

# THE INFLUENCE OF THE ACTIVITY OF WATER ON THE PHASE COMPOSITION OF ALUMINUM HYDROXIDES FORMED BY REACTION OF AMALGAMATED ALUMINUM WITH WATER

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**Abstract**—The influence of the activity of water on the phase composition of aluminum hydroxides obtained by reaction of amalgamated aluminum with water has been studied. The reaction was carried out in solutions of water and dioxane, and in sodium chloride solutions of different concentrations; amorphous aluminum hydroxide was precipitated initially. The aging of this primary product to bayerite, pseudoboehmite, or an amorphous gel was controlled by the water content of the system. The pseudoboehmite has shown a significant reactivity when used as a source of alumina in the hydrothermal syntheses of kaolinite at relatively low temperature and pressure.

**Key Words**—Alumina, Aluminum, Bayerite, Hydroxide, Pseudoboehmite, Water.

## INTRODUCTION

The study of the composition and structure of aluminum hydroxides and oxyhydroxides has been the subject of a large number of publications during the past fifty years. In this paper we report results of our work concerning the preparation, structure and properties of aluminum hydroxides obtained by reaction of amalgamated aluminum with water. Many authors have reported on the nature and properties of aluminum hydroxides prepared by this reaction but with considerable diversity of opinion. Among the numerous references that should be mentioned are those of Watson et al. (1957) and de Souza Santos (1958), who gave, as we have done (Šarc-Lahodny, 1963, 1964), a very detailed review of the literature concerning the nature, structure, and morphology of the product obtained by this reaction.

Aluminum exposed in a solution of mercury salt displaces the mercury from the solution, which is then deposited on the surface of the aluminum metal. Due to the large difference in electrochemical potential between both metals, local electromotive cells are formed. The resulting anodic dissolution produces aluminum ions which react with hydroxyl ions from water to form aluminum hydroxide. Hydrogen ions are discharged at the sites where the amalgam forms and may recombine to produce hydrogen gas or form a hydride; the reaction is highly exothermic.

The contradictory nature of the data often reported in the literature concerning the nature of the aluminum hydroxide produced in the reaction of amalgamated aluminum with water is due to differences in procedure of amalgamation or in the aging of the primary product.

We were led to reexamine previous work in this area because of results which we obtained in the study of kinetics of the synthesis of kaolinite (Lahodny-Šarc et al., 1977) in which we used, as a source of alumina, aluminum hydroxide obtained from amalgamated aluminum whose nature and properties were controlled by the method of preparation and aging. Chesworth (1971) used amalgamated aluminum as a source of alumina in the synthesis of some hydrated aluminosilicates. Chesworth (1971, 1972) attempted to demonstrate the stability of gibbsite and boehmite at the earth's surface through experiments carried out in the laboratory at room temperature. In the laboratory experiments he used amalgamated aluminum in water, but the system  $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$  was undersaturated with respect to  $\text{H}_2\text{O}$  (i.e.,  $\text{H}_2\text{O}$  was absent as a separate phase) in order to realize the conditions necessary for the precipitation of the aluminum oxymonohydrate. The lowering of the chemical potential of water was accomplished by using water solutions of different salts of appropriate concentration, or conducting the reaction in an atmosphere with lowered water vapor pressure.

## EXPERIMENTAL

In our work we have lowered the activity of water in the system using solutions of water in dioxane, water in acetone, and water solutions of sodium chloride of different concentrations. In another series of experiments we carried out syntheses in the atmosphere, but over solutions which produced the desired water vapor pressure.

