

FORMATION OF ALUMINUM HYDROXIDES AS INFLUENCED BY ALUMINUM SALTS AND BASES

K. P. PRODROMOU¹ AND A. S. PAVLATOU-VE²

¹ Laboratory of Applied Soil Science and

² Laboratory of Soil Science, Aristotelian University of Thessaloniki
540 06 Thessaloniki, Greece

Abstract—The influence of different ions in the formation of Al(OH)₃ polymorphs has been studied experimentally by promoting stoichiometric reactions between the aluminum salts (AlCl₃, Al(NO₃)₃, Al₂(SO₄)₃) and bases (NaOH, KOH, NH₄OH). In all cases the polymorphs obtained were a mixture of gibbsite, bayerite and nordstrandite or pseudoboehmite with the exception of the reaction between KOH, or NH₄OH and Al₂(SO₄)₃, which produced amorphous gels. Ageing of these gels at ambient temperature and pressure for 180 days or at 60°C for 20 days resulted in crystalline structure. Specifically, pseudoboehmite was crystallized from the reaction between Al₂(SO₄)₃ and NH₄OH. Significantly, of all ions present in solution in the present experiment, only the sulphate ones were observed to have a marked influence in the precipitation of Al oxyhydroxides.

Key Words—Aluminum hydroxides, Pseudoboehmite, Sulfates.

INTRODUCTION

The crystalline forms and chemical behavior of aluminum hydroxides, oxyhydroxides and oxides have been the subject of many studies (Ross and Turner 1971, Violante and Violante 1980, Kodama and Schnitzer 1980, Violante and Jackson 1981, Violante and Huang 1985, Hsu 1989).

The crystalline aluminum hydroxide is the most common form and occurs in three polymorphs; gibbsite, bayerite and nordstrandite. All these polymorphs can be synthesized in the laboratory. Gibbsite, α -Al(OH)₃, was identified by the presence of the three principal diffraction lines at 4.85, 4.37 and 4.32 Å. Bayerite, β -Al(OH)₃, was distinguished by strong diffraction lines at 4.72 and 4.36 Å along with isolated major diffraction lines at 2.21 and 1.72 Å. Nordstrandite, γ -Al(OH)₃, was detected by the appearance of the set of the three major lines at 4.79, 4.33 and 4.22 Å as well as by weaker but nonetheless distinct triplet bands between 3.9 and 3.3 Å. Of these forms, pseudoboehmite, can also be formed from boemite, α -AlO(OH), as it was identified by a series of broad diffraction peaks at 6.6, 3.2, 2.35, 1.85, 1.43, 1.31 and 1.13 Å (Kodama and Schnitzer 1980).

Several factors may affect the formation of these polymorphs such as the pH and OH/Al ratio of the solution, the presence of organic and inorganic ligands and their concentration, the presence of clay minerals, the aluminum and base concentration in the solution, the rate of base addition, the stirring and finally the presence of foreign ligands in the solution.

Many workers (Barnhisel and Rich 1965, Schoen and Roberson 1970) have reported that alkaline media favor the formation of bayerite, whereas acidic media

favor that of gibbsite. In the intermediate pH range, a mixture of nordstrandite with bayerite or gibbsite or both of them was obtained. Further, Hsu (1989) found that the reaction product is gibbsite if the system is kept above pH 12, and bayerite for pH values between 9 and 12. Bayerite and nordstrandite have frequently been prepared by neutralization of an aluminum salt solution with a base.

Another factor that influences the formation of these polymorphs is the ratio NaOH/Al, which depends on the pH of the medium. The presence of a base, especially of NaOH, not only increases the pH of the solution but also the localized high alkalinity could help to pull monomeric species together. Then polymerization of monomeric Al(OH)₃ begins according to the scheme $m\text{Al(OH)}_3 \rightarrow \text{Al(OH)}_{3m}$. For values of the ratio NaOH/Al lying in the range from 2.2 to 2.4 the inclusion of Al in the basic ring is complete. Additional OH⁻ transforms these ring units into larger polymers which gradually increase in size and simultaneously decrease in net positive charge per aluminum atom. At NaOH/Al ratio equal to 3, aluminum is completely neutralized and then crystalline Al(OH)₃ is formed rapidly (Hsu 1989).

