

The Kinetics of the Formation of Aluminium Hydroxyde by Seeding Sodium Aluminate Solutions with Hydrargillite Crystals.

II. Experiments with Particle-size-classified Seed

S. Maričić and I. Markovčić

Institute of Light Metals, Zagreb, Croatia, Yugoslavia

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The decomposition of sodium aluminate solutions by seeding with hydrargillite-crystals occurs simultaneously in three different ways by: (a) crystal-growth, (b) formation of firm-binded-agglomerates (intercrystallization) and (c) creation of new crystallites. By the experimental technic applied only the predominations of (b) or (c) are proved, but not their relative intensities. The last two mechanisms are exclusively characteristic for the particle-size-range < 20 microns (especially for the particles ~ 10 microns). The way of the acting of the seed depends on the absolute amount as well as on its size distribution.

INTRODUCTION

The complexity of the decomposition of sodium aluminate solutions caused by seeding was verified in a preceding paper¹. Both the creation of new crystallites and the crystal growth can be found in this system. The former process is characteristic for the beginning of the decomposition while the latter is predominant at the end. The aim of the present report is to supply further data necessary for a quantitative treatment of the problem.

EXPERIMENTAL

Material used was the same as before.¹ From Bayer-alumina trihydrate three separate size-ranges were obtained by the Andreasen-method², glass-apparatuses being used for hydro-elutriation³. For the sake of simplicity distilled water instead of a stabilizing solution was taken as fluid. After a period of elutriation the flocculation becomes perceivable causing an apparent end of the hydro-separation. To eliminate this effect the flow was interrupted and the suspension allowed to settle. A few minutes later the liquid was allowed to flow again. In this way, by repeated deflocculations, the limit in getting »monodispersed« systems was obtained.

Because of the small amounts of the seed-fractions the experiments were performed with 150–200 ccm portions of aluminate solution having a composition of 150 g $\text{Na}_2\text{O}_{\text{tot}}/\text{l}$, 130 g $\text{Na}_2\text{O}_{\text{free}}/\text{l}$ and 115 g $\text{Al}_2\text{O}_3/\text{l}$. In every experiment the charge of the seed was 150% (usual terminology). The temperature was 50°C. All other details were the same as before.¹

RESULTS

The results are represented in the same way as in the first report. Every field in Fig. 1 and 2 refers to two seeding-experiments with a given seed-fraction. In Fig. 1 the numbers on the ordinate (but not on the curves) represent the total amount of $\text{Al}(\text{OH})_3$ -crystals in the system at the end of

the experiments. The difference between the mentioned points and the each next one equally marked (on the curve) indicates the amount of alumina trihydrate with particle diameters surpassing the greatest value of the class.

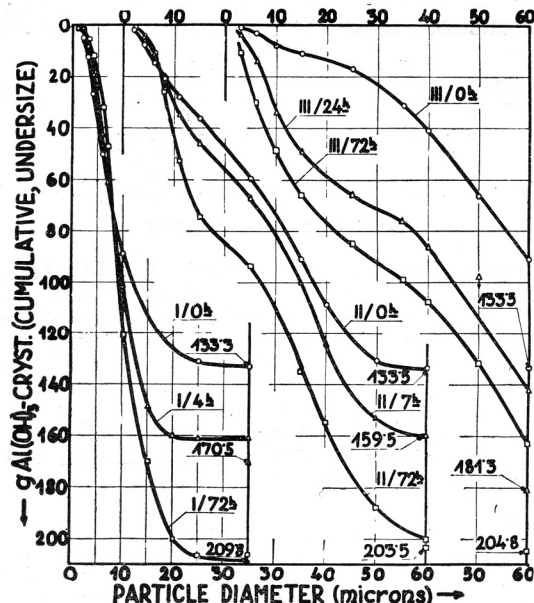


Fig. 1. — Particle size cumulative distribution curves.
Sl. 1. — Sumarne krivulje raspodjele veličine čestica.

