The Reaction of Aluminum Sulfate and Calcium Carbonate. I. Preparation of Basic Aluminum Sulfate Sol and its Hydrolysis

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Introduction. It has been known that basic aluminum sulfate may be produced by dissolving aluminum hydroxide in aluminum sulfate solution. The solubility of the oxide measured by R. Kremann, K. Hüttinger[1] was relatively small at room temperature and the ratio of Al_2O_3: SO_3 is about 1 mol:2 mol. N. Grüstein[2] has claimed in his patent that pure aluminum hydroxide is prepared by the hydrolysis of basic aluminum sulfate solution containing ferrous sulfate. The solution was produced by reacting iron powder on the concentrated solution of aluminum sulfate containing iron salts. Another patent claimed by G.H. Hultman[3] is that the pure basic aluminum sulfate is precipited by calcium carbonate from the dilute solution of aluminum sulfate and ferrous sulfate.

If we assume that the reaction of calcium carbonate and aluminum sulfate is as follows,

$$Al_2(SO_4)_3+3CaCO_3+3H_2O=2Al(OH)_3+3CaSO_4+3CO_2,$$

3 mols of $CaCO_3$ are necessary for 1 mol of $Al_2(SO_4)_3$. But the reaction is neither so simple nor so perfect.

Change of the Composition of Aluminum Sulfate Solution with the Amount of Reacting Calcium Carbonate. In this experiment a known amount of calcium carbonate in milky state was added little by little in 100c.c. of aluminum sulfate solution under a vigorous agitation in the course of 4–5 hrs. An unvigorous agitation or a quick addition of calcium carbonate is unfavorable for the reaction, because they often induce the formation of large crystals of calcium carbonate or the covering of the carbonate with small crystals of calcium sulfate.

After the whole amount of calcium carbonate was added, the agitation was continued for 30 minutes, and then the precipitate was filtered. The analysis of the filtrate was carried out in the usual manner: i.e. Al_2O_3 by the gravimetric method and SO''_4 by the volumetric method using benzidin hydrochloride as the precipitation agent. The pH of the filtrate was observed by the test paper.

(1) R. Kremann, K. Hüttinger, *Jahresb. Geol. Reichsanst., Wien*, **58**, 637, (1908).
(2) N. Grünstein, Brit. P., 472, 229 (1937).
(3) G. H. Hultman., U. S. P. 1,607,279 (1926).

Table 1.

The relation between the amount of the reacted carbonate and the composition of the filtrate.

No.	$CaCO_3$ add. % to equivalent	Al_2O_3 concn		SO_3 concn.		SO_3/Al_2O_3 molar ratio
		g./c.c.	% to original concn.	g./c.c.	% to original concn.	
Solution I	—	0.0856	100	0.2040	100	2.97
1	60.0	0.0879	102.7	0.1021	50.1	1.47
2	75.0	0.0355	41.5	0.0392	19.3	1.33
3	89.9	0	0	0.0035	1.7	—
4	99.9	0	0	0.0018	0.9	—
Solution II	—	0.1178	100	0.2810	100	3.03
1	58.6	0.1221	103.6	0.1613	57.5	1.68
2	76.2	0.1205	102.2	0.1262	44.9	1.33
3	93.9	0.0521	44.2	0.0525	18.7	1.28
4	117.3	0	0	0.0043	1.6	—
Solution III	—	0.1231	100	0.2758	100	2.85
1	59.9	0.1288	104.6	0.1651	60.0	1.63
2	74.5	0.1316	106.9	0.1218	44.3	1.18
3	85.5	0.1274	103.5	0.1103	40.1	1.10
4	99.3	0.0516	41.9	0.0533	19.3	1.31

The Solutions II and III correspond to the saturated solution at ca. 20° and 38–40°C respectively.

In the above table, some data which overrun from the original concentration of Al_2O_3 wouuld be accounted for the concentration of the solution being taken off some water for the crystallization of calcium sulfate. The results obtained are shown in Fig. 1.

While the concentration of SO''_4 decreases linearly in proportion to the amount of the $CaCO_3$ added, the aluminum content in the solution does not decrease in the same manner and the more concentrated solution can retain more aluminum in the solution. As a result, highly basic aluminum sulfate sol may easily be obtained from the concentrated solution of aluminum sulfate by this process.

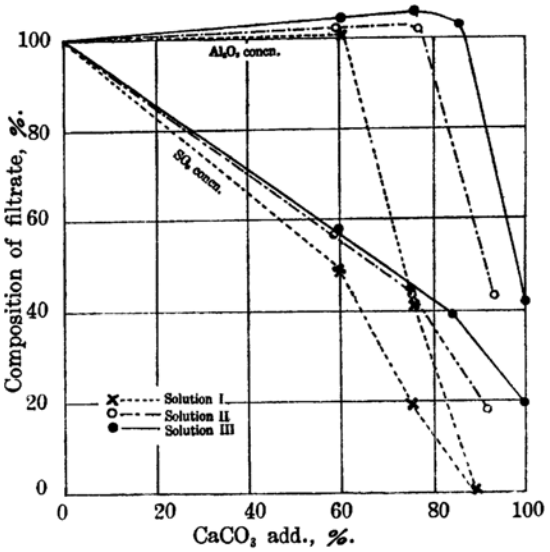

Fig. 1. The relation of the amount of reacted $CaCO_3$ and the composition of the filtrate.