Violante and Violante (1980) showed that the chelating organic acids hampered the hydrolytic reactions of Al and affected the nature of the crystalline aluminum hydroxides. Chemical composition, structure, size, nature of functional groups and concentration of each organic anion, as well as the pH of the system, controlled the rate of Al(OH)₃ crystallization. The order of effectiveness of the various acids was as follows: glutaric < succinic = phthalic < glucine < malonic < glutamic < aspartic < oxalic < salicylic = malic < citric < tartaric. An increase in the stability of com-

Table 1. The pH values of the ligand phases (A) after precipitation and (B) after the second washing and the products of aluminum hydroxides were obtained.

Reactions	pH		Time and temperature of ageing		
	A	B	After precipitation	180 days at ambient temper.	20 days at 60°C
AlCl ₃ + NaOH	9.6	8.6	G, B, P	—	G, (B)
AlCl ₃ + KOH	11.0	9.5	G, B, N	—	G, (B)
AlCl ₃ + NH ₄ OH	8.5	8.1	G, B, N, P	—	N, B, G
Al(NO ₃) ₃ + NaOH	10.6	8.0	G, B, P, (N)	—	G, (B)
Al(NO ₃) ₃ + KOH	10.4	9.5	G, B, N, P	—	G, (B)
Al(NO ₃) ₃ + NH ₄ OH	8.5	8.1	G, B, P	—	N, B, G, (P)
Al ₂ (SO ₄) ₃ + NaOH	10.5	9.0	G, B, P	G, B, (P)	G, B, P
Al ₂ (SO ₄) ₃ + KOH	9.8	9.1	A	(P)	(P)
Al ₂ (SO ₄) ₃ + NH ₄ OH	8.7	8.1	A	G, (P)	G, (P)

A = Amorphous aluminum gels G = Gibbsite B = Bayerite P = Pseudoboehmite N = Nordstrandite () = traces — = same crystalline form with previous form.

plexes formed between the organic ligands and Al decreased the rate of crystallization and changed the final products from bayerite to nordstrandite and/or gibbsite and them to pseudoboehmite and/or amorphous material.

Violante and Jackson (1981) demonstrated that in neutral and alkaline solutions, citrate anions favor the crystallization of nordstrandite and/or gibbsite, partic-

ularly in the presence of montmorillonite which acts as a catalyst.

Hsu (1964) suggested that the rate of OH⁻ addition can influence the formation of these polymorphs. He reported that rapid precipitation favored the bayerite structure, while slow crystal growth favored the gibbsite structure. The nature and concentration of anions may play an important role in the formation of the various polymorphs of aluminum hydroxide, and influences the stability of the basic salts formed. With anions such as Cl⁻, ClO₄⁻ and NO₃⁻, which do not have strong affinity for aluminum, the basic salts are highly soluble and yield clear solutions. Also, the OH-Al polymers continue to hydrolyze and polymerize into larger units during prolonged ageing unless a high concentration of a counter anion is present. In the presence of anions that exhibit strong affinity for Al, such as sulphate, phosphate and silicate, precipitation of basic salts occurs rapidly after mixing with the counter anions. Therefore, most of the basic salts formed are amorphous. Because of the affinity for Al, these anions prevent or at least retard the Al-OH polymers from further hydrolysis and polymerization into crystalline Al(OH)₃ (Hsu 1989).

Kodama and Schnitzer (1980) have studied the effect of fulvic acid (FA), on the crystallization of aluminum hydroxides. They showed that in the absence of FA, gibbsite was formed at pH 6, a mixture of nordstrandite and bayerite at pH 8, and bayerite crystallized at pH 10. At pH 6 and 8, the addition of increasing amounts of FA first delayed and then inhibited the crystallization of these aluminum hydroxide polymorphs but tended to favor the crystallization of pseudoboehmite. At pH 10, the addition of FA totally inhibited crystallization and precipitation.

