Effect of sulfate on the crystallization of $Al(OH)_3$ from aging hydroxy-aluminum solutions[1]

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A series of samples were prepared by adding varying amounts of Na_2SO_4 to a hydroxy-aluminum solution (NaOH/Al mole ratio = 2.6; 0.02 M in Al) and diluting to 0.002 M in Al. Crystalline $Al(OH)_3$ was found in the control shortly after preparation and its amount increased with time, accounting for 79% of the total Al after 3 years. The presence of sulfate greatly inhibited the crystallization of $Al(OH)_3$. With 0.1 eq. of $SO_4^{=}$ per mole of Al, only 12% of the total Al was converted to crystalline $Al(OH)_3$ after 3 years. With 0.2 eq. or more $SO_4^{=}$ per mole of Al, the reaction products were either amorphous or crystalline basic aluminum sulfate even after prolonged aging.

1. INTRODUCTION

By slowly adding dilute NaOH to an aluminum salt solution, true solutions containing polynuclear OH-Al species less than 10 Å in size can be obtained up to NaOH/Al mole ratio = 2.4. With NaOH/Al mole ratio = 2.55 or 2.7, the products showed a very weak Tyndell effect (< 1 JTU) but were still clear to the naked eye (Hsu and Bates, 1964). Many such partially neutralized aluminum solutions, however, are only meta-stable and eventually turn turbid, with crystalline $Al(OH)_3$ precipitate developed as a separate phase after prolonged aging (Hsu, 1966; Hem and Roberson, 1967; Turner, 1968; Turner and Ross, 1970; Ross and Turner, 1971; Smith, 1971). It was also reported that the process of $Al(OH)_3$ crystallization can be inhibited by adding extra Cl^- or accelerated by lowering the concentration of Cl^- in the medium (Gastuche and Herbillon, 1962; Hsu, 1966). Ross and Turner (1971) showed that Cl^- was more effective than NO_3^- in inhibiting thecry stallization of $Al(OH)_3$ while ClO_4^- ion did not show inhibition at all. The $Al(OH)_3$ crystallization was also inhibited in the presence of vermiculite (Hsu and Bates, 1964b) and, to a less extent, by montmorillonite (Turner and Brydon, 1967; Hsu, 1968). This report presents results illustrating that the crystallization of $Al(OH)_3$ is greatly inhibited in the presence of sulfate.

(1) Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University-The State University of New Jersey, New Brunswick, N. J. 08903, U.S.A.

2. METHODS

2.1. Sample Preparation

A stock solution of NaOH/Al mole ratio = 2.6 and 0.02 M in Al was prepared by adding 1,040 ml. of 0.1 N NaOH to 200 ml. of 0.2 M $AlCl_3$, drop by drop, at a rate of 100 ml/hr., under vigorous stirring, and then diluting to 2 l. This solution is known to consist mainly of positively charged polynuclear OH-Al species of average net positive charge 0.4 eq. per mole of Al (Hsu and Bates, 1964). To avoid any possible complication caused by irregular preparation, this solution was aged for 3 days or until its turbidity decreased to less than 1 JTU before using. Eight samples of SO_4/Al mole ratios = 0 to 1 were prepared by mixing appropriate amounts of the stock OH-Al solution and 0.1 N Na_2SO_4 and diluting to 0.002 M in Al. These samples were periodically analyzed during aging up to 3 years.

2.2. Chemical analysis

An aliquot was taken from each sample and centrifuged. The precipitate was washed twice with 70% alcohol and dispersed in 10 ml. of 1 N HCl for 20 min. The residual precipitate, if any, was re-centrifuged at the end of 20 min. and dissolved in another 10 ml. of 1 N HCl at 70 °C. The Al and SO_4 contents of both HCl extracts were determined and the SO_4/Al ratio in the precipitate was assumed to be equivalent to the residual positive charge of the polynuclear OH-Al units. The Al in the first HCl extract is referred to as basic aluminum sulfate or amorphous aluminum hydroxide. The Al in the second HCl extract is referred to as crystalline Al $(OH)_3$. Only a small amount of Al precipitate in the control and no Al precipitate at all in the two low-sulfate samples were separated after being centrifuged at 1000 G for 30 min. Then, 2 ml. of 0.1 N Na_2SO_4 were added to 100 ml. aliquots of these three samples, allowed to stand for 1 hr. and centrifuged. The precipitate was then analyzed as others.

