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Decomposition of Sodium Aluminate Solutions. V. Coarse Grained Hydrargillite Seed and Induced Nucleation*

Ž. Hlobik, E. Jungman-Horvat, and S. Maričić**

Institute of Light Metals, Zagreb, Yugoslavia

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Decompositions of sodium aluminate solutions of different molar ratio ($\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$) were carried out by seeding with coarse grained hydrargillite. The induced nucleation is greater the more supersaturated the decomposing solution. An outline of the actual mechanism of induced nucleation is given. The importance of the initial formation of new solid phase on the seed surface is stressed. Its kinetics are highly dependent on supersaturation.

INTRODUCTION

Kuznetsov and Derevyankin have recently shown¹ that coarse grained hydrargillite can induce nucleation in the decomposition of sodium aluminate solution. This is at variance with our results², and also against our interpretation of their previous experiments³. It appears now that different techniques of washing out fine particles from the coarse grained seed do not play as decisive a role as we thought at first.

On comparing other details of the experimental techniques one finds that Kuznetsov and Derevyankin have been working with solutions more supersaturated than ours. We therefore carried out a set of similar experiments. The primary purpose was to establish the effect supersaturation might have on nucleation induced by coarse grained seed, but the results threw some light on the actual mechanism of this process as well.

EXPERIMENTAL

Sodium aluminate solutions were prepared by dissolving commercial hydrargillite in warm technical caustic soda solution with subsequent filtering. Concentrated stock solutions of different molar ratios were diluted to about 130 g $\text{Na}_2\text{O}_{\text{free}}/\text{l}$ before each experiment.

The seed was prepared by sieving and sedimentation of commercial hydrargillite in order to remove all particles smaller than 50 μ . We were again unable to achieve this by using only water as sedimentation medium. For the sake of completeness we give here the Andreassen-pipette analysis results for the seed at various stages of removing the fines. Three batches of coarse grained seed were prepared starting from the same commercial hydrargillite, confirming in each case the absence of particles smaller than 50 μ by the Andreassen method.

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** Present address: Institute »Ruder Bošković«, Zagreb, p. p. 171.

TABLE I

10 X in dist. water \longrightarrow + 5 X in 0.005 M $\text{Na}_4\text{P}_2\text{O}_7$ /l solut.

$D_{\text{Stokes}} [\mu]$	batch I	batch II	batch I	batch II
	weight	weight	%	%
50	24.8	38.9	2.0	0.0
40	16.4	24.3	0.8	0.0
35	16.4	21.6	0.5	0.0

The decomposition was performed at $55 \pm 0.1^\circ\text{C}$ in steel cylinders ($\varnothing = 95$ and $h = 150$ mm) immersed in a water bath. It was first checked with a similar glass beaker that two propellers ($\varnothing = 80$ mm) bent at 45° , one near bottom and the other in the middle of the vessel, were sufficient to avoid any sediment at the bottom if the mixing speed was 100 r/min. The steel cylinders were filled with either 250 or 700 ml of corresponding aluminate solution. After the bath temperature had been attained the seed was added. The seeding ratio (Al_2O_3 of the seed: Al_2O_3 in solution) for the solution of $\text{MR} = 1.67$ was 1:1 as in experiments of Kuznetsov and Derevyankin. The same absolute amount of seed was present in all the other experiments. After decomposition filtered solutions were analysed and part of the washed product used for particle size measurements by the Andreasen method.

RESULTS AND DISCUSSION

A. Supersaturation and induced nucleation

In planning the present experiments we had in mind rechecking of our earlier results². An aluminate solution was therefore prepared with a similar molar ratio and Na_2O -concentration. The temperature was 5°C higher in this new experiment, and the amount of seed four times larger, because we also wanted to work under conditions chosen by Kuznetsov and Derevyankin¹.

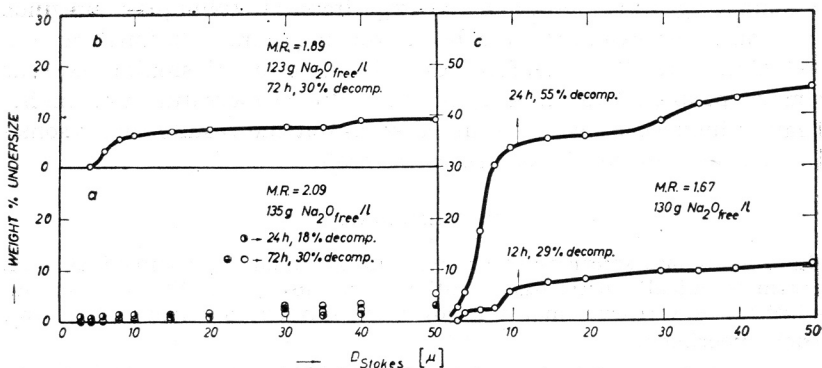


Fig. 1. The cumulative undersize curves of different decompositions products as indicated.