The curves marked O^h belong to three different seed-fractions. The fraction I. contains only 95% particles finer than 20 microns. The next two fractions are not monodisperse due to the above mentioned flocculation. The fraction II. is an intermediate case with approximately uniform dispersity having no crystals coarser than 60 microns. Even the last (III.) fraction contains 17% of particles with a diameter less than 30 microns, though the elutriation was adjusted in such a way to exclude all particles smaller than 45 microns.

The other curves marked 4, 7, 24 and 72 h belong to the end-products in the experiments lasting as indicated.

As to the positions of the maxima in Fig. 2 and the earlier hypothesis, the results are rather unexpected. The most »active« part of the seed having particle-diameters about 5 microns seems to be subjected only to crystal-growing, while it is with the most »inactive« part having 83% particles coarser than 30 microns that the new crystallites are formed.

For further discussion it was necessary to transfer all the results into the so-called Rosin-Rammler-Bennet-nomogram.⁴ In order to obtain linear-plots the dispersity curves were divided into two fields according to their form (Fig. 2.), every field being treated separately. The obtained »subfractions« may be seen in the Table I. It is evident that for the fraction I. no such subdivision was needed.

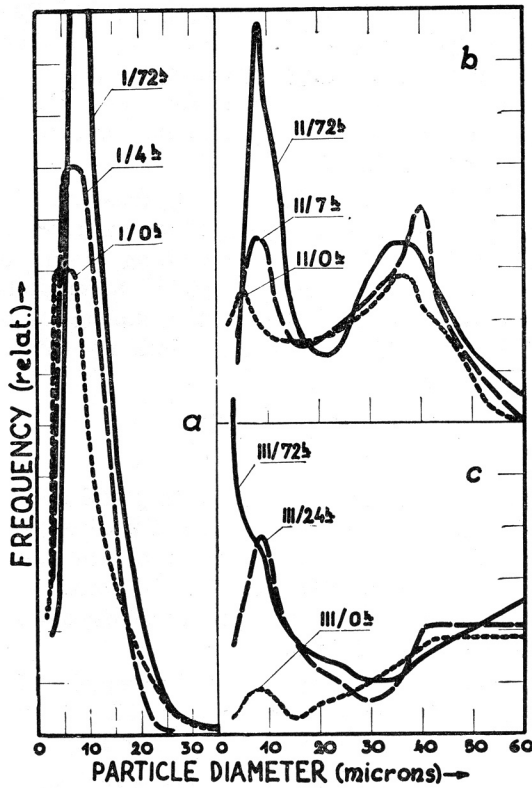


Fig. 2. — Particle size frequency distribution curves.
Sl. 2. — Krivulje učestalosti veličina čestica.

TABLE I

F r a c t i o n

	I.			II.						III.					
				< 17.5 μ			> 17.5 μ			< 30 μ			> 30 μ		
d' [μ]	9.5	10.8	12.5	10.0	10.0	11.0	37.0	39.0	41.5	16.5	13.3	12.8	60.0	60.0	60.0
n	1.98	2.25	2.35	1.89	2.50	3.10	4.00	4.00	3.90	1.98	1.96	1.35	4.00	> 5	> 5
O' [m ² /kg]	1100	900	730	1000	900	740	200	190	180	600	750	1090	130	130	130
O_{obs} [m ²]	147.0	153.5	153.0	42.0	45.5	59.2	42.0	20.7	22.2	13.8	53.3	108.0	14.3	14.4	14.6
No	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
O'_{theor} [m ²]	190	206		42.0	55.0		20.3	23.5							
$F = O_{\text{obs}} / O_{\text{theor}}$	0.81	0.74		1.08	1.07		1.02	0.95							

The mean-diameter (\bar{d}), the uniformity factor (n), the specific surface (o') obtained by this graphical method are all collected in Table I. The density and shape-factor were not taken into account because the purpose of this discussion is to compare the results in a narrow range. In multiplying O' by the amount of crystals present in each particular case the absolute surfaces were obtained as listed in Table I.