The purpose of this paper is to study the synthesis of Al(OH)₃ forms by using aluminum salts and bases in proportions dictated by the synthesis reactions. Aluminum chloride, nitrate and sulphate salts were allowed to react with sodium, potassium hydroxide and

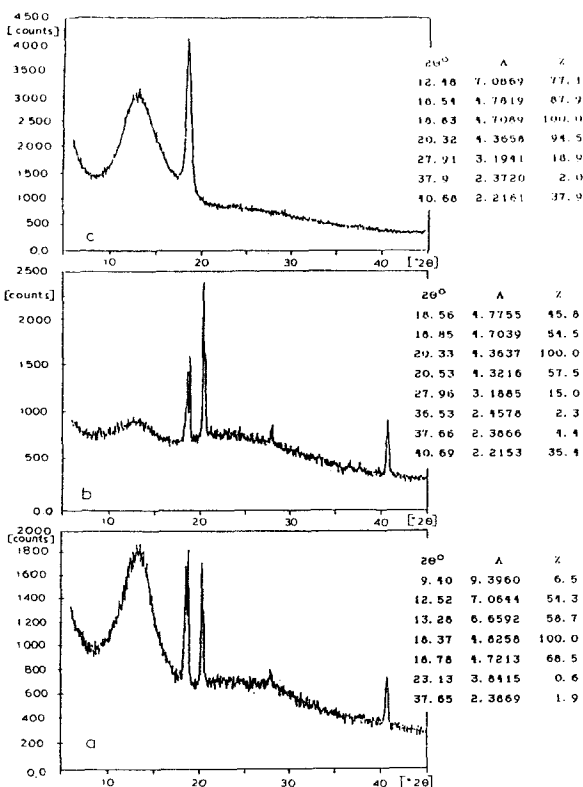


Figure 1. X-ray diffractograms were obtained after precipitation, from reactions AlCl₃ with NaOH (a), KOH (b) and NH₄OH (c).

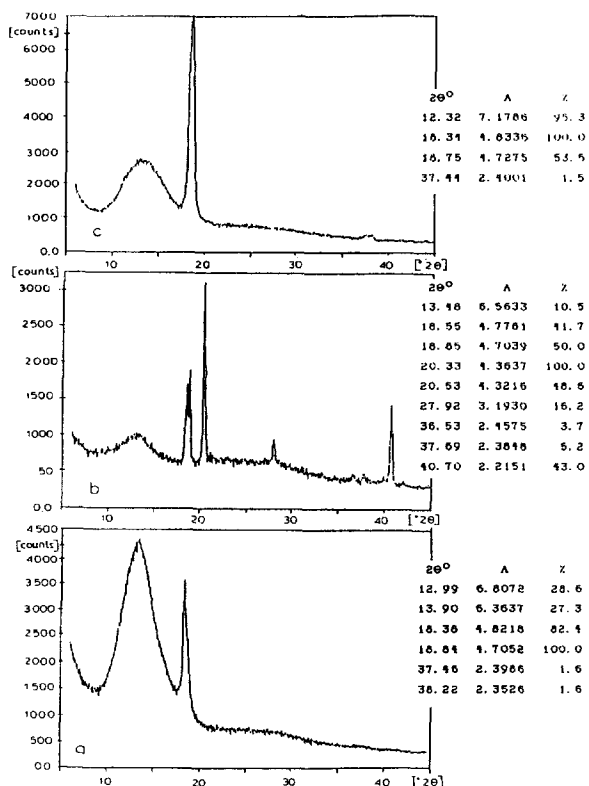
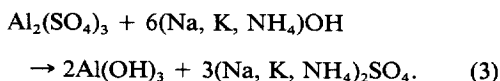
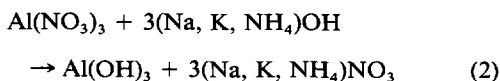
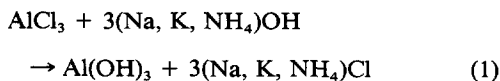


Figure 2. X-ray diffractograms were obtained after precipitation, from reactions $\text{Al}(\text{NO}_3)_3$ with NaOH (a), KOH (b) and NH_4OH (c).

ammonia solution, and the products were examined using X-ray diffraction in order to detect the influence of different anions and cations in the formation of aluminum hydroxide forms.