The products obtained by the reaction of amalgamated aluminum with water were investigated by X-ray

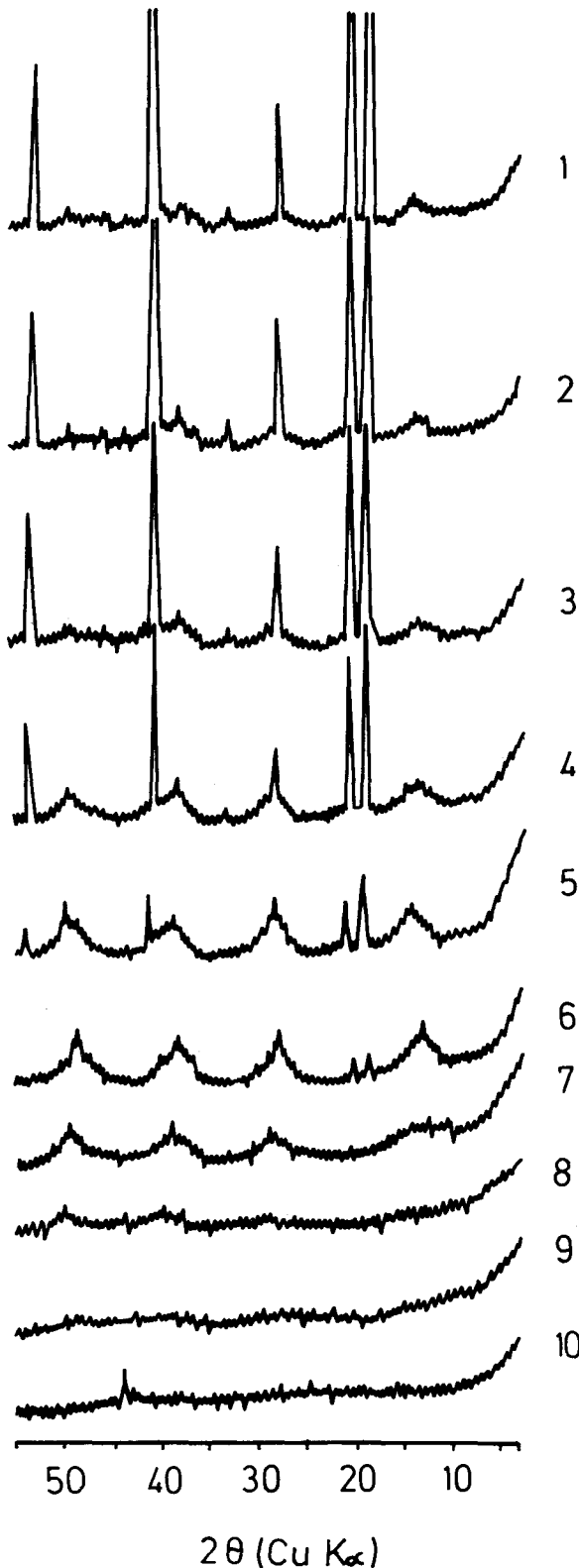


Fig. 1. X-ray data for samples of aluminum hydroxides obtained in solutions as follows: 1, in distilled water, and 2 to 10 in solutions with increasing concentrations of dioxane in water: 5%, 10%, 20%, 30%, 40%, 50%, 90%, 95%, and 98%, respectively.

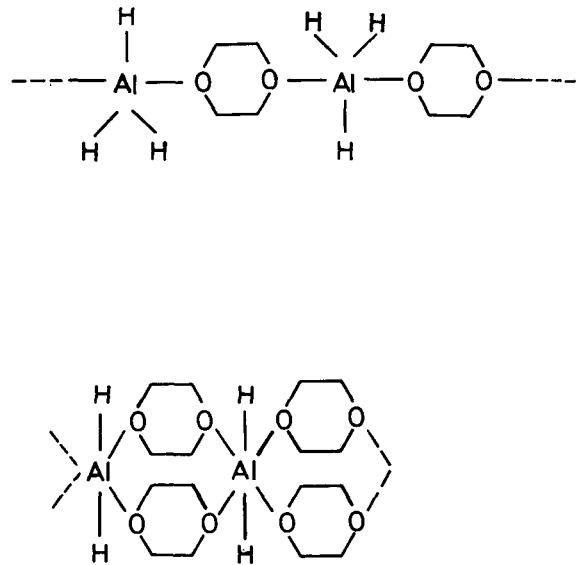


Fig. 2. Complex compound formed between aluminum hydride and dioxane.

powder diffraction measurements, thermal analysis, and infrared spectroscopy.