2.3. X-ray diffraction

A suitable sample aliquot was centrifuged through Millipore filters of predetermined pore size. The filter containing the precipitate was pasted onto a glass slide and x-rayed.

3. RESULTS

3.1. Solution pH, turbidity and precipitation of aluminum

The initial pH values of all samples were about 5.5, but their changes in pH with time were noticeably different (Table 1). The pH value of the control, to which no sulfate was added, began to decrease approximately 15 days after preparation and reached 4.1 after 8 months, with no further change thereafter. The presence of sulfate markedly prolonged the induction periods and reduced the magnitude of pH change. With 0.6 eq. or more of $SO_4^=$ added per mole of aluminum, no significant decrease in pH was observed up to at least 3 years.

The control was initially clear with a turbidity reading of 0.1 JTU. Its turbidity began to increase after 15 days and rapidly developed to a dense turbid suspension shortly afterwards. Settleable precipitate was first observed some 40 days after preparation but it accounted for only 13% of the total Al at the end of 3 years. With 0.1 and 0.2 eq. $SO_4^=$ added per mole of aluminum, the turbidities were 0.3 and 2.8 JTU, respectively, when freshly prepared, the former being clear to the naked eye and the latter being slightly visibly turbid. Both of these two samples increased their turbidities very slowly during

TABLE I

Change in pH during aging of a partially neutralized Al solution in the presence of sulfate
Time of aging, days

$SO_4^=$ Added *	0	5	10	15	30	60	180	240	525	1080
0	5.52	5.76	5.74	5.26	5.10	4.53	4.36	4.09	4.12	4.10
0.1	5.57	5.49	5.48	5.42	5.41	5.36	5.15	4.90	4.53	4.43
0.2	5.44	5.34	5.40	5.36	5.36	5.42	5.20	5.10	5.12	4.89
0.3	5.35	5.32	5.37	5.33	5.35	5.38	5.26	5.14	5.08	4.98
0.4	5.30	5.30	5.34	5.35	5.35	5.38	5.27	5.18	5.08	4.97
0.6	5.50	5.49	5.55	5.57	5.73	5.80	5.64	5.31	5.56	5.48
1.2	5.51	5.68	5.73	5.80	5.84	5.72	5.83	5.51	5.70	5.72
2.0	5.62	5.98	6.03	6.13	6.13	5.78	6.05	5.69	5.52	5.73

* Eq. per mole of Al. The concentration of Al was 0.002 M in all samples.

aging. At the end of 3 years, the turbidities of these two samples were 37 and 25 JTU, respectively and no precipitate was observed after being centrifuged at 1000 G for 30 min. With 0.4 eq. or more $SO_4^=$ added per mole of Al, precipitation took place almost immediately after preparation, resulting in a relatively light suspension.

3.2. **Nature of reaction product**

The results of x-ray diffraction indicate that crystalline $Al(OH)_3$ was observed in the control as soon as it became visibly turbid, 19 days after preparation. The crystallinity slightly improved with time but no other change was observed (curves 1 and 2, Fig. 1). The amount of crystalline $Al(OH)_3$ gradually increased with time and accounted for 79.2% of the total Al at the end of 3 years (Table 2). In this determination, the suspended particles were precipitated by adding excess $Na_2\ SO_4$ and standing for 1 hr. prior to the regular procedure of HCl extraction. The portion of Al dissolved in the 1 N HCl-20 min.