MATERIALS AND METHODS

In the present study $\text{Al}(\text{OH})_3$ was synthesized according to reactions (1), (2), and (3) below. The quantities of the salts (AlCl_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Al}_2(\text{SO}_4)_3$) and bases (NaOH , KOH and NH_4OH) used are those dictated by the synthesis reactions themselves.



The precipitation of $\text{Al}(\text{OH})_3$ took place in 50 ml centrifuge tubes. 20 ml of 0.5 M AlCl_3 or $\text{Al}(\text{NO}_3)_3$ solutions were titrated with 20 ml of 1.5 M (Na , K , NH_4) OH solution. 20 ml of 0.25 M $\text{Al}_2(\text{SO}_4)_3$ solution

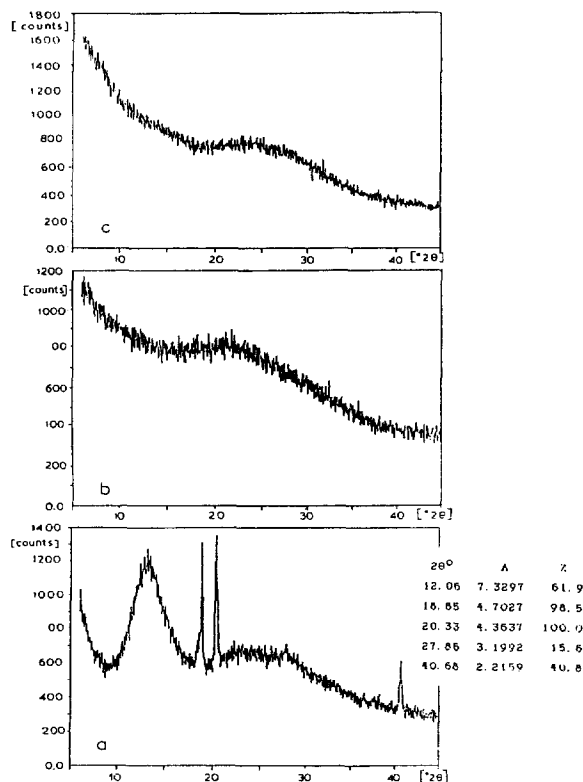


Figure 3. X-ray diffractograms were obtained after precipitation, from reactions $\text{Al}_2(\text{SO}_4)_3$ with NaOH (a), KOH (b) and NH_4OH (c).

were titrated with 20 ml 1.5 M (Na , K , NH_4) OH solution.

The bases were added at a rate of 1 ml per 15 sec. The tubes were then sealed and agitated at ambient temperature and pressure for 20 min and subsequently centrifuged at 3000 rpm for 10 min. The pH of the gels formed in the tubes as measured (Table 1). Afterwards the gels were washed twice with distilled water. These two washes aimed at lowering the pH value and remove the ions of the formed salts, in order to have no strong effect during the ageing phase. Hence, the pure effects of the anion of the aluminum salts and of the cation of the bases used in the synthesis experiments are restricted only in the phase after the precipitation.

In two sets of experiments, the gels were left to age at ambient temperature and pressure for a) 10 days and b) 6 months. In another set of experiments the gels were left to age for 20 days at 60°C.

The $\text{Al}(\text{OH})_3$ polymorphs synthesized by reactions (1), (2) and (3) were identified using X-ray diffraction.