Aluminum used in the experiments had a purity of 99.998% and was obtained from Pechiney. Samples were degreased in acetone, washed in distilled water, and exposed for a short time in a saturated solution of  $\text{HgCl}_2$ , then washed again with water and left in the specific solution being studied.

Samples exposed in water until all the aluminum was transformed into a white precipitate were identified as bayerite. In solutions with decreasing activity of water, pseudoboehmite was formed.

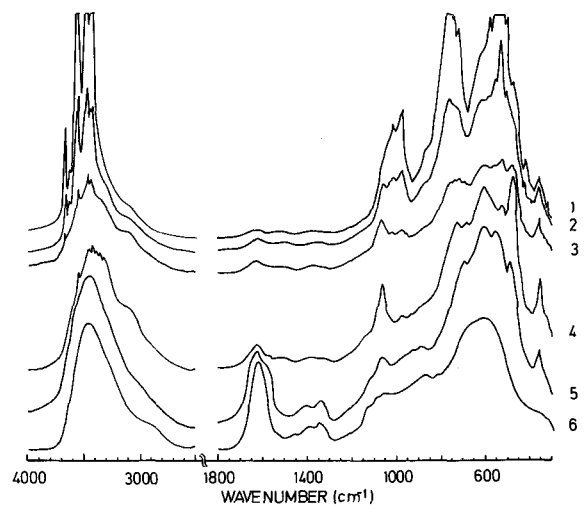


Fig. 3. IR data for samples prepared in solutions as follows: 1, distilled water, 2 to 6: in 20%, 30%, 40%, and 90% dioxane in water, respectively.

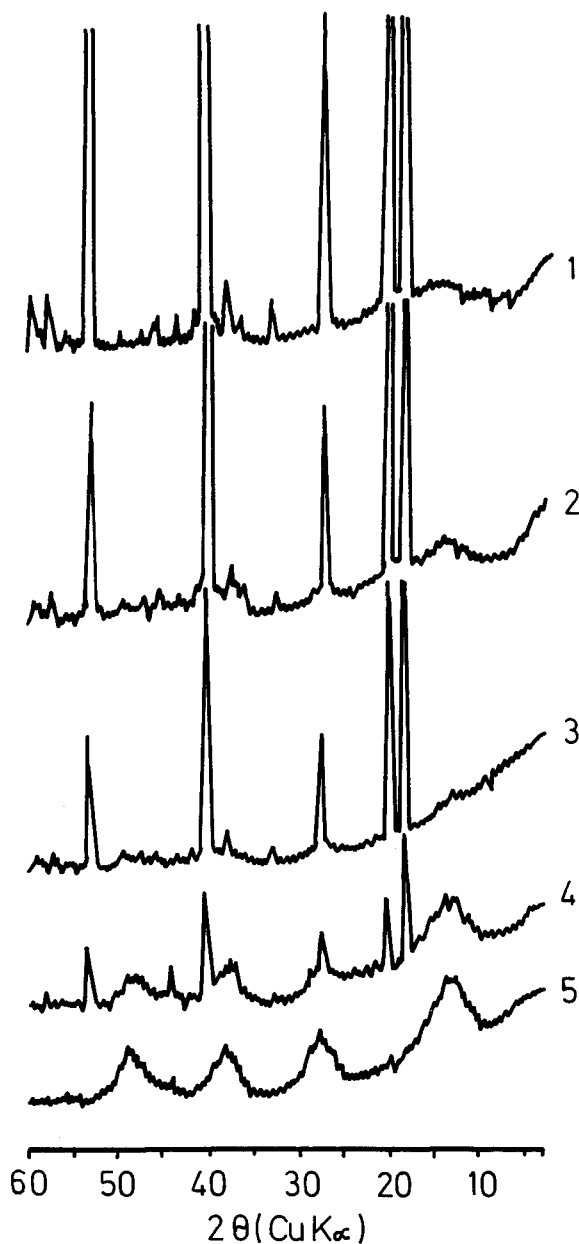


Fig. 4. X-ray data for samples prepared in distilled water, diffractogram 1, and in solutions of NaCl as follows: diffractograms from 2 to 5: in 0.5 M, 2 M, 3 M, and 5 M, respectively.