In Fig. 1/b we have the cumulative undersize curve up to 50μ for the product of a 72 hour decomposition of a solution with $\text{MR} = 1.89$. One notes that about 6% of the product is comprised of particles smaller than 10μ . In our earlier work² we observed no particles at all smaller than 50μ . One possible cause of this difference might be the larger amount of seed in the present experiment.

The fine particles are indeed newly formed, for the amount of particles above $50\ \mu$ in the product is slightly greater than the amount of introduced seed, which is plausible in view of the simple crystal growth to which the coarse particles are subject in decomposition.

Finally, in this experiment there are practically no particles between 20 and $50\ \mu$, which is indicative of the absence of any kind of breakage of the large crystallites.

In the decomposition of a less supersaturated solution with a $MR = 2.09$, one can hardly detect any newly formed small crystallites (see Fig. 1/a). This graph comprises the results of three independent experiments; two 72 hour decompositions using batch I and II seed, and one 24 hour decomposition with batch II seed. A very small amount (about 1%) of small crystallites has been newly formed in the first 24 hours and the crystallites appear to have slightly grown in the remaining 48 hours.

In the decomposition of a more supersaturated solution, such as used by Kuznetsov and Derevyankin¹, with a $MR = 1.67$, the situation is quite different (see Fig. 1/c). Induced nucleation took place in the first 12 hours, and after 24 hours there are seven times more particles smaller than $20\ \mu$, than in 72 hour decomposition of the solution with a $MR = 1.89$.

Let us now compare results in Fig. 1/c with the relevant data in Table I of Kuznetsov and Derevyankin¹. (Strictly speaking one may do this only with the last but one set in that table.)

Interestingly enough, we obtained even more pronounced induced nucleation. It would be superfluous to speculate on what caused this difference, because, naturally, we did not use the same seed.

It may appear that pronounced nucleation in more supersaturated solutions is due to spontaneous decomposition. However, there is ample evidence by Kuznetsov and coworkers⁴ that such solutions under the same conditions are stable for several days. Because of the use of technical chemicals in our experiments we checked on this point. A solution of $MR = 1.67$ was mixed for 72 hours under the same conditions as in seeding experiments and no change in its composition was established afterwards.

As regards the fracturing of large crystals, due to internal stresses as suggested by Kuznetsov and Derevyankin, we cannot find clear-cut evidence of it in our experiment (cf. Fig. 1/c). While the 12 hour curve is negative in this respect, the second one shows presence of some 10% of $15\text{--}50\ \mu$ particles, and the amount of $+50\ \mu$ particles in the product is less than the initial amount of the seed. On the other hand, in every single experiment with $+63\ \mu$ seed of Kuznetsov and Derevyankin there is a surplus of $+63\ \mu$ particles in the product as compared with the initial seed amount. We feel that sieving analysis, by which these medium size particles were found by Kuznetsov and Derevyankin, is not a suitable technique for two reasons: a) fine aluminium hydroxide has appreciable and active surface area, which favours formation of clusters larger in size than their constituent crystallites; b) it is likely that in the course of sieving some breakage of the irregular parts of the large crystals may take place.

We should also like to mention the possibility of an intercrystallization mechanism⁵ and overlapping of fracturing effects with simple growth of large

crystals*, which further complicates the interpretation of the present results. It seems to us that the »internal stress fracture« theory is still open here to further experimental checking.

Whatever the answer to the questions raised the following conclusions may be drawn fairly safely:

- 1) Decomposition of aluminate solutions by nucleation can be induced even with coarse grained hydrargillite (all particles larger than $50\ \mu$).
- 2) The kinetics of this process are highly dependent on the supersaturation of the aluminate solutions. At 55°C formation of new crystallites is pronounced for Bayer-decomposition caustic concentrations if the molar ratio is about 1.7 and weak or almost suppressed if the molar ratio is larger than 1.9 as encountered in the classical Bayer process.

This last fact explains the observation of Kuznetsov and Derevyankin about the seed-recycling problem. They write:¹ »In certain decomposition experiments (at temperatures above 50°C), when the seed was coarse grained hydroxide ($+63\ \mu$) with fine particles not removed by sedimentation we got precipitates in which $-40\ \mu$ fraction content was negligibly small — not more than 0.5%.« Then follows Fig. 3 in their article, representing results of decompositions with the temperature decreasing from $73-50^\circ\text{C}$. This, of course, means lower supersaturation, especially in the most important part — the beginning of decomposition when the temperature was close to 70°C .