TABLE II

Changes in the contents of crystalline $Al(OH)_3$, % total Al, during aging
Time of aging, days

$SO_4^=$ added *	30	60	180	525	1080
0	9.2	32.3	51.5	77.5	79.2
0.1	nil	nil	nil	—	12.0

* Eq. per mole of Al. No crystalline $Al(OH)_3$ were found in all other samples of 0.2 eq. or more $SO_4^=$ added per mole of Al.

TABLE III

Change in sulfate content in precipitate, eq. SO_4/mole Al,
with time and with the SO_4/Al ratio in sample preparation
Time of aging, days

SO_4/Al in prep. eq./mole	15	30	60	180	525	1080
0*	—	0.24	0.23	0.20	0.17	0.16
0.1*	—	0.26	0.23	0.22	—	0.21
0.2*	—	0.25	0.23	0.23	—	0.23
0.3	0.25	0.24	0.27	0.26	0.25	0.25
0.4	0.24	0.27	0.28	0.28	0.26	0.29
0.6	0.32	0.32	0.34	0.31	0.32	0.33
1.2	0.32	0.33	0.33	0.31	0.30	0.32
2.0	0.32	0.32	0.37	0.34	0.32	0.32

* Excess Na_2SO_4 was added to precipitate aluminum from solution before analysis. Crystalline Al was not included in calculation.