A series of experiments was carried out in solutions with increasing content of dioxane in water. The results of the diffraction measurements of a series of samples prepared in those solutions are shown in Figure 1. The first diffractogram corresponds to the sample obtained in distilled water and shows the reflections of bayerite with traces of amorphous material. The diffractograms from 2 to 10 are those of samples in dioxane-water systems having the following concentrations of dioxane: 5%, 10%, 20%, 30%, 40%, 50%, 90%, 95%, 98%. It is

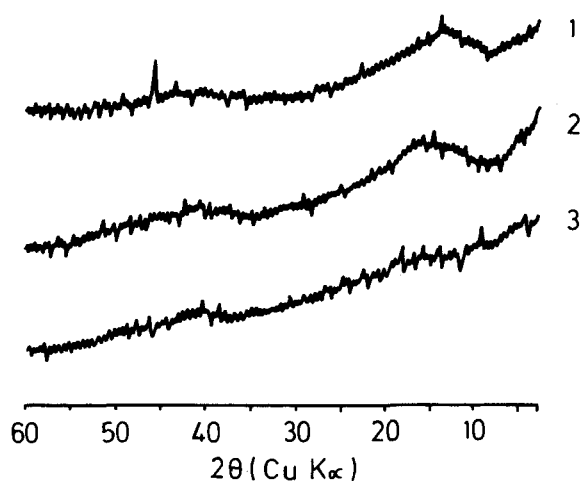


Fig. 5. Samples prepared in a 3-minute treatment period and separated from the mother liquor in solutions as follows: (1) in distilled water, (2) in 50% dioxane, and (3) in 98% dioxane.

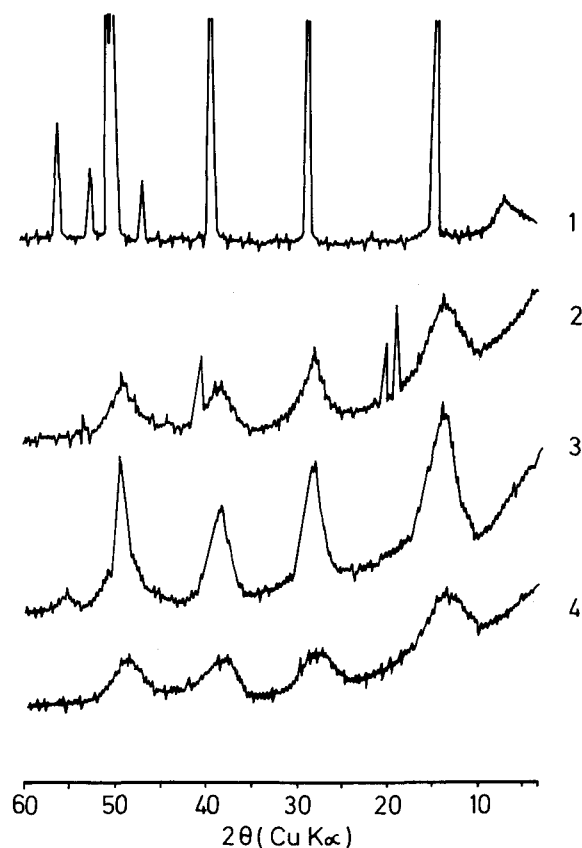


Fig. 6. X-ray data for samples: diffractogram 1, boehmite; diffractogram 2, pseudoboehmite treated 4 days at 100°C; diffractogram 3, pseudoboehmite treated 4 days at 80°C; and diffractogram 4, pseudoboehmite prepared at room temperature.

