temperature of 70°C. The water content was determined by a gravimetric method, Al_2O_3 – complex-metric, phase composition – with 08 Advance diffractometer of company Bruker AXS (Germany).

Main part. Production conditions and the composition of the sediments are given in the Table. In the interaction of the aluminum reagent with a precipitant, precipitations of hydrated alumina are formed, characterized by the phase structure and a molar ratio of $\text{Al}_2\text{O}_3 : \text{H}_2\text{O}$. As shown by the experimental data, the type and form of precipitation of hydrated aluminum oxides depend on the conditions of the chemical deposition. During the precipitation of sodium aluminate a precipitate is formed, which lays over and is characterized by a high value of the filter factor, during the deposition of the aluminum salt solution a gel-like precipitate is formed which does not practically lay over.

As the authors note [5], the formation of residues during chemical precipitation from solutions of salts of polyvalent metals is as follows: at the beginning of the interaction, the formation of the monomer is observed, in which the aluminum cation is coordinately unsaturated. The increase in the coordination number of aluminum occurs in the interaction of monomers, resulting in the formation of dimers, but even as a part of dimers both aluminum cations are coordinately unsaturated. This circumstance is the driving force for further combining the dimers into a more complex structure, which leads to the formation of an inorganic polymer.

These processes occur at the origin of a solid phase both in acidic and alkaline medium. However, depending on the conditions of deposition of the hydrated alumina the resulting monomers differ in mutual arrangement of aluminum cations, and OH groups that leads to the formation of polymers of different structure. The resulting polymers are disoriented in the reaction chamber, and therefore precipitate is X-ray amorphous. The exceptions are the precipitates obtained by precipitation at a pH value of the reaction medium heated to 12.0–

12.5°C solution of 80 (samples No. 4 and 8). On the radiographs of these samples (Fig. 1, curve 4) diffraction peaks are present, indicating the presence of a crystalline phase, which corresponds to the structure of aluminum oxy-hydroxides boeh-

mite. The formation of the crystalline phase in the precipitation stage is caused by the fact that as the temperature increases, the crystallization processes of hydrolytic recrystallization proceed more rapidly.

Table

Conditions for obtaining hydrated aluminum oxides and results of their research

Sample No.	Synthesis conditions					Results of the study			
	Aluminum containing reactant	Precipitant	Temperature of deposition, °C	pH	Aging temperature, °C	Content, wt. %		Phase composition	Molar ratio Al ₂ O ₃ : H ₂ O
						Al ₂ O ₃	H ₂ O		
1	Solution NaAlO ₂ with ratio Na ₂ O : Al ₂ O ₃ = 1,93	HNO ₃ 35 wt. %	20	8.0–8.5	100	75.4	24.6	Pseudo-boehmite-AIOOH	1 : 1.8
2			20	10.0–10.5	20	62.8	37.1	Bayerite Al(OH) ₃	1 : 3.3
3			20	12.0–12.5	20	65.4	34.5	Gibbsite Al(OH) ₃	1 : 3.0
4			80	12.0–12.5	–	78.8	21.2	Boehmite AIOOH	1 : 1.5
5	Solution Al(NO ₃) ₃ with concentration 1 M	NH ₄ OH 25 wt. %	20	8.0–8.5	100	74.3	25.7	Pseudo-boehmite-AIOOH	1 : 1.9
6			20	10.0–10.5	20	62.4	37.8	Bayerite Al(OH) ₃	1 : 3.4
7	1 M	NaOH 1 M	20	12.0–12.5	20	65.9	34.1	Gibbsite Al(OH) ₃	1 : 2.9
8			80	12.0–12.5	–	77.2	22.9	Boehmite AIOOH	1 : 1.7

