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On the Ability of Coarse Grained Aluminium Hydroxide to Induce Nucleation in Decomposition of Aluminate Solutions*

S. I. Kuznetsov and V. A. Derevyankin

Urals Polytechnical Institute, Sverdlovsk, USSR

Received November 19, 1959

Experiments are reported by which the presence of new fine crystallites was established after seeding aluminate solutions with coarse grained hydrargillite. The presence of the newly formed fines is attributed to chipping off the dendrites formed on the surface of large crystals as shown by electron micrographs. The intermediate range of particle sizes is due to fracture of large crystal growing. These are cases when some time is needed for the coarse particles to become able to induce nucleation.

INTRODUCTION

Many different aspects of the physical chemistry of decomposition of aluminate solutions have been studied in recent years in our country and abroad. Conclusions drawn from these investigations have broadened our understanding of the process in question. Thus, for instance, it was proved that decomposition is not only a process of simple growth of seed hydroxide crystals. As a rule the formation of new nuclei accompanies growth. The mechanism of formation of new nuclei is not yet quite clear, but some details of this process may be considered as proved.

Observations prove that the probability of spontaneous origination of hydrargillite nuclei in aluminate solutions under the conditions of decomposition is exceedingly small[1,5,6]. Therefore the main source of new nuclei should be found in the ability of aluminium hydroxide seed to chip off small particles when being agitated with aluminate solutions. The chipping off of small particles by hydrargillite crystals may take place in the following ways.

Elecron microscopic observations proved[15,7] that the hydrargillite particles grow unevenly in the process of decomposition. At certain points on the surface of these crystals formation of dendrites may be observed quite frequently. During agitation these dendrites are easily broken. Highly perfect cleavage of hydrargillite crystals favours this breaking. Broken pieces of dendrites become new nuclei. In the process of decomposition they have no time to coarsen, and thus highly dispersed hydroxide appears in the product. There is still another way of formation of small particles in the final product of decomposition.

As is well known from the literature, internal stresses appear in crystals during growth. This results from the fact that equilibrium distances among the atoms in the surface layer of crystals are somewhat greater than in their

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* In connection with articles by S. Maričić[1,2,3,4]

bulk[8]. When the crystals coarsen outside layers begin to intergrow in the former bulk with lattice parameters increasing continuously[9]. If correction of these distortions lags behind the growth of crystals then at a certain stage the formation of nuclei with normal lattice parameters becomes more advantageous than completion of crystal formation (Dankov-Konobeevsky principle). An opinion exists that such growth causes mosaic structure of crystals[10]. Growth of mosaic bulk leads to increase of internal stresses on the boundaries of parts with different lattice parameters, and causes fracture[10]. The above phenomenon seems to be observed in the process of hydrargillite crystallization from aluminate solutions. Similar views have been expressed in literature. Thus Ginsberg and Hüttig[7] consider that well crystallized coarse