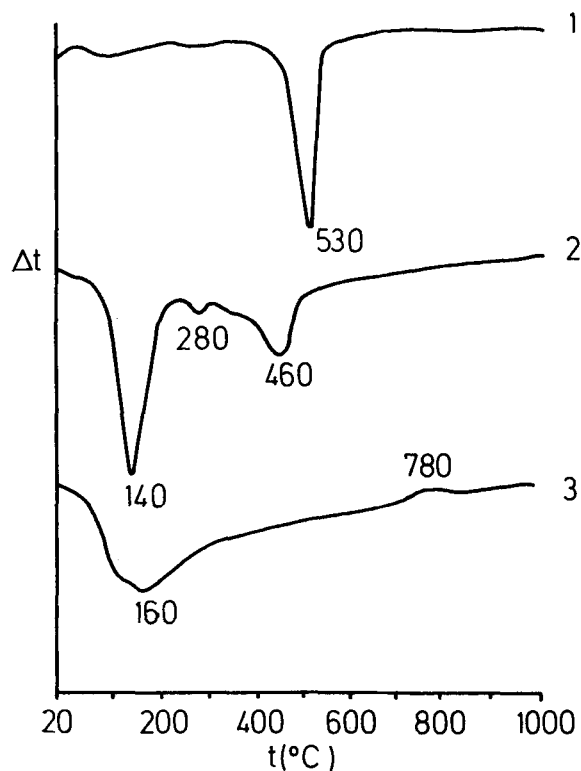


Fig. 7. DTA: curve 1, boehmite; curve 2, pseudoboehmite; curve 3, amorphous gel.

evident that with increasing concentration of dioxane the ratio of pseudoboehmite to bayerite increases, reaching a maximum in solutions of 40 to 50% of dioxane. With further increases in dioxane the product becomes more amorphous.

One might expect the formation of some kind of addition compounds between dioxane and aluminum hydroxide, as for example those presented in Figure 2. These are addition compounds of aluminum hydride with dioxane, the existence of which was established by Dautel and Ziel (1960). In all of our experiments the precipitates obtained after all aluminum was transformed were washed carefully with distilled water to remove dioxane and obtain the hydrolyzed products, which were then dried at room temperature. The aging period for all samples was 30 days and the pH after formation of the precipitate was approximately 8.

Figure 3 shows the results of the infrared absorption measurements. The spectra were made using the KBr pellet technique with a Model 180 Perkin-Elmer infrared spectrophotometer. From the series presented in Figure 1 we have chosen six samples as follows: spectrum 1 corresponds to the sample of bayerite, and spectra 2 through 6 correspond to samples obtained in dioxane-water solutions having the following concentrations of dioxane: 20%, 30%, 40%, 90%, and 98%. The infrared analyses confirm the X-ray powder dif-

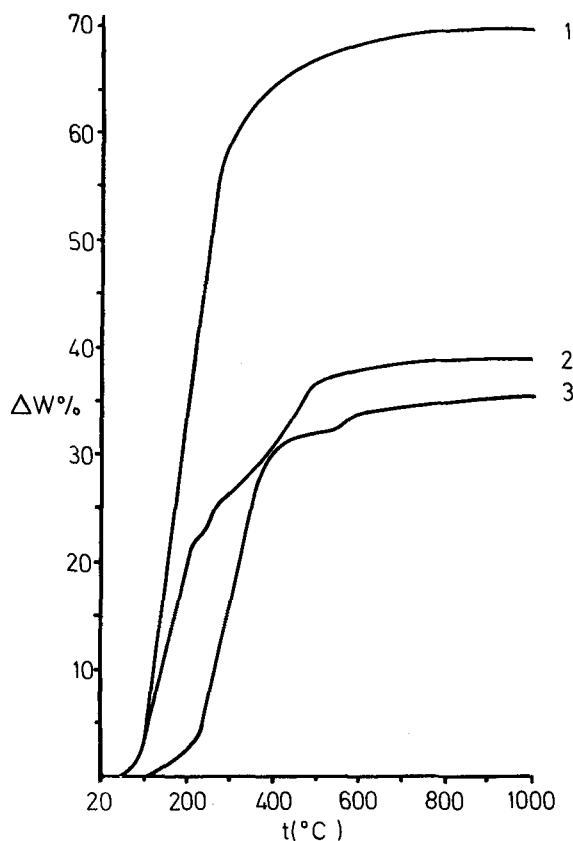


Fig. 8. TGA: curve 1, amorphous gel; curve 2, pseudoboehmite; curve 3, boehmite.

