Effect of the Addition of Some Carbohydrates on the Decomposition Rate of Sodium Aluminate Solutions with Seeding[*]

By Taichi SATO

(Received December 26, 1956)

Introduction

The Bayer process is today the most widely used method for the production of alumina. Of this process it is usually said that the precipitation of crystalline aluminum hydroxide from a sodium aluminate solution is actually performed in the presence of organic matter[1-3]. When alumina hydrate in bauxite is dissolved with a solution of caustic soda, some organic matter found in bauxite such as humus etc. dissolves too and accumulates in the alkali solution. Two methods have been proposed to avoid this phenomenon. The first is the destruction of organic matter by a calcination of bauxite at temperatures from 350° to 400°C before grinding. The second is the separation of organic matter by concentrating an alkali solution after the precipitation cycle.

Recently, however, the calcination of bauxite before grinding is not carried out in most of the alumina plants. The omission of this calcination is a debatable problem. At present, we can not answer whether this calcination will be necessary or not. From an industrial view point, the effect of the presence of organic matter on the precipitation of aluminum hydroxide from a sodium aluminate solution has an important meaning as it relates to the problem of the necessity of calcination. On the other hand this study will, beside being an academic problem, give us interesting results with regard to crystal growth and to reaction between inorganic compound, organic matter, etc. But the reports on this problem are few till now, because the phenomenon in which the presence of organic matter has influence on the precipitation of aluminum hydroxide from a sodium aluminate solution is a complicated one. Therefore this study was undertaken as the continuation of the writer's former studies[4], and it has the object of investigating fundamentally the influence of the presence of organic matter on the decomposition of sodium aluminate solution. As the first step, the investigation on the decomposition rate of sodium aluminate solution with seeding and some carbohydrates has been made.

Experimental Methods

Various amounts (0.1, 0.3, 0.5, 1, 3, 5, 10 and 20 g./l.)[*1] of glucose, sugar and starch as the representatives of carbohydrate were added to sodium aluminate solution (NaOH 140.0 g./l., Al_2O_3 105.0 g./l., mol. ratio $Na_2O/Al_2O_3=1.7$). These solutions were decomposed with seeding of hydrargillite[*2] (5 or 10 %[*3]) at a temperature of 30°C, and those decomposition rates were measured. Here the decomposition rate is given by a change of decomposition ratio expressed as follows;

$$\frac{x_1-x_2}{x_1}\times 100(\%)$$

where x_1 and x_2 are the concentrations of alumina contained in sodium alminate solutions before and after decomposition.

The carbohydrates used were as follows. Glucose of dehydrated reagent class, and cane sugar was purified by a reprecipitation of ordinary sugar obtained in the market. Starch was made by refining white potato. The contained moistures were measured with Abderhalden's drying apparatus[*4]. The obtained values were as follows; 0.26 % in glucose, 1.25 % in sugar and

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[*] This paper is written as the 16th report of Studies on the Hydrolysis of Sodium Aluminate Solutions.

A partial report was made at the Autumn Meeting of Kanto Subgroup of the Chemical Society of Japan, held in Tokyo on November 6th, 1955.

1) "Gmelins Handbuch der anorganischen Chemie", Nr. **35**, Al〔B〕, (1933), S. 34.

2) J. D. Edwards, F. C. Frary and Z. Jeffries, "Aluminum Industry, Aluminum and its Production", Mc. Graw-Hill, New York (1930), p. 128, 160.

3) F. Ullmann, "Enzyklopädie der technischen Chemie", Bd. I, (1928), S. 306.

[*1] These values designate net weight of carbohydrate exclusive of moisture.

4) T. Sato, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), **54**. 266, 755 (1951); **55**, 66, 198 (1952); **56**, 399, 478, 743, 840 (1953); **57**, 20 111, 355, 540. 805 (1954); **58**, 325, 556 (1955).

[*2] This was previously precipitated by decomposition with seeding of sodium aluminate solution of NaOH 140.0 g./l., Al_2O_3 105.0 g./l., mol. ratio $Na_2O/Al_2O_3=1.7$ at 30° C.

