

FORMATION OF X-RAY AMORPHOUS AND CRYSTALLINE ALUMINUM HYDROXIDES

by

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EXTENDED ABSTRACT

Various crystalline and X-ray amorphous forms of aluminum hydroxides and hydroxy-aluminum solutions were prepared by adding 0.1 N NaOH to 0.2 N $\text{Al}_2(\text{SO}_4)_3$ or 0.5 N AlCl_3 solution dropwise with vigorous stirring. The amount of NaOH was adjusted to give a NaOH/Al ratio in the final suspension of from 0.0 to 3.3. In most of the preparations, the concentrations of aluminum, chloride or sulfate were all 0.05 eq./liter. In some samples in the $\text{AlCl}_3 + \text{NaOH}$ system, higher aluminum and chloride concentrations were used in order to obtain a precipitate product. Extra sulfate was added to some samples in the $\text{Al}_2(\text{SO}_4)_3 + \text{NaOH}$ system to study its effect on the composition of the product.

The precipitate products were analyzed for their aluminum and OH^- contents, and for the sulfate content in cases where it was involved in the preparation. The OH^- content was determined by treating the precipitate with NaF solution to complex the aluminum and by then titrating the OH^- released to the solution with HCl. The precipitate was treated with N HCl and the aluminum dissolved was determined to measure the resistance of the product to this acid. The structure of the precipitate was studied by X-ray diffraction.

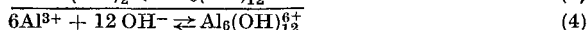
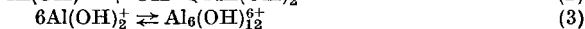
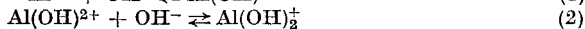
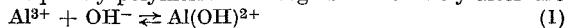
The hydroxy-aluminum solutions which were obtained in the $\text{AlCl}_3 + \text{NaOH}$ system when the concentration of aluminum was 0.05 eq./liter, were treated with Dowex-50, $\times 8$ in order to separate Al^{3+} from the hydroxy-aluminum species and permit the determination of each.

The results showed that the products could be separated into two categories according to the NaOH/Al ratio involved in their preparation. When NaOH/Al = 3 and 3.3, crystalline $\text{Al}(\text{OH})_3$ in the form of bayerite, nordstrandite and/or gibbsite appeared to be the main constituent in the precipitate. The X-ray diffraction peaks appeared several hours after preparation, and became sharper and larger as the period of aging increased. The products became highly resistant to acid shortly after preparation. A broad X-ray peak with its maximum at 6.5 Å spacing was also observed. This peak corresponds to that of pseudoboehmite proposed by Calvet *et al.* (1953) (see also Papee, Tertian and Biais, 1958). Despite the huge area of this peak as compared with that of the $\text{Al}(\text{OH})_3$ peaks, the chemical analysis indicated that this component accounted for only a minor portion of the aluminum in the precipitate.

When the NaOH/Al ratio was 2.75 or below, the products were basic aluminum sulfates or chlorides, as indicated by the chemical analyses. They were completely dissolved in N HCl in 20 minutes and amorphous to X-ray diffraction even after 6 months of aging. In the 0 to 2.1 range of NaOH/Al ratio, the composition of the products was constant, being approximately $\text{Al}(\text{OH})_{2.2}\text{X}_{0.8}$. In the 2.1 to 2.75 range a continuous series of basic salts was obtained. Seeding the amorphous precipitate with bayerite and subsequent aging for two months did not produce any crystalline $\text{Al}(\text{OH})_3$.

The following hypothesis is proposed to account for the amorphous or crystalline character of the various products in these systems.

When NaOH is added to an aluminum salt solution, the initial reaction should be expressed by equations 1 and 2 given below. However, neither the $\text{Al}(\text{OH})^{2+}$ nor the $\text{Al}(\text{OH})_2^+$ unit is stable and consequently polymerization begins immediately after the



OH^- ion is attached to the Al^{3+} ion. The most probable structure of the resulting hydroxy-aluminum polymer is a ring unit composed of six $\text{Al}(\text{OH})_2^+$ units (eq. 3), and the reaction is summarized by equation 4. At $\text{NaOH}/\text{Al} = 2$, the transformation of Al^{3+} into the 6 member ring is complete. Still further OH^- then goes to the single ring unit, thereby providing a bridge to another such unit forming, upon rearrangement, a double ring. After this transformation is complete, the further addition of NaOH then transforms the double ring into a triple ring, and so on. Based on this reasoning, increased addition of NaOH results in increased polymer size and the formation of a continuous series of species.

The net charge per aluminum ion decreases with increasing NaOH/Al ratio, but all of the aluminum polymers remain positively charged until the ratio reaches 3. Thus, up to this point the hydroxy-aluminum polymers repel one another.

In order to maintain electro-neutrality, there must be some anions between these positively charged polymers thereby giving rise to basic aluminum sulfate or chloride salts. Although, under certain conditions, these salts may be crystalline, the large amount of hydration of the polymers and the effect of the anions connecting them apparently promotes the formation of amorphous products.

The net charge per Al^{3+} vanishes at $\text{NaOH}/\text{Al} = 3$. Consequently, the repulsion among polymers, as well as their hydration water, vanishes and all the polymers cluster together and form crystalline $\text{Al}(\text{OH})_3$ in a matter of hours.

REFERENCES

- Calvet, E., Boivinet, P., Noel, M., Thibon, H., Maillard, A., and Tertian, R. (1953) Contribution to the study of aluminum gels; *Bull. Soc. Chim. France*, pp.99-108.
 Papee, D., Tertian, R., and Biais, R. (1958) Studies of the constitution of gels and crystalline hydrates of alumina; *Bull. Soc. Chim. France*, pp.1301-1310.