fraction data. Samples prepared with very small amounts of water (spectra 4, 5, 6) are essentially amorphous and the large amount of molecular water, as evidenced by the deformation band at  $1620\text{--}1640\text{ cm}^{-1}$ , indicates a high surface area material. The intensity of this band may be influenced by the presence of traces of the complex compound, aluminum hydride with dioxane, shown in Figure 2 (Dautel and Ziel, 1960). These spectra show a broad OH-stretching band centered at  $3450\text{ cm}^{-1}$ , the same as that for liquid water. With increasing water concentration one can recognize the gradual appearance of bands at  $3300$ ,  $3100$ , and  $1060\text{ cm}^{-1}$ , characteristic OH-stretching vibrations in boehmite, and a decrease in the intensity of the molecular water deformation band at  $1640\text{ cm}^{-1}$ . We obtained the same sequence of results for solutions of acetone as in the dioxane-water systems, i.e., with increasing concentration of acetone the ratio of pseudoboehmite to bayerite increased.

In Figure 4 are shown the X-ray data for experiments carried out in solutions of sodium chloride. The first diffractogram corresponds to bayerite obtained in distilled water, and diffractograms 2 through 5 to the following concentrations of NaCl solutions: 0.5 M, 2 M, 3 M, and 5 M. One can observe the relative amount of