Though there are other ways of interpreting these results, we have chosen this one in order to be able to compare them with those of Wrigge and Ginsberg⁵ criticized in the first article¹. According to this authors the seed-crystals in our system are exclusively subjected to crystal-growth. In such a case the number of particles should be constant during the process of growth. Assuming that the shape of the particles does not change, the following equation can be easily derived:

$$O_2 = O_1 \cdot \left(\frac{d_2}{d_1}\right)^2 \quad (1)$$

where O_1 , O_2 are absolute surfaces of the starting and end-product resp., and d_1 , d_2 their (mean-)diameters. According to eq. 1 the results for O_{abs} (Tab. I.) were multiplied by the ratio of the squares of the mean-diameters for each pair of successive experiments. For instance, 1—2... $O_{\text{theor}} = 190$; 2—3... $O_{\text{theor}} = 206$ and so on. If the proposed hypothesis is correct, the ratio $O_{\text{abs}}/O_{\text{theor}}$ should be equal to 1.

From Tab. I it may be seen that F is neither equal to 1, nor constant. On the contrary, this factor becomes in any case smaller toward the end of the decomposition. But the most striking fact is that F may be smaller than one.

There is no explanation for the last mentioned fact according to the hypothesis put forward till now. If only crystal-growth takes place F ought to be constantly equal to one. With nucleation in addition to the crystal-growth it might be even larger than one without being constant. But F can by no means be smaller than one. Therefore, it should be supposed that another mechanism tends to diminish the absolute surface of the final product in the decomposition process.

Let us suppose that such a process is the aggregation of seed-crystals followed by agglomeration of aggregates by the freshly crystalized alumina trihydrate. This case may be roughly compared to the condensation of several droplets into a bigger one. The number of particles is variable during this process while their volume remains constant. (This assumption is not, of course, strictly justified in our case.) Assuming that there are no changes in the shape of the particles either, we should have:

$$O_2 = O_1 \cdot \frac{d_1}{d_2} \quad (2)$$

A few years ago the importance of aggregation during the crystalization was clearly pointed out by B. Težak.⁶ By using Oden's⁷ results on reversible aggregation he showed that the well-known maxima of von Weimarn's precipitating curves are due to the aggregation processes.⁸ He verified later this fact in many systems.⁹

The evidence that aggregation is taking place in our system too may also be obtained from Herrmann and Stipetić's results.¹⁰ They found, in (apparent) contradiction to Volmer's theory¹¹ that the product of the first day's decomposition was coarser than that of the second.

Microscopical observations confirmed the hypothesis of $\text{Al}(\text{OH})_3$ -crystals being firm agglomerates. Apart from this, there is strong evidence for this fact in the recent work of Amstein and Scott¹².

Quite generally, the following ways of interaction between the seed and the supersaturated solution may be assumed.

1. Every particle is growing up by enlarging its own volume at the expense of the solute («simple-growing»).

2. Larger particles are formed by aggregation of smaller ones owing to the new crystalized solid phase («intercrystalization»).

3. Seed-particles induce the formation of the new independent crystallites («nucleation»).

4. The larger particles enlarge themselves partially at the expense of the finer ones, which in their turn dissolve.

The last possibility may be discarded. The finer particles had already before (Bayer-process!) been in contact with a not too supersaturated solution. Under our experimental conditions they are stable owing to the high degree of supersaturation.

The first three mechanisms mentioned above are probably simultaneously present from the very beginning of the decomposition process. Their relative importance in the course of decomposition depends on the size-distribution as well as on the absolute amount of the seed.