The formation of the phase composition of other residues occurs in the stage of aging. In accordance with the experimental data the main parameter affecting the phase composition of products is pH deposition. According to X-ray studies, the phase composition of the samples, which were obtained by precipitation at pH of the reaction medium 10.0–10.5 corresponds to hydrated alumina bayerite structure (Fig. 1, Curve 2). Sample No. 3 and 7 are identified as hydrated aluminas with gibbsite structure (Fig. 1, Curve 3). Should be noted that hydrated alumina with the structure of bayerite and gibbsite are crystallized as a result of aging at a temperature of 20°C. At pH 8.0–8.5 and temperature of aging at 100 °C, a precipitate is formed, the composition of which corresponds to the aluminium oxy-hydroxide. Radiograph for

samples No. 1 and 5 (Fig. 1, Curve 1) does not have distinct reflexes, they are unclear and blurred, which indicates a weak crystallinity of the compounds obtained. According to the results of radiographic studies it was determined that the diffraction peaks on this radiograph are characteristic of the compounds with the structure of pseudo-boehmite AIOOH.

As the authors note [6], the crystallization of hydrated alumina occurs at the stage of aging by the mechanism of "oriented capacity". According to this mechanism, the hydrated aluminum oxide polymers under the action of hydrogen forces combine in the primary particles. The convergence of polymers promotes water displacement from the space between them, which leads to their ordering. Thus, polymers are par-

tially dehydrated and disintegrated. The crystallization becomes possible after achieving some degree of dehydration and it occurs within a certain amount of primary particles due to decomposition products of the polymer structure, rather than by dissolution of one particles and transfer of crystal-forming substance through the stock solution to other solutions. After reaching in the sediments "critical" degree of ordering, the formation and growth of crystals becomes possible. This is due to the fact that Al-OH-groups which are capable to attach other primary particles to certain verge of the growing crystal are present at the edges of the primary particles. According to [7], during the crystallization of aluminum oxy-hydroxides inert oxygen anions are present between polymers, thus reducing the ability to displace water molecules in the space between approaching polymers. Therefore aluminum oxy-hydroxides have a much larger number of water molecules as compared to tri-hydroxide in the interlayer space. As shown in [8], pseudo-boehmite and boehmite consist of the same packets, but differ in the magnitude of the interlayer distance and consequently the amount of interlayer water. Therefore pseudo-boehmite radiograph (Fig. 1, Curve 1) in comparison with X-ray diffraction of boehmite (Fig. 1, curve 4) has several features: line broadening, redistribution of the intensity peaks, the first peak shift towards lower angles. Interlayer water molecules form hydrogen bonds with the oxygen of the

OH groups coordinated by the cation, and thus the cleavage of the molecules of water may take place until the beginning of the removal of structural OH groups. This is confirmed by thermal studies (Fig. 2). The course of the mass loss curves for the samples with the structure of oxy-hydroxide is different from the curves of mass loss samples, chemical and phase composition of which corresponds to the aluminum tri-hydroxide. Thus, for samples № 5 and 8 mass loss in the temperature range of 70–300°C is 10.1 and 7.9 wt. %, respectively. A large weight loss of samples of aluminum oxy-hydroxides to 300°C, probably is caused by the presence of molecules of adsorbed and interlayer water, as mentioned above. This is due to cleavage of structural OH groups. Losing weight by samples No. 5 and 8 in the temperature range 300–800°C is 15.6 and 15.1 wt. % which corresponds to the theoretical content of water in the composition of oxy-hydroxide (15.0 wt.%).

Adsorbed water molecules are likely to be removed at a temperature of 100°C. Losing weight by samples No. 4 and 8 to 100°C is 3.8 and 4.7 wt. %, respectively. Thus, 6.3 and 3.2 wt. % of interlayer water is contained in samples of oxy-hydroxides No. 4 and 8, respectively. Samples No. 6 and 7 at a temperature of 300°C lose 3.0 and 1.9 wt. %, respectively. The total weight loss by samples No. 6 and 7 is 37.8 and 34.1 wt. %, respectively, indicating the insignificant content of "nonstructural" water.