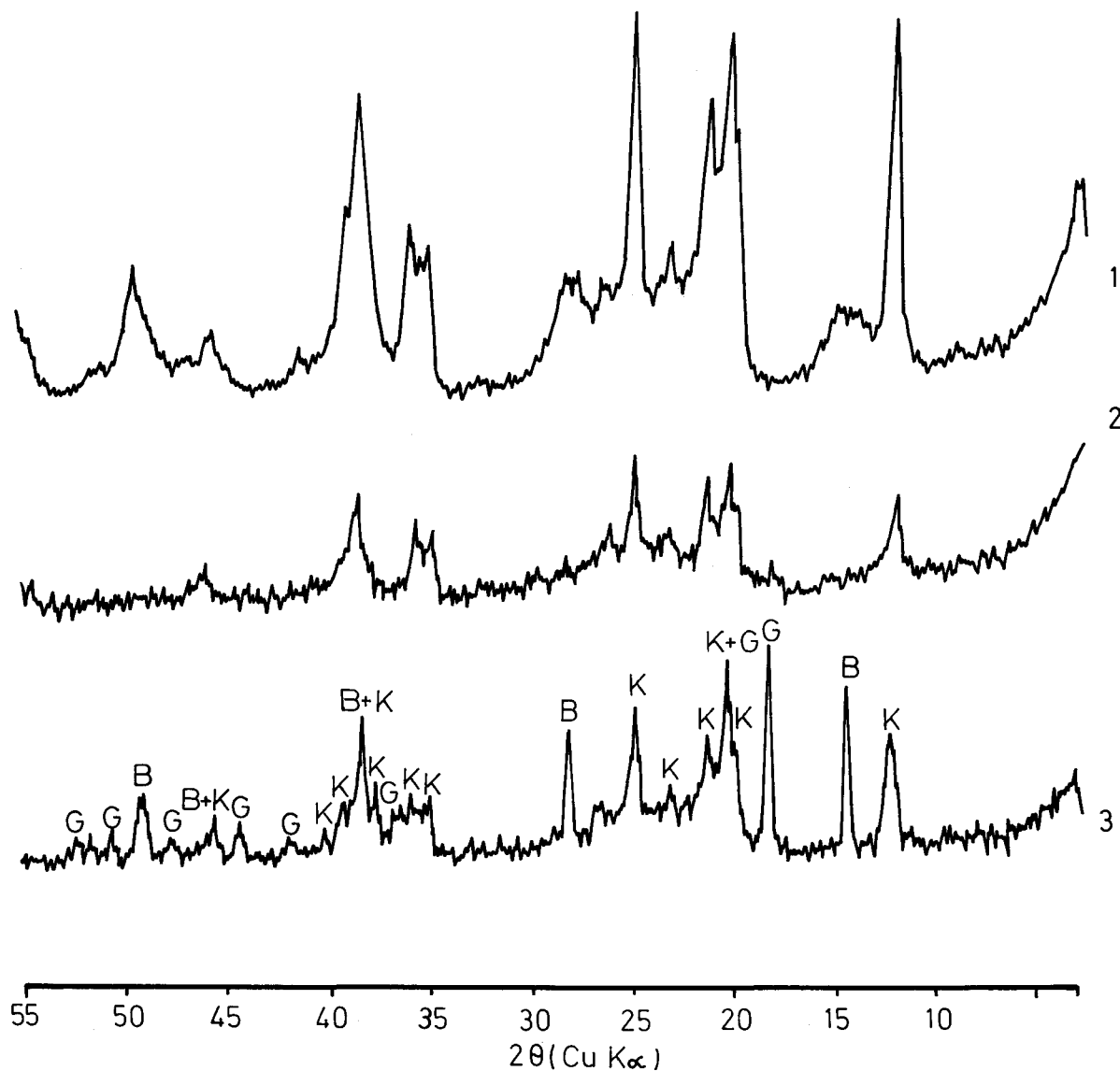


Fig. 9. X-ray data for samples of kaolinite obtained by hydrothermal synthesis: diffractogram 1 for the sample when pseudoboehmite was used as a source of alumina; diffractogram 2, with allophane; and diffractogram 3, with gibbsite as a source of alumina.

pseudoboehmite increases with decreasing activity of water (increasing concentration of NaCl).

Our X-ray powder diffraction measurements show that samples of aluminum hydroxide formed during a short time of treatment (3 minutes), and which are separated from the mother liquor, are always amorphous, whether obtained in distilled water or in water-dioxane solutions, as shown in Figure 5. These precipitates are transformed into bayerite, or into pseudoboehmite, or remained as an amorphous gel if left in the mother liquor, i.e., in water, in 50% dioxane, or in 98% dioxane, respectively.

In some diffractograms of the amorphous gel one can

recognize a reflection at  $2\theta = 46.6^\circ$  (Cu  $K\alpha$ ) which corresponds to  $d = 1.947 \text{ \AA}$ ; this indicates the presence of traces of aluminum metal. These samples have a grayish color.

In Figure 6 the X-ray diffractograms of the following samples are given: a sample of pseudoboehmite obtained at room temperature, diffractogram 4; diffractogram 3 is of the same sample, but treated 4 days at  $80^\circ\text{C}$  in the mother liquor; diffractogram 2 is of the same sample treated 4 days at  $100^\circ\text{C}$ ; diffractogram 1 corresponds to boehmite. It is evident that raising the temperature to  $80^\circ\text{C}$  produces an increase in the intensity of the diffuse X-ray reflections, but the material is still

a pseudoamorphous product and not crystalline boehmite. The name pseudoboehmite was derived from the fact that its diffuse X-ray reflections are similar to those of the mono-oxyhydrate, boehmite (Tertian et al., 1953). The same features were observed by Papée et al. (1958) in the X-ray pattern of pseudoboehmite obtained by precipitation from ionic solutions. They suggest that, although the structure resembles that of boehmite in certain respects, the order is only very short range and of an intramolecular or intramicellar nature. They characterized the pseudoboehmite as having an amorphous character rather than a crystalline one on the basis that it possessed diffraction properties attributed to amorphous materials, namely, that the intensity of diffuse reflections of the pseudoboehmite do not decrease significantly at higher angles, which is common for gels. In fact, the reflections at higher angles become sharper. The sample treated at 100°C (diffractogram 2) shows the reflections of bayerite along with pseudoboehmite.