[*3] This is a percentage to the amount of alumina contained in sodium aluminate solution.

[*4] Aceton was used.

18.47 % in starch. These substances were added to sodium aluminate solution in the dry state.

The method of decomposition of sodium aluminate solution with seeding is as follows⁵⁾. Sodium aluminate solution was prepared by the dissolution of aluminum (99.85 %) into a solution of caustic soda (NaOH 140.0 g./l.). 250 cc. of the solution was put in a wide-mouthed bottle of 500 cc. capacity and it was agitated with a seed charge of the prepared hydrargillite in a constant temperature water bath. The amount of alumina contained in sodium aluminate solution was determined gravimetrically.

As the viscosity of sodium aluminate solution may be influenced by the swelling of added starch particles, it was measured with Ostwald's viscosimeter at a temperature of 30°C. In this case its viscosity has to be measured after the attainment of swelling-equilibrium of starch particle. Therefore, at first, the swelling behavior of starch was investigated, and then the time within which the starch particle will attain the swelling-equilibrium was determined. Namely 1 g./l. of starch added to the caustic soda solution of prescribed concentration (NaOH 140.0 g./l.) was swollen under agitation at a temperature of 30°C. the same as in the case of decomposition with seeding of sodium aluminate solution, and the viscosity of its solution was measured after some prescribed times. Next, the sodium aluminate solutions containing 1, 3, 5 and 10 g./l. of carbohydrates were left for a prescribed time*⁵, and then these amounts of viscosity were measured.

The Effect of the Addition of Carbohydrate on the Decomposition Rate

The decomposition rates, with seeding of 5 % hydrargillite, of sodium aluminate solutions containing glucose, sugar and starch are given in Figs. 1, 2 and 3. Furthermore the decomposition curve of auto-precipitation is shown in these Figs.

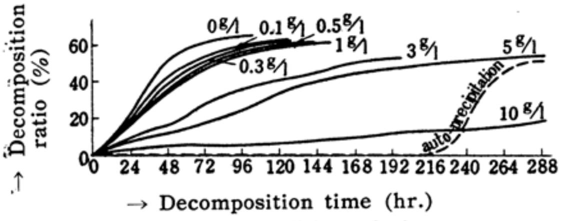

Fig. 1. Effect of addition of glucose on decomposition rate with 5% seeding.

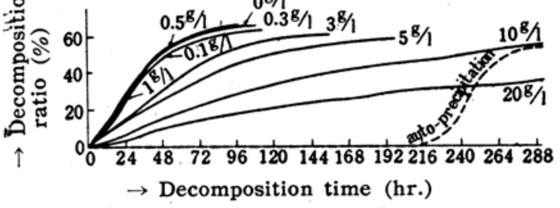

Fig. 2. Effect of addition of sugar on decomposition rate with 5 % seeding.

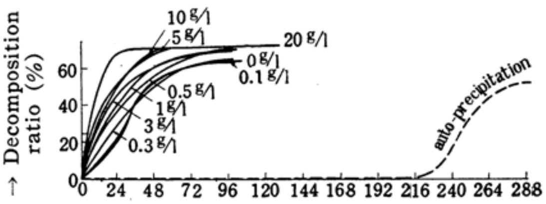

Fig. 3. Effect of addition of starch on decomposition rate with 5 % seeding.