RESULTS AND DISCUSSION

The forms of $\text{Al}(\text{OH})_3$ synthesized according to these reactions are given in Table 1 and Figures 1–5. In all

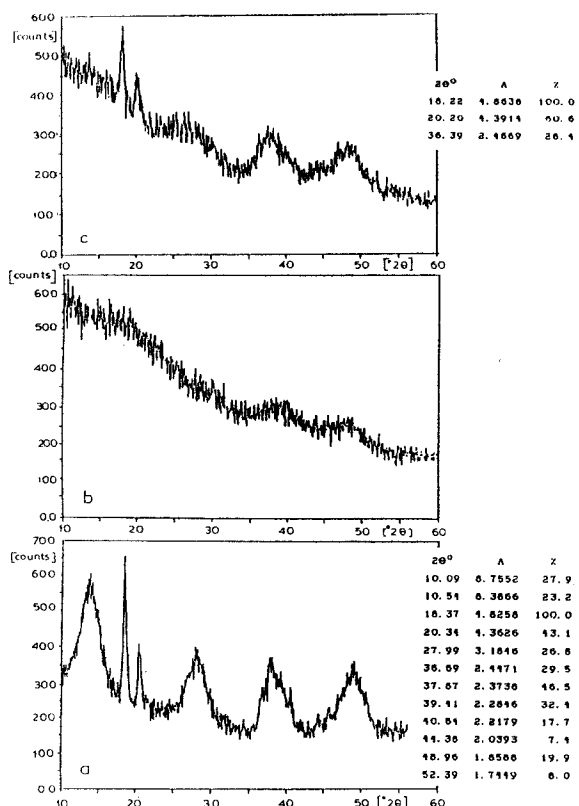


Figure 4. X-ray diffractograms were obtained after 180 days from the precipitation, from reactions $\text{Al}_2(\text{SO}_4)_3$ with NaOH (a), KOH (b) and NH_4OH (c).

cases the X-ray diffraction traces of the reaction products revealed the formation of a mixture gibbsite (G), bayerite (B), nordstrandite (N) or pseudoboehmite (P), with the exceptions of the reactions between $\text{Al}_2(\text{SO}_4)_3$ and KOH or NH_4OH which gave amorphous products.

The reactions of the aluminum salts with NaOH resulted in the formation of a mixture of G, B, P and traces of N. On the other hand, the reactions of the aluminum salts with NH_4OH produced a mixture of G, B, N and P.

The mixtures of G, B, N and P are formed because Cl^- and NO_3^- do not have strong affinity for aluminum. On the contrary, amorphous gels are formed because of the strong affinity of SO_4^{2-} for aluminum (Hsu 1989).

To the best of our knowledge the use of KOH to precipitate $\text{Al}(\text{OH})_3$ is not mentioned in the literature. Our results showed that the reaction of AlCl_3 and $\text{Al}(\text{NO}_3)_3$ with KOH gave mixtures of G, B, N and P. Amorphous gels were obtained from the reaction between $\text{Al}_2(\text{SO}_4)_3$ and KOH.

Mixtures of $\text{Al}(\text{OH})_3$ polymorphs similar to those of the present study have been reported by many researchers (Ross and Turner 1971, Violante and Vio-

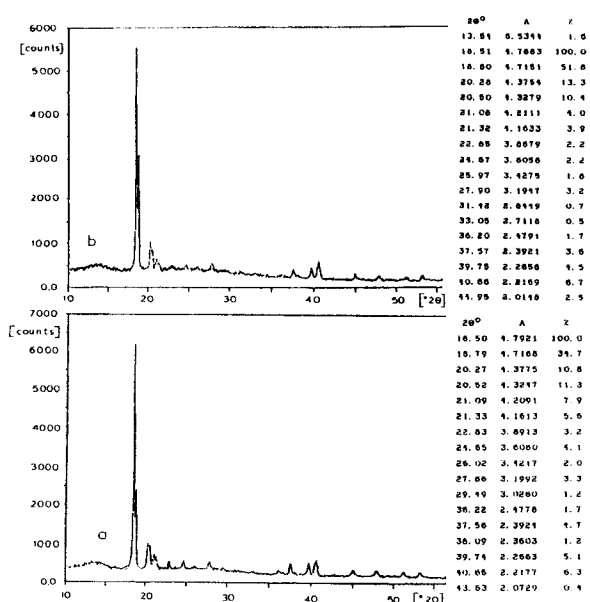


Figure 5. X-ray diffractograms were obtained after ageing for 20 days at 60°C , from reactions AlCl_3 with NH_4OH (a) and $\text{Al}(\text{NO}_3)_3$ with NH_4OH (b).