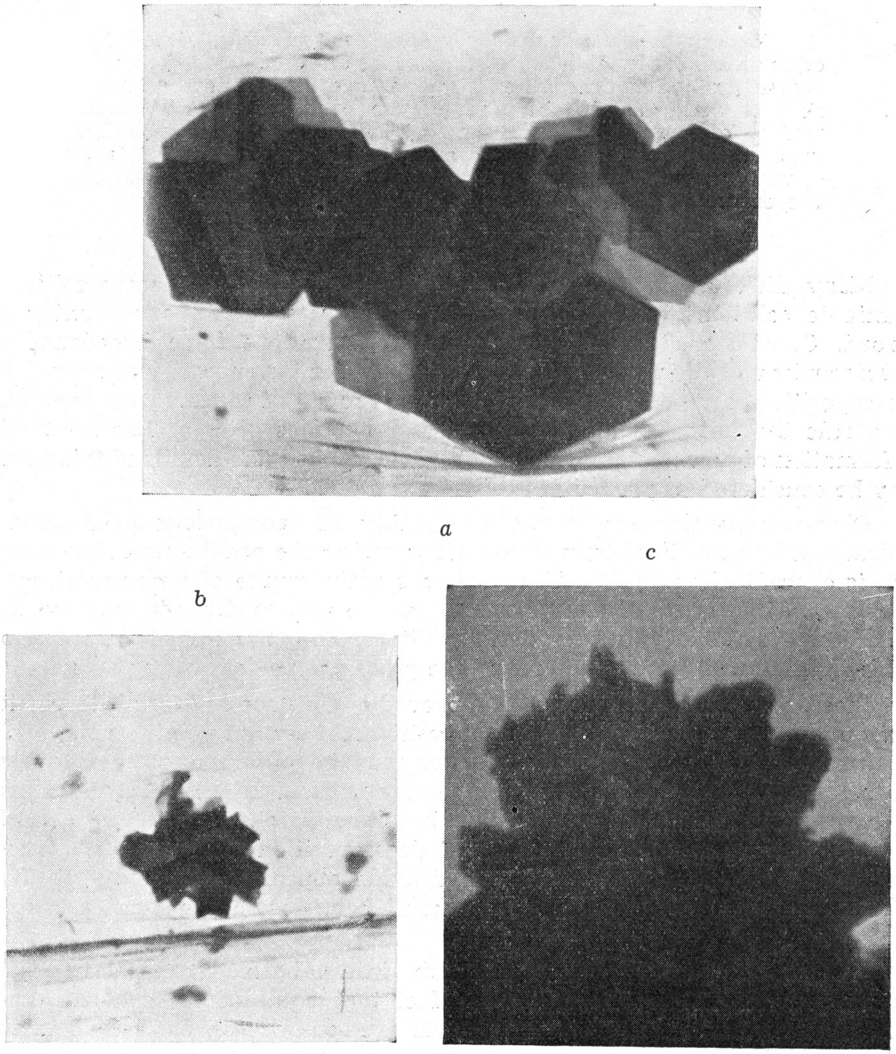

Fig. 1. Electron micrographs of small crystals of hydrargillite, formed in the process of decomposition of aluminate solutions. a, b × 11 400; c × 13 000.

particles of hydrargillite can be fractured during decomposition owing to the dissolving action of locally unsaturated liquor.

During agitation different mechanical effects contribute to the breaking of crystals. It is quite possible that just for this reason aluminium hydroxide particles which are in circulation do not grow above a definite size. We think that breaking of crystals under the influence of internal stresses as well as formation and breaking of dendrites are the main reasons of formation of new hydrargillite particles in the process of decomposition of aluminate solutions.

Ability of hydrargillite crystals to chip off new nuclei depends on many factors including the coarseness and surface condition of particles of original seed.

S. Maričić and his coworkers[2,3] are of opinion that only fine hydroxide with particle size less than 10 μ is able to chip off new nuclei. Coarse grained hydroxide is absolutely unable to induce nucleation. These conclusions were reached after studying the particle size distribution of aluminium hydroxide obtained in decomposition of aluminate solutions with seeds of various coarseness. In particular inactivity of coarse crystalline seed in formation of

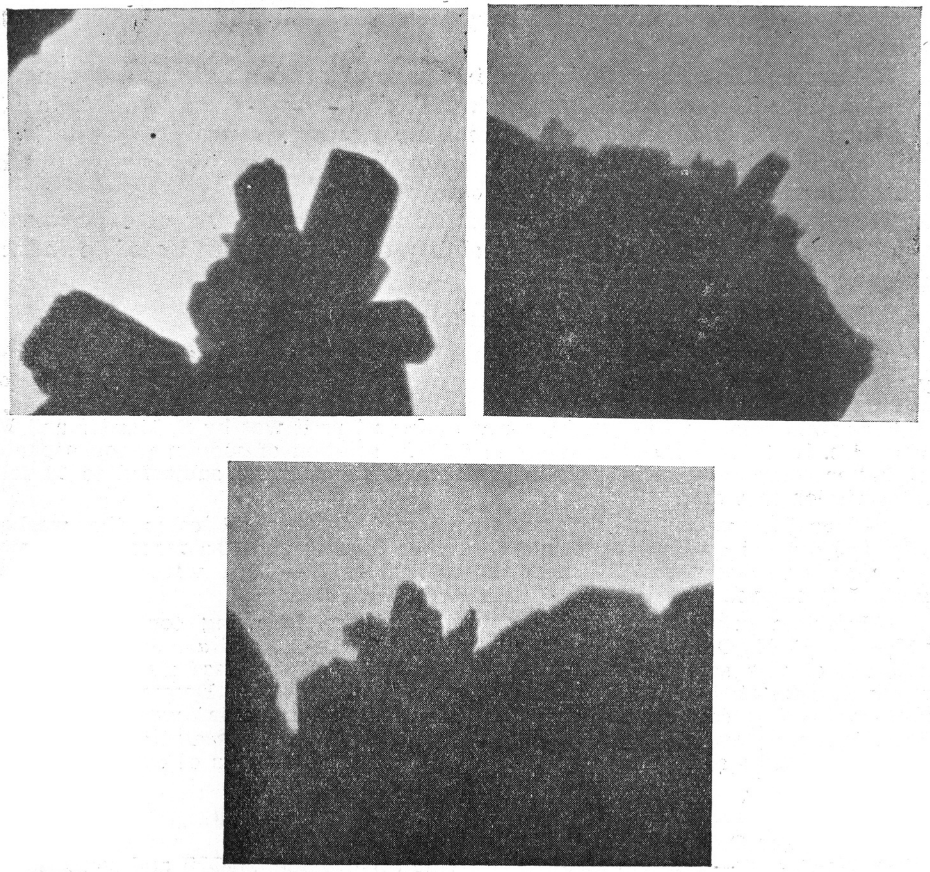

Fig. 2. Electron micrographs of individual parts of coarse hydrargillite crystals, formed in the process of decomposition of aluminate solutions. × 13 000.