Figure 7 shows the differential thermal analysis of well crystallized boehmite prepared from gibbsite by hydrothermal synthesis and recorded here only for comparison with other data (curve 1). Curve 2 is that of pseudoboehmite. A high content of low temperature bound water (endothermic maximum at 140°C) is evidence in favor of the high surface area of pseudoboehmite. Curve 3 is that of a completely amorphous sample. Figure 8 shows the thermogravimetric analysis of the samples as in Figure 7: curve 3 is that of boehmite, curve 2 of pseudoboehmite, and curve 1 is that of the amorphous gel. These data confirm the DTA results.

The pseudoboehmite and amorphous gels prepared in this investigation in solutions of water with dioxane or acetone were found to be very stable after being air-dried. X-ray and infrared measurements indicate that samples prepared by the amalgamation reaction have not changed over a period of 15 years.

The samples of pseudoboehmite used for the synthesis of kaolinite under hydrothermal conditions at a relatively low temperature show an appreciable reactivity in comparison with gibbsite, amorphous gel or allophane, when used as a source of alumina. X-ray data for samples of kaolinite prepared at 200°C and corresponding saturated water vapor pressure during 15 days of treatment are shown in Figure 9. One can recognize by the increasing intensity of the basal reflections of kaolinite that the rate of formation was highest when pseudoboehmite (diffractogram 1) was used for the syn-

thesis and the rate decreases in the order: allophane and gibbsite (diffractograms 2 and 3).

The more pronounced reactivity was observed with samples of pseudoboehmite which contained traces of amalgamated aluminum which had not yet reacted with water.

## CONCLUSIONS

From this work we may conclude that the primary aluminum hydroxide formed by reaction of amalgamated aluminum with water is always amorphous, and that the phase composition of the aged product depends, if other parameters (i.e., temperature and pH) are constant, on the activity of water.

Well-crystallized boehmite could not be obtained at the low temperatures (up to 100°C) used in these experiments.

It would be of interest to establish the possibility of forming aluminosilicates at low temperature and pressure using amalgamated aluminum as a source of alumina; this would aid in applying laboratory methods of synthesis to the study of mineral formation under conditions prevailing at the surface of the earth.

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Резюме- Изучалось влияние активности воды на фазовый состав гидроокисей алюминия по результатам реакции амальгамированного алюминия с водой. Реакция проводилась в растворах воды и диоксана и растворах хлористого натрия различной концентрации. Первоначально осаждалась аморфная гидроокись алюминия. Созревание этого первичного продукта до стадии бейерита, псевдобемита или аморфного геля контролировалось по содержанию воды в системе. Псевдобемит показал значительную реактивность при использовании в качестве источника алюминия в гидротермальном синтезе каолинита при относительно низких температуре и давлении.

Kurzreferat- Der Einfluß der Aktivität des Wassers auf die Phasenzusammensetzung von Aluminiumhydroxyden, welche durch Reaktion von amalgamiertem Aluminium mit Wasser erhalten wurden, ist untersucht worden. Die Reaktion wurde in Wasser- und Dioxanlösungen und in Natriumchloridlösungen, verschiedener Konzentrationen, ausgeführt. Das Aluminiumhydroxyd, welches zuerst ausfällt, ist amorph. Das Altern dieses primären Produkts zu Bayerit, Pseudobohemit oder einem amorphen Gel wurde durch den Wassergehalt des Systems kontrolliert. Pseudobohemit zeigte eine erhebliche Reaktivität, wenn es als Ausgangsmaterial für Alumina in der hydrothermalen Synthese von Kaoliniten bei relativer niedriger Temperatur und Druck benutzt wurde.