lante 1980, Kodama and Schnitzer 1980, Violante and Jackson 1981, Violante and Huang 1985), who precipitated $\text{Al}(\text{OH})_3$ either at particular pH values or by keeping the NaOH/Al ratio constant.

Ageing of the synthesis products for 10 or 180 days at ambient temperature and pressure has no effect on the form of aluminum hydroxides produced by reactions (1) and (2). In the mixtures obtained by reaction with KOH (3) only small amounts of P have been detected. On the other hand, the aluminum hydroxides synthesized using NH_4OH are mixtures containing mainly G and small amounts of P.

$\text{Al}(\text{OH})_3$, produced by reactions (1) and (2) transforms after ageing for 20 days at 60°C , mainly to crystalline formed G with traces of B. The absence of P and N implies that thermal annealing brought about polymerization of P or N to G. By contrast, in the case of reaction 3, thermal annealing seems to have no effect at least under the same conditions, on the composition of the products (e.g., the synthesized $\text{Al}(\text{OH})_3$ still contains G, B, N and small amount of P).

In conclusion, we have shown that the aluminum hydroxides synthesized according to reaction types (1), (2) and (3) are mixtures of G, B, P or N. The mixture composition is stable under certain ageing conditions. We have found that both the anion of the aluminum salts and the cation of the bases used in the synthesis reactions have no influence on the form of the gels produced. The only influence we have noticed is that of SO_4^{2-} , which in the presence of KOH or NH_4OH gave amorphous gels.

REFERENCES

- Barnhisel, R. I., and C. I. Rich. 1985. Gibbsite, bayerite and nordstrandite formation as affected by anions, pH and mineral surfaces. *Soil Sci. Soc. Am. Proc.* **29**: 531–534.
- Hsu, Pa Ho, and T. F. Bates. 1964. Formation of X-ray amorphous and crystalline aluminum hydroxides. *Mineral. Mag.* **33**: 749–768.
- Hsu, Pa Ho. 1989. *Minerals in Soil Environments*. Madison, Wisconsin: Soil Sci. Soc. Am., 331–378.
- Kodama, H., and M. Schnitzer. 1980. Effect of fulvic acid on the crystallization of aluminum hydroxides. *Geoderma* **24**: 195–205.
- Kwong Ng Kee, K. F., and P. M. Huang. 1977. Influence of citric acid on the hydrolytic reaction of aluminum. *Soil Sci. Soc. Am. J.* **41**: 692–697.
- Ross, G. J., and R. C. Turner. 1971. Effect of different anions on the crystallization of aluminum hydroxide in partially neutralized aqueous aluminum salt systems. *Soil Sci. Soc. Am. Proc.* **35**: 389–392.
- Schoen, R., and E. C. Roberson. 1970. Structures of aluminum hydroxide and geochemical implication. *Am. Mineral.* **55**: 43–77.
- Violante, A., and P. Violante. 1980. Influence of pH, concentration, and chelating power of organic anions on the synthesis of aluminum hydroxides and oxyhydroxides. *Clay & Clay Miner.* **28**: 425–433.
- Violante, A., and M. L. Jackson. 1981. Clay influence on the crystallization of aluminum hydroxide polymorphs in the presence of citrate, sulfate or chloride. *Geoderma* **25**: 199–214.
- Violante, A., and P. M. Huang. 1985. Influence of inorganic and organic ligands on the formation of aluminum hydroxides and oxyhydroxides. *Clay & Clay Miner.* **33**: 181–192.

(Received 29 April 1993; accepted 8 August 1994; Ms. 2374)