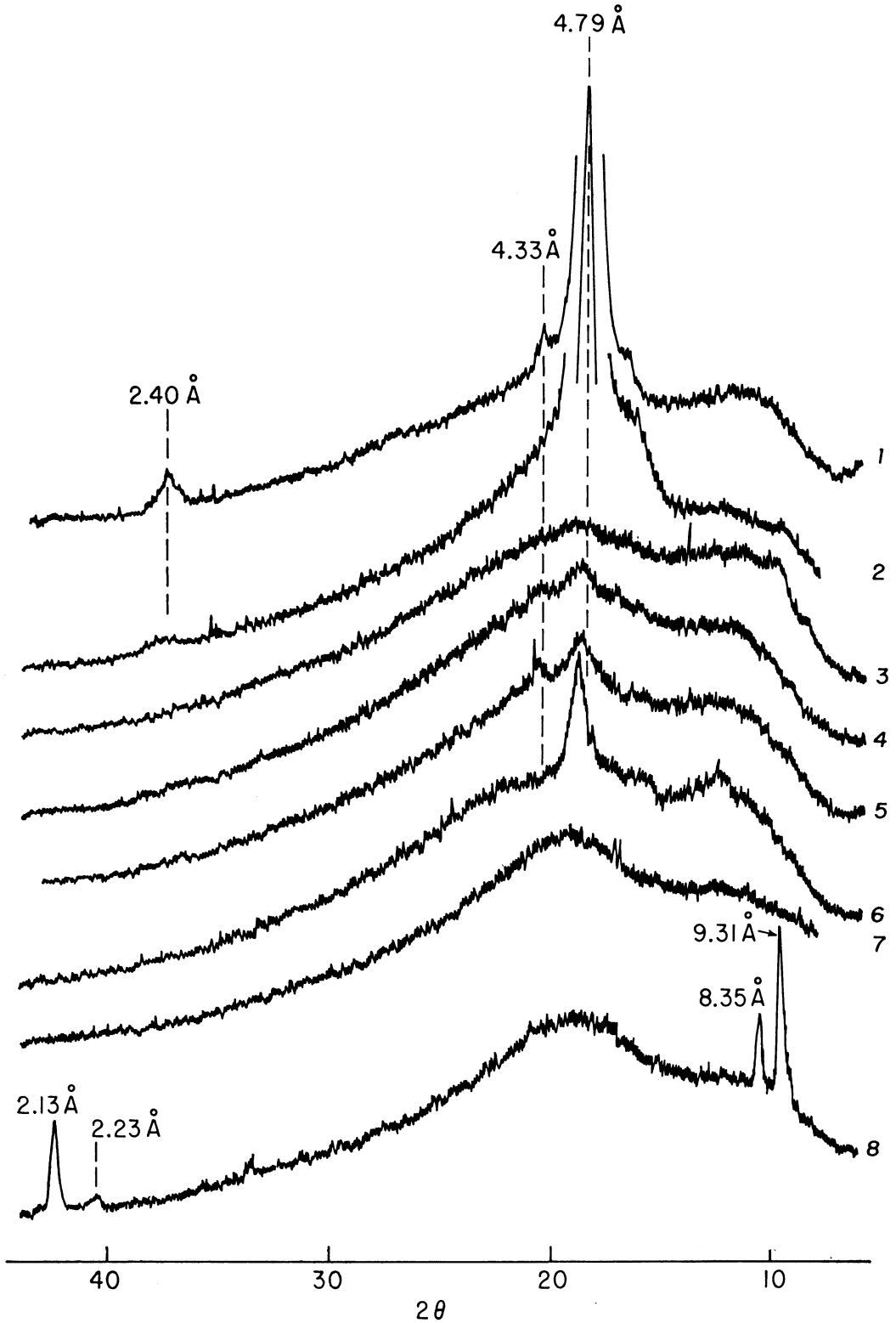

Fig. 1. — X-Ray diffraction patterns of representative reaction products:
Curve 1: Control, 3 years, settled precipitate. — Curve 2: Control, 19 days, suspended particles, > 0.25μm
Curves 3-6: 0.1 eq. $SO_4^{=}$ added per mole of Al, 3 yr., suspended particles:
3: > 3 μm. — 4: 1.2-3μm. — 5: 0.65-1.2 μm. — 6: 0.45-0.65 μm
Curve 7: 0.4 eq. $SO_4^{=}$ added per mole of Al, 3 yr., precipitate.
Curve 8: 0.6 eq. $S_4^{=}O$ added per mole of Al, 14 days, precipitate

extraction is referred to as amorphous $Al(OH)_3$ whereas the residual Al, as crystalline $Al(OH)_3$. This separation, although arbitrary, provides useful information for comparison. Chemical analysis indicates that amorphous $Al(OH)_3$, after being precipitated with Na_2SO_4, contains a considerable amount of $SO_4^=$. By assuming that $SO_4^=$ does not disrupt the internal structure of aluminum hydroxide, the SO_4/Al ratio in the precipitate may then be considered to be its residual positive charge. It is shown in Table 3 that the residual positive charge of the amorphous aluminum hydroxide gradually reduced during aging. The results also show that crystalline $Al(OH)_3$ contains a small amount of $SO_4^=$ equivalent to 0.01 eq. per mole of Al. This charge, although small, probably is the key factor keeping $Al(OH)_3$ particles from precipitation. It should be noted that only a fraction of the total crystalline Al $(OH)_3$ can be separated by centrifugation at 1000 G for 30 min.

With 0.1 eq. of $SO_4^=$ added per mole of Al, the reaction product up to a least 6 months was amorphous to x-ray diffraction and dissolved rapidly in 1 N HCl. A mixture of crystalline $Al(OH)_3$ and amorphous basic aluminum sulfate was observed at the end of 3 years, however. When a sample aliquot was filtered through a series of Millipore filters and x-rayed, crystalline $Al(OH)_3$ was found largely in the 0.45-0.65 μm fraction (curves 3-6, Fig. 1). Chemical analysis indicates that crystalline $Al(OH)_3$ accounted for 12% of the total Al and was also slightly charged, approximately 0.01 eq. per mole of Al. The amorphous component was basic aluminum sulfate with its basicity increasing slightly with time. No analysis was made between 6 months and 3 years and therefore, the time for the first appearance of crystalline $Al(OH)_3$ is not known.

With 0.2, 0.3, or 0.4 eq. of $SO_4^=$ added per mole of Al, the reaction products, suspended particles or settled precipitate, were amorphous to x-ray diffraction (curve 7, Fig. 1) and dissolved rapidly in 1 N HCl even after prolonged aging. The precipitates of these three samples contained 0.23, 0.25 and 0.28 eq. of $SO_4^=$ per mole of Al, respectively, and no significant change during aging was observed.