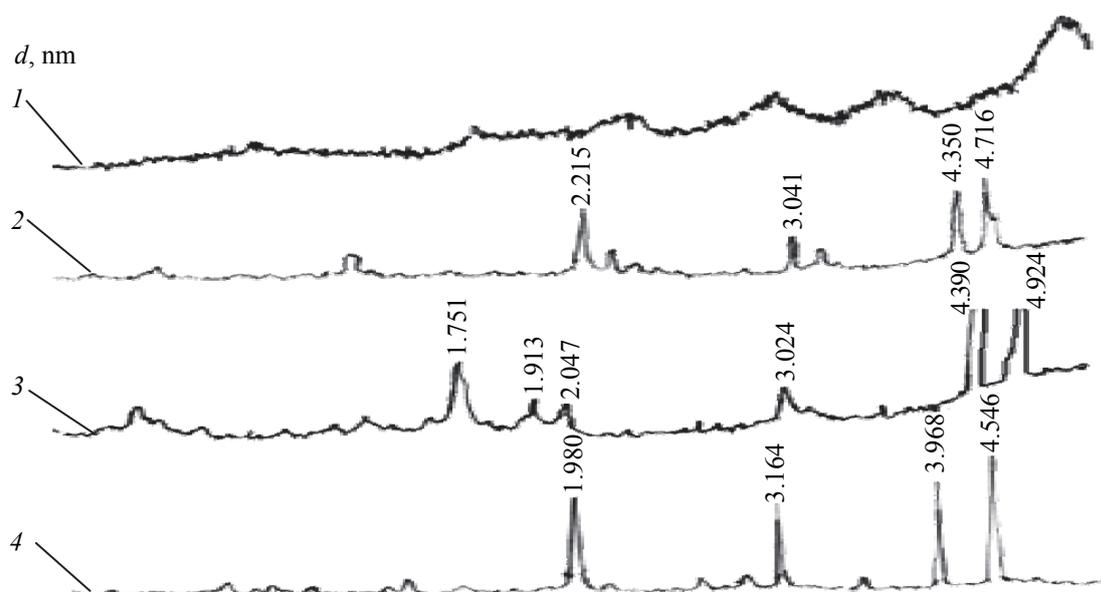


Fig. 1. Radiographs of hydrated alumina samples:
 1 – samples No. 1 and 5; 2 – samples No. 2 and 6;
 3 – samples No. 3 and 7; 4 – samples No. 4 and 8

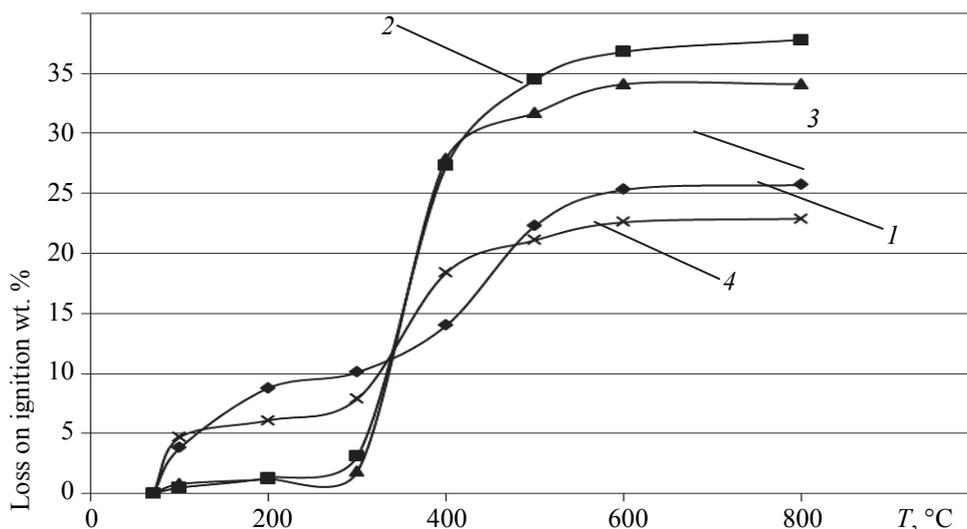


Fig. 2. Weight loss curves of hydrated alumina:
1–4 – weight loss curves of samples No. 5–8 respectively

Conclusion. It was shown that the main parameter affecting the phase and chemical composition of hydrated aluminum oxides is pH of the reaction medium and conditions of aging. Values of pH of the reaction medium at which the formation of aluminum tri-hydroxides and oxy-hydroxides with different crystal structures is possible were determined. The peculiarities of the crystal structure of hydrated aluminum oxides by the mechanism of "oriented capacity" were noted.

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