We do agree with Kuznetsov and Derevyankin that »it takes time till the coarse particles are prepared to nucleation«, and that this is the cause of the apparent discrepancy between theirs and our earlier results². However, we hope to have produced enough evidence showing that this kinetic aspect is a consequence of the degree of supersaturation of the decomposing solution.

B. On the mechanism of induced nucleation

So far in this paper, and also in the earlier ones in this series, we deliberately have not been explicit on the mechanism of induced nucleation. We think that our present results enable us to do this partially now.

We did find most useful in interpreting our first results⁶ the ideas put forward independently by Herrmann et al.⁷ and Calvet et al.⁸ They came to the conclusion that disordered and very active fragments (»Splittern«) are being detached from the seed crystal surface to act as nuclei, which in the course of decomposition grow to some extent.

There are generally two ways of creating such irregularities on the crystal surface: (i) by specially preparing so-called active seed independently of the solution which is to be decomposed; (ii) in the very process of classical Bayer decomposition whereby part of the plant product is being recycled as seed.

There is an important difference between the two cases. In the first one the decomposition kinetics are dominated by a vast number of »disseminated« new nuclei, as soon as the seed comes into contact with the liquor. The parent crystals offer suitable surface for deposition of new irregularities, i. e. new potential nuclei irrespective of the previous detachment, and this, of course,

* This was pointed out by S. I. Kuznetsov in a private communication to S. M.

is dependent on supersaturation. However, no pure simple crystal growth can take place by this method, because always there will be present an appreciable amount of detached new nuclei.

The reverse is true of the second case. Here, the potential nuclei have first to be formed in the decomposition process. Now the solution plays the important part as shown here and elsewhere^{1,2}, although the surface properties of the recycled seed must certainly be taken into account^{7,8,9,10}. That higher supersaturation favours dendritic depositions on the seed surface is quite plausible and has already been mentioned by Pearson¹¹. We should only like to stress that this mechanism, and therefore induced nucleation, can completely be suppressed and pure simple crystal growth achieved. This is equivalent to our earlier conclusion^{6,10} that in the latter part of decomposition (higher MR) simple crystal growth prevails, while induced nucleation is characteristic of the beginning of decomposition (low MR).

We have confined the above discussion to the first step of induced nucleation, that of the formation of dendrites, the existence of which has been confirmed by Sato¹², Ginsberg and Hüttig¹³ and Kuznetsov and Derevyankin¹. In view of the meager experimental evidence on the final step — the detachment of dendrites from the parent crystals — we would rather defer the discussion about it to another occasion. It still remains to find the causes of the reproducible size of newly formed nuclei, which is about 5 μ .

There is a general agreement between Kuznetsov and Derevyankin and ourselves as regarding the mechanism of induced nucleation. However, we attach much importance to the first step, i. e. to the formation of new disordered solid phase capable of rapid growth on the crystalline surface, while Kuznetsov and Derevyankin pay more attention to the mechanical aspect of the chipping off. As already shown in section A., our point of view helps in interpreting the recycling experiments. In these, there are two or three cycles with negligible or no induced nucleation at all before the effect is established in a subsequent cycle. This can happen if the supersaturation is rather low. Under such conditions newly deposited phase is less disordered and the overall number and rate of growth of dendrites is smaller. Hence, it takes more than one cycle until there are detectable amounts of irregularities on the surface of parent seed, and which have grown enough to be detached.

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IZVOD

Dekompozicija Na-aluminatnih otopina. V. Krupnozrnato hidrargilitno cjepivo i inducirana nukleacija

Ž. Hlobik, E. Jungman-Horvat i S. Maričić

Izvršeni su pokusi kristalizacije $\text{Al}(\text{OH})_3$ iz Na-aluminatnih otopina različenog prezasićenja i to molarnih omjera ($\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$) 1,67, 1,89 i 2,09 uz ~ 130 g $\text{Na}_2\text{O}/\text{l}$ kod 55°C . Nađeno je, da je krupnozrnato hidrargilit (čestice $> 50 \mu$), koji je bio upotrebljen kao cjepivo inducirao stvaranje novih sitnih čestica ($< 10 \mu$) ako je prezasićenje veliko. Pod uvjetima klasičnoga Bayerova postupka ovaj je efekt neznan. U diskusiji mehanizma inducirane nukleacije podvučena je važnost početnoga formiranja nove čvrste faze na površini cjepiva. Kinetika ovoga procesa jako zavisi od prezasićenja, čime se tumače razni efekti iz prakse i rezultati drugih autora.

INSTITUT ZA LAKE METALE
ZAGREB

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