Fig. 1 shows that the addition of glucose gives a retarding action on the decomposition with seeding, and that its action grows with the increase of the added amount. Thereafter the decomposition rate with the addition of 10g. glucose/l. is much smaller than in the case of auto-precipitation. Fig. 2 shows that the addition of sugar retards the decomposition of sodium aluminate solution as in the case of the addition of glucose. In this case we observe the tendency that the decomposition is retarded with the increase of the added amount but with the exception of the addition of 0.3, 0.5 and 1 g. sugar/l. As the addition of 0.3, 0.5 and 1 g. sugar/l. are considered the same, with no addition in the decomposition curves, the addition of 0.1 g. sugar/l. will have no influence on the decomposition. Though the tendency of Fig. 3 is different from those of Fig. 1 or 2, yet Fig. 3 suggests that the addition of starch promotes the decomposition. The decomposition is not promoted with the addition of 0.1 g. starch/l., but it begins to be promoted with the addition of 0.3 g. starch/l. Then the decomposition rate is rapidly improved with the addition of more than 0.5 g. starch/l. However, on the addition of starch to sodium aluminate solution its viscosity becomes as large as Fig. 9 indicates.

In order to investigate the actions on the decomposition of glucose, sugar and starch in all of the results of Figs. 1, 2 and 3, the comparison of decomposition rate with the addition of 1, 5 and 10 g./l, for example, is made in Fig. 4.

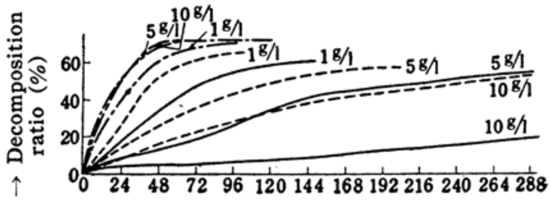

Fig. 4. Comparison of decomposition rate with 5 % seeding in presence of 1, 5 and 10 g./l. of glucose, sugar and starch respectively.

——— glucose
- - - - sugar
— — — starch

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[5] T. Sato, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **58**, 325 (1955).

*5 This time is six hours in Fig. 8.

Fig. 4 shows that the retarding action of glucose is obviously larger than that of sugar. In Fig. 4 the decomposition rate with the addition of 5 g. glucose/l. coincides with those of the addition of 10 g. sugar/l. Such a result may be due to the difference in molecular formulas ($C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$) of glucose and sugar. Because the numbers of molecules of glucose contained in the same weight are about twice the number in the case of sugar.

Relation between the Amount of Seed and the Addition of Carbohydrate

As Figs. 1, 2, 3 and 4 are given with 5% seeding, the decomposition rate was next investigated with 10% seeding. Then the comparison of decomposition rate between 5 and 10% seeding was made with the addition of carbohydrate. In this experiment the added amounts of carbohydrates were 1 and 3 g./l. in the case of glucose or sugar, and 0.5, 1, 3 and 5 g./l. in starch. These results are given in Figs. 5, 6 and 7.

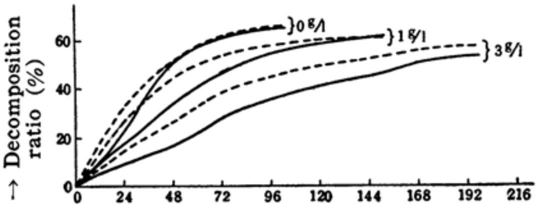

Fig. 5. Relation between amount of seed and addition of glucose.
—— 5% seeding
- - - 10% seeding

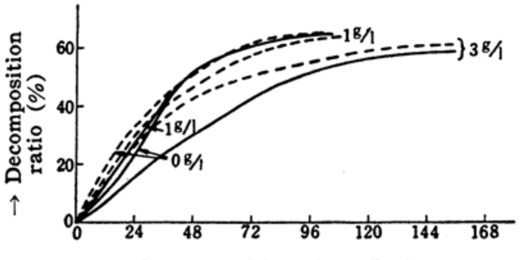

Fig. 6. Relation between amount of seed and addition of sugar.
—— 5% seeding
- - - 10% seeding

Fig. 5 shows that the decomposition rate with 10% seeding is larger than that of 5% seeding by the addition of glucose. This result suggests that the presence of seed charge acts stronger on the decomposition than glucose does. Fig. 6 shows that though with an exception of addition of 1 g. sugar/l., the decomposition rate with much seeding is larger than that with a little seeding on the addition of sugar the same as in the case of glucose. On the addition of starch as shown in Fig. 7, 10% seeding promotes the decomposition the same as 5% seeding, but its effect is smaller than the effect of 5% seeding.