From Fig. 2/a and the values in Tab. I/1, 2, 3 it may be easily understood that in this case the intercrystalization is predominant. Though all the particles were in the «active» range of size-distribution¹ the creation of new crystallites is only of minor importance. The lower value of F for the second part of the process indicates that new surfaces are developed to a lesser extent than before. According to the crystalization-theory the rate of crystalization is a linear function of the supersaturation while the rate of nucleus-formation depends on the square of the supersaturation. Thus, it is more probable to suppose that such a variation of the nucleation-rate (the evidence of this mechanism being so implicit) is for the greatest part responsible for the lowering of F .

In the second extreme (see Fig. 2/c) there are no such rapid changes of Al_2O_3 -concentration in the solution during the process as in the former case. That may only be explained by the practically complete inactiveness of the larger particles (> 35 microns). The «active» part of the seed in this system is only about one tenth of the amount used in the seeding with fraction I. Here the finer particles do not condense neither among themselves nor with the larger ones. Moreover, their action is quite independent of the larger particles and independently they can produce new crystallites. Such a nucleation is impossible if the seeding is done exclusively by a large portion of the finest crystallites. (See Fig. 2/a.) The high concentration of such a suspension favours a primary (reversible) aggregation. This is followed by a rapid precipitation of the new alumina trihydrate acting as binder in the new

agglomerates. As a consequence, the supersaturation is rapidly decreasing from the very beginning of the process. Thus there is no possibility for nucleation to prevail as it might be expected according to the particle-size of the seed.¹

The results shown in Fig. 2/b and Tab. I/4—9 may be treated as an intermediate case among the two extremes described above. There are quite enough particles capable of simple-growing (Tab. I/7—9) which causes the lowering of the Al_2O_3 -concentration of the solution. Thus, of course, the nucleation is not supported in a predominant way but still it takes place. (Note the shape of the 7 and 72 h maxima in Fig. 2/b, where constant increase of new crystalites during the process is clearly visible.) Still it is not possible yet to decide if in such a case intercrystallization takes place too. Should F be exactly equal to one it might be attributed to a proper combination of the three mechanisms. For the same reason it is still impossible to elucidate the relation between simple growth and intercrystallisation in the region of low supersaturation ($\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 > 3$). It might be expected that Na_2O -content in the solution is mostly responsible for the primary aggregation of the particles, while the Al_2O_3 -component for their final binding. Further experiments in this line are in course.

This and the preceding report mostly deals with the size of the seed-particles. To support the view of a special activity of the finer particles we mentioned the morphology of Kohlschütter's »somatoids«¹³. But both the size and the morphology of the hydrargillite-crystals are a consequence of a more essential process known as the ageing of $\text{Al}(\text{OH})_3$. The crystals may be enlarged in the Bayer-process by recycling through the decomposition-operation. Thus the finest of the crystals are not »older« than 2 or 3 cycles. The crystals are the larger the longer they have been in the aluminate solution. Such a contact with a strong alkaline solution is known to promote the ageing of $\text{Al}(\text{OH})_3$ -crystals. Thus the behaviour of the finer particles (~ 10 microns) as manifested in nucleation and intercrystallization can be explained by their high surface-disorder.

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IZVOD

Kinetika stvaranja aluminijeva hidroksida cijepljenjem otopine natrijeva aluminata kristalima hidrargilita. II. Eksperimenti s cjepivom određene veličine čestica

S. Maričić i I. Markovčić

Kod cijepljenja otopina natrijeva aluminata kristalima hidrargilita zbivaju se istodobno tri procesa (a) rast kristala, (b) stvaranje čvrsto vezanih aglomerata (interkristalizacija) i (c) nastajanje novih kristalita. Eksperimentalnom tehnikom, koja je bila primijenjena, bilo je moguće utvrditi samo prevladavanje mehanizma (b) ili (c), ali ne i relativni značaj pojedinog procesa. Posljednja su dva karakteristična jedino za područje veličina čestica < 20 mikrona (osobito za čestice ~ 10 mikrona). Način djelovanja cjepiva zavisi koliko od apsolutne njegove količine, toliko i od raspodjele veličina čestica u njemu.

INSTITUT ZA LAKE METALE
ZAGREB

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