A crystalline basic aluminum sulfate was observed in all samples with 0.6 eq. or more $SO_4^=$ added per mole of Al. With 0.6 eq. of $SO_4^=$ added, the precipitate yielded a weak peak at 9.31 Å one day after preparation, and well defined peaks at 9.31 Å, 8.35 Å and 2.13 Å after 14 days (curve 8, Fig. 1). With 2 eq. of $SO_4^=$ added, the same well-defined peaks were observed only 1 day after preparation. When a random specimen was x-rayed, additional peaks at 7.4 Å, 4.55 Å, 4.31 Å, 3.74 Å, 3.30 Å, 3.26 Å, 2.71 Å and 2.28 Å were observed. The diffraction pattern is close to that of basaluminite (Brydon and Singh, 1969). All samples dissolved rapidly in 1 N HCl when freshly prepared. Although their resistance to acid gradually increased with time, they were still completely dissolved in 1 N HCl in less than 20 min. even after three years of aging. All precipitates contained 0.32 eq. $SO_4^=$ per mole of Al, corresponding to the composition $Al(OH)2.68\ (SO_4)0.16$. This composition is considerably more basic than basaluminite and other reported basic aluminum sulfate (Brydon and Singh, 1969); Hollingworth and Bannister, 1950, Hsu and Bates, 1964).

4. DISCUSSION

It can be concluded from the results that the formation of crystalline $Al(OH)_3$ is markedly inhibited in the presence of $SO_4^=$. According to Hsu and Bates (1964), the polynuclear OH-Al species in a fresh, partially neutralized aluminum solution is composed of two planes of closely packed OH^- ions with Al^{3+} sandwiched between them and distributed as hexagonal rings, following the same pattern as gibbsite. The Al^{3+} ions at the edge, however, are not fully neutralized by OH^- ions, resulting in a positively charged edge. Crystallization involves the combination of such units vertically as well as horizontally,

the latter case requiring the introduction of addition OH^- linkages. Thus, unless adequate OH^- ions are added to neutralize the residual positive charge, the additional OH^- required for crystallization can only be acquired through the hydrolysis of edge Al^{3+}. This explains that the development of crystalline $Al(OH)_3$ must be accompanied by a decrease in pH. On the basis of this mechanism, any anion that can be bonded to the edge Al with adequate strength will be able to prevent the secondary hydrolysis and the development of crystalline $Al(OH)_3$. $SO_4^=$ is an example. As compared with $SO_4^=$, $PO_4^=$ forms a stronger complex with Al^{3+} and is thus more effective in inhibiting $Al(OH)_3$ crystallization (unpublished data). On the other hand, Cl^- forms only weak complexes with Al^{3+} and therefore the crystallization of $Al(OH)_3$ is inhibited only in the presence of high Cl^- concentration (Hsu, 1966). ClO_4^- has generally been assumed not to form complexes with Al^{3+} and therefore does not inhibit the process of $Al(OH)_3$ crystallization (Ross and Turner, 1971). Vermiculite and montmorillonite can be considered to be anions in solid state and therefore their effects on $Al(OH)_3$ crystallization can be interpreted similarly (Hsu and Bates, 1964; Hsu, 1968; Turner and Brydon, 1967). In short, the ionic environment in a system must be taken into consideration in elucidating the formation or non-formation of $Al(OH)_3$. Furthermore, if there is not an adequate amount of $SO_4^=$ present, part of the edge Al^{3+} may hydrolyze further and form a more basic sulfate. The product may be present as precipitate or stable suspension, depending on the residual charge and particle size, but there should be no difference in the formation mechanism.

The above interpretation is based on the assumption that $SO_4^=$ can be bonded to the edge Al^{3+} with moderate strength but is not able to disrupt the internal Al-OH linkage. This assumption is corroborated by the results that the three samples of high sulfate content (0.6 to 2 eq. $SO_4^=$ per mole of Al) have nearly the same pH and same composition during the entire period of study. Substitution of $SO_4^=$ for structural OH^- should result in increases in pH and sulfate content.

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