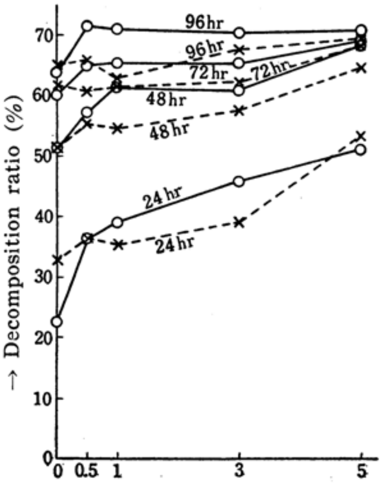

Fig. 7. Relation between amount of seed and addition of starch.
○ 5% seeding
× 10% seeding

Discussion

From the above-mentioned results it is obviously seen that the addition of glucose or sugar retards the decomposition of sodium aluminate solution, and that the addition of starch promotes its decomposition. But the viscosity of sodium aluminate solution is improved with the addition of starch. Hence the viscosity of sodium aluminate solution containing carbohydrate was measured in order to investigate the effect of the viscosity of solution on the decomposition. On the addition of starch to sodium aluminate solution, as starch particle is steadily swollen by alkali, the viscosity of the solution in the swelling-equilibrium of starch is different from that which occurs before swelling. W. Ostwald and G. Frenkel⁶⁾ reported that the swelling of starch by alkali had taken a long time to attain the equilibrium. C. E. Mangels and C. H. Bailey⁷⁾ measured the viscosity of the solution left for three hours after the addition of alkali to starch particle, and H. Suzuki and N. Taketomi⁸⁾ measured the viscosity of solution left for from five to ten minutes after the addition of alkali. In these studies, however, the concentration of alkali solutions are below 1 N, and they are not so high as this study treats. Hence the viscosity of sodium hydroxide solution (NaOH 140.0g./l.) with the addition of 1 g.starch/l. has been measured in order to investigate the swelling behavior of starch. This result is given in Fig. 8.

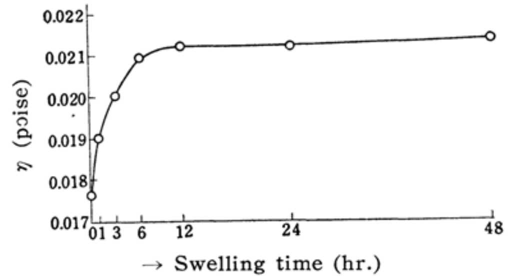

Fig. 8. Swelling behavior of starch in sodium hydroxide solution at 30°C. (1 g./l. of starch in NaOH 140.0 g./l.)

Fig. 8 shows that the starch particle may attain the equilibrium of swelling within about from six to twelve hours. Therefore the viscosity of sodium aluminate solutions with the addition of carbohydrates have been measured, six hours after their addition to the solution. These results are contained in Fig. 9.

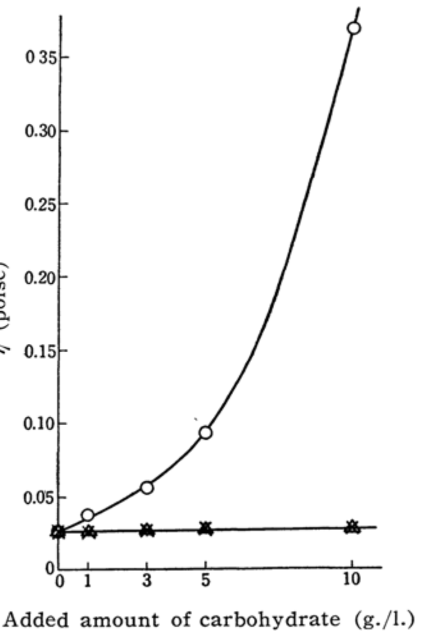

Fig. 9. Changes of viscosity of sodium aluminate solutions in presence of glucose, sugar and starch at 30°C.
△ glucose
× sugar
○ starch