The reaction of $CaCO_3$ with the solution of aluminum sulfate, however, is somewhat delicate. If the addition of $CaCO_3$ is too quick, an insoluble form of basic aluminum sulfate deposits with $CaSO_4$. In such a

case, the decrease of molar ratio SO_3/Al_2O_3 of the solution stops at an unsatisfactory extent. It is also interesting that the small overcharge of calcium carbonate causes the almost perfect precipitation of the insoluble basic aluminum sulfate.

Sol-Gel Transformation. The concentrated and highly basic aluminum sulfate solutions, like solutions II-No. 3 in Table 1, are viscous and transparent with a faint blue fluorescence. They are relatively stable and unvariable for the stock of several months at room temperature, although some samples deposit, in these standings, the white fairly dense precipitates. When the stable and highly basic aluminum sulfate solutions are heated up to 50-70°C, they coagulate to opaque gelatineous gels. Since this sol-gel transformation is reversible according to temperature, it again changes to the original sol form when standing at room temperature. This remarkable phenomena of highly basic aluminum sulfate solution is assumed to be accounted for the change of hydration degree of associated aluminum hydroxysulfate molecules. The details are left for a future study.

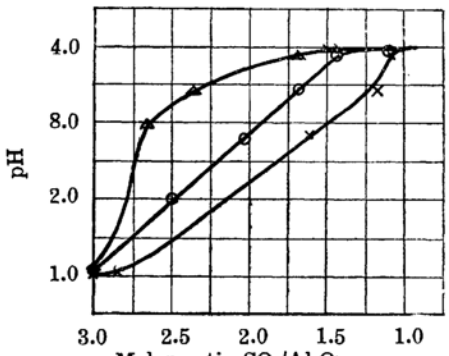

Fig. 2. The relation of pH and SO_3/Al_2O_3 of solution.
△, ○, × are the solutions I, II, III in Table 1 respectively.

pH of the Basic Aluminum Sulfate. The relation of pH and molar ratio SO_3/Al_2O_3 of the basic aluminum sulfate solution is not definite. It differs with the concentration of Al_2O_3. The more dilute solution of basic aluminum sulfate shows the larger value of pH at the same value of SO_3/Al_2O_3, though in all cases, the pH becomes about 4.0 after all.

Hydrolysis of the Basic Aluminum Sulfate. When the basic aluminum sulfate solution is thrown into water, a while precipitate is readily produced. This precipitate is a kind of basic aluminum sulfate having the molar ratio $Al_2O_3:SO_3=1:0.5$–0.6. It corresponds to the com-

Table 2.
The relation between SO_3/Al_2O_3 of the solutions and the yields of Al_2O_3 by their hydrolysis.

No.	Composition of solution Al_2O_3 g./c.c.	SO_3/Al_2O_3	Yield of the precipitate (observed as Al_2O_3) %
1–1	1.274	1.10	79.8
1–2	,,	,,	81.4
2	0.502	1.27	64.9
3	0.282	1.44	57.6
4	0.202	1.58	52.9
5	0.125	1.73	52.0

No. 1–2 was thrown into the water at 20°C. and not heated.

The concentration of solution observed as Al_2O_3 g/c.c.: (1) 0.0501, (2) 0.104 (3) 0.123

position of $2Al_2O_3 \cdot SO_3 \cdot xH_2O$. It is fairly dense and can easily be filtered.

Five c.c. of the basic aluminum sulfate are thrown into 50 c.c. of water at 80°C. and well stirred and then filtered. The relation of SO_3/Al_2O_3 of the basic aluminum sulfate and the yield of the precipitate are shown in Table 2. and Fig. 3.

It seems that in spite of the distinction of the concentration of the basic aluminum sulface solution, the yield of Al_2O_3 is in a linear relation with SO_3/Al_2O_3 of the basic solution.

The preparative method of aluminum hydroxide or alumina studied by the present authors is also of much interest for the separation of aluminum and iron from their sulfate solution, because ferrous sulfate does not show such hydrolytic change.

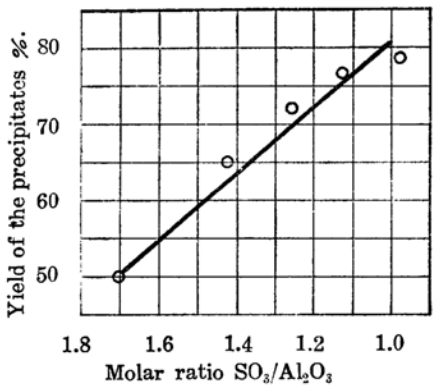

Fig. 3.

Summary

1. By the moderate reaction of calcium carbonate and the concentrated solution of aluminum sulfate, highly basic aluminum sulfate sol is easily obtained.

2. Some kinds of the basic aluminum sulfate sol become gel on heating and the sol-gel transformation is perfectly reversible at the neighbourhood of 40-50°C.

3. On dilution with water, the highly basic aluminum sulfate (SO_3/Al_2O_3=1.1–1.6) hydrolyses and precipitates the insoluble basic aluminum sulfate ((SO_3/Al_2O_3=0.5–0.6).

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