Fig. 9 shows that the viscosity of sodium aluminate solution is not improved with the increase in an added amount of glucose or sugar, and that it is very much influenced by the addition of starch. However the viscosity of sodium aluminate solution with added starch may be improved by the swelling of starch at first, and then it may be rapidly lowered with the hydrolysis of starch initiated by the action of alkali, because the concentration of alkali is high. Though the viscosity of solution is almost unchanged after the swelling as shown in Fig. 8, then starch will not be influenced by alkali for the period of decomposition with seeding in this study. These results suggest the viscosity of solution is not a factor of first order for the decomposition.

On the one hand, from the results of decomposition rate, the action of starch on the decomposition is obviously different from that of glucose or sugar. Hence, the writer thinks, glucose or sugar (or their oxidation products by alkali in solution) binds with Al^{3+} or $Al(OH)_3$ molecules, and they must be soluble in solution forming some compounds (for example such as saccharate). R. K. Gupta and H. E. Buckley[9] who investigated the effect of the presence of dye on the solubility of a solution considered a binding of dye and solute. The writer believes this idea may be applied to this study too. However, if the phenomena in this study should be discussed only by Gupta's thought, this decomposition has to give us such an induction period as auto-precipitation[10], because the addition of glucose or sugar makes lower the degree of supersaturation of alumina to caustic soda in solution. Auto-precipitation has an induction period and is rapidly promoted after passing that period. On the other hand, the seeding decomposition with the addition of glucose or sugar has not an induction period, and it progresses very slowly. This shows obviously the difference of decomposition mechanism between auto-precipitation and seeding decomposition with the addition of carbohydrate. In auto-precipitation, crystal nuclei are gradually formed in an induction period, and then the formation of these certain definite numbers promotes

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6) W. Ostwald and G. Frenkel, *Kolloid-Z.*, **43**, 296 (1927).

7) C. E. Mangels and C. H. Bailey, *J. Am. Chem. Soc.*, **55**, 1981 (1933).

8) H. Suzuki and N. Taketomi, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **59**, 45 (1956).

9) R. K. Gupta and H. E. Buckley, *Z. physik. Chem.*, **204**, 165, 175 (1955).

10) T. Sato, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **54**, 755 (1951).

rapidly the precipitation of aluminum hydroxide. On the addition of glucose or sugar these bind with solutes in solution, and the degree of supersaturation of alumina to caustic soda becomes lower. Further, in this case, the activity of seed is decreased by a binding of seed charge and these carbohydrates. Therefore it seems that the formation of new crystal nuclei is retarded on the seeding decomposition with the addition of glucose or sugar. But it is obviously seen from the decomposition curves of Figs. 5 and 6 that the binding of glucose or sugar with solute is weak. In the meanwhile, it is observed from Fig. 4 that the binding between glucose and solute is stronger than that of the binding between sugar and solute.

On the other hand, the action of starch on the decomposition will be considered in relation to the facts[11] that starch is added in order to promote the separation of red mud from sodium aluminate solution. The starch added to the solution will bind with seed charge at first. E. Herrmann and others[12,13] who studied the separation of red mud in the sodium aluminate solution with the addition of starch as one of the colloid-chemical problems, pointed out that the addition of 0.25 g. starch/l. gives the optimum aggregation to red mud, and that at high starch concentration starch acts as a protective colloid for individual particles. Therefore, in this study too, more or less amounts of added starch will have a great influence on the agglomeration of particles. As the starch particle is apt to suffer hydration, it is chemisorped by OH^- on the surface of seed and it causes the aggregating phenomena of individual particles by the bridge action towards other particles. When starch particles chemisorped on the surface of seed are increased, these act as a protective colloid for individual particles and disturb the aggregation of particles. However, as the active surface of seed is diminished by the absorption of starch on its surface, the decomposition with seeding of sodium aluminate solution is retarded, and the effects on the decomposition grow remarkably with the increase in the added starch. And then the decomposition is evidently promoted with the addition of starch as shown in Figs. 3 and 7. Therefore, in the opinion of the present writer the presence of starch in itself must have a promotive action*[6]. From the above discussion this writer believes two counter phenomena play an important role in the action of starch on the decomposition rate. First, starch is retarding in the active surface diminished by the chemisorption on the surface of seed-crystallites (negative action). Second, starch is promoting in some way on the decomposition rate (positive action). As mentioned above, Fig. 7 shows that the decomposition rate with 5 % seeding on the addition of starch is larger than that of 10 % seeding. This may owe to aggregating phenomena of seed caused by starch. It seems that the condition of this experiment with 5 % seeding and starch addition has not been necessary (for example, the dispersed concentration of seed in solution) to get the aggregation by starch-bridge. Therefore, as seed charge of 10 % seeding is aggregated by starch more than in the case of 5 % seeding, the surface area of seed under 10% seeding may be diminished by the formation of a big agglomeration of particles.

Moreover the sedimentation behavior of a particle precipitated by the decomposition of sodium aluminate solution with seeding and starch addition has been investigated. Consequently the sedimentation behavior of a particle precipitated with 5 % seeding indicates an aggregated sedimentation (that is, suspension layer settles in forming clearly a boundary from dispersed phase), and that of 10 % seeding points a tendency of free sedimentation (that is, with the state of suspension, dispersed particles settle steadily from a large particle to a small one, and a boundary of suspension layer is not clear). As these results may be closely connected with the action mechanism of starch, the writer intends to investigate these problems in his next report.

In this study the influence of temperature on carbohydrate need not be considered, because the decomposition of sodium aluminate solution has been made at the temperature of 30°C.

Summary

In order to study the influence of the

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[11] W. Kerr, "Chemistry and Industry of Starch", Academic Press, Inc., New York (1950), p. 645.

[12] E. Herrmann, I. Dvornik, O. Korelić and V. Matković, *Kolloid-z.*, **123**, 22 (1951).

[13] I. Dvornik and E. Herrmann, ibid., **128**, 75 (1952).

*[6] It seems that the effect of starch on the decomposition is owing to amylose or amylopectin. This point will be investigated in a later report.

presence of the organic matter in a sodium aluminate solution the decomposition rate was investigated by the addition of some carbohydrates as first step of study. Three kinds of carbohydrate, i. e. glucose, sugar and starch (white potato) were chosen and added to a sodium aluminate solution in verious amounts. These solutions were decomposed with seeding of hydrargillite, and these decomposition rates were compared in each case. Consequently it had been observed that the addition of glucose or sugar acts to retard the decomposition, and that the increase of an added amount of starch promotes the decomposition. But the retarding action of glucose is larger than that of sugar. On the other hand, the relation between the added amount of seed and the addition of carbohydrate was investigated. It had been seen that the presence of seed is stronger than that of glucose or sugar in the action of decomposition, and that this relation is different upon the presence of starch. Further the viscosity of sodium aluminate solution mixed with carbohydrate was measured. It has been observed from this measurement that the viscosity of sodium aluminate solution is almost unchanged with the addition of glucose or sugar, and that its viscosity is improved with the addition of starch. Then these results have been compared with the decomposition rate. From this result, it is concluded that the viscosity of solution does not always act on the decomposition as the factor of first order. Hence the action mechanism of these carbohydrates on the decomposition are discussed, and it is clearly concluded that there is a very large difference among the actions of each carbohydrate on the decomposition. In these results one must obtain some informations upon the action mechanism on the decomposition of sodium aluminate solution in the presence of organic matter.

The author wishes to express his hearty thanks to Dr. Erich Herrmann of Martinswerk G. m. b. H., Bergheim and Mr. Siniša Maričić of Institute of Physics Zagreb for their very helpful discussion.

Government Chemical Industrial
Research Institute Tokyo
Yoyogi p.o. Tokyo