new nuclei was demonstrated by the following direct experiment. Coarse-grained hydroxide (+53 μ) carefully separated from fine particles by 10 fold sedimentation in 0.005 *M* solution of sodium pyrophosphate was used as seed when decomposing aluminate solution[3]. After 69 and 77 hour agitation with seed at 50°C there were detected no particles smaller than 53 μ in decomposition products.

The conclusion of Maričić and his coworkers about the ability of fine crystalline aluminium hydroxide to chip off new nuclei is no doubt correct. Numerous observations using electron microscope carried out by us recently* showed that dendrite branches are formed on the surface of many small particles of hydrargillite during decomposition (Fig. 1). Breaking of these particles results in formation of new nuclei. Another conclusion of the above authors about absolute passivity of coarse particles of hydrargillite as to nucleation is quite doubtful. Observations made using electron microscope prove that dendrite branches are formed on coarse hydroxide crystals as well (Fig. 2). Thus coarse grained hydroxide also must chip off new nuclei during decomposition. Our experiments[11] showed that when coarse grained hydroxide + 74 μ separated from small particles by 8 fold sedimentation in water was used as seed, many small crystals were formed in the decomposition product.

S. Maričić thinks[4] that difference in the results of his and our experiments is caused by different conditions under which they were carried out. In his opinion we were unable to separate completely coarse grained hydroxide from small particles because sedimentation in our experiments was carried out in water, and not in sodium pyrophosphate solution.

We considered that possibility and carried out a new set of experiments to get a better understanding of the ability of coarse grained seed to induce nucleation.

EXPERIMENTAL

In the following experiments +40 —63 μ and + 63 μ hydroxide fractions separated by means of sieves from sediments obtained in the decomposition process at Bogoslovsky and Urals aluminium plants were used as seeds. Separation of these fractions from retained fine particles was done just as it was by S. Maričić and M. Vidan[3] *i. e.* by 10 fold sedimentations in 0.005 *M* solution of sodium pyrophosphate. For better comparison some portions of both fractions were subjected to 10 fold sedimentation in water.

Observation under the microscope showed that in all cases the washed hydroxide did not contain any particles smaller than 40 and 63 μ respectively (very fine crystals smaller than 0.5 μ near the crytical — 0.1 — 0.3 μ were not detected by the microscope.)

Aluminate solution to be decomposed had the following content: $Al_2O_3 = 128—130$ g/l, $Na_2O_{caustic} = 130—132$ g/l** ($\alpha_{total} = 1.66 — 1.7$ and $\alpha_{caustic} = 1.65—1.69$). Agitation of this solution with seeds was carried out in glass flasks placed in an air thermostat. Seeding ratio in all experiments was 1.0. Decomposition temperature was lowered mainly from 55 to 37°C. In some experiments it was kept constant (55°C). Sieving was used for particle size analysis with subsequent checking by microscope and in some cases by Figurovsky's[12] method. Results of experiments are given in Table I.

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* Engineer O. K. Shabalina took part in that work.

** $Na_2O_{caustic}$ — Na_2O in solution as sodium hydroxide (NaOH) and sodium aluminate. α_{total} and $\alpha_{caustic}$ are molar ratios of Na_2O_{total} and $Na_2O_{caustic}$ to Al_2O_3 in solution.

RESULTS AND DISCUSSION

TABLE I

Results of experiments for decomposition of aluminate solution with coarse crystalline aluminium hydroxide seeds (+ 40 — 63 μ and + 63 μ).

Seed, part. size fraction	Sedimentation medium	Agitation time, hours	Decomposition of solution, %	Part. size distr. of the product, w. %				
				—40 μ	—50 μ	—63 μ	—100 μ	+100 μ
1	2	3	4	5	6	7	8	9
+ 40 —63 μ (Urals aluminium Plant)	0.005 *M* solution $Na_4P_2O_7$	24	41.5	5.68	18.08	78.58	99.85	0.15
		48	48.5	7.95	21.72	81.85	99.80	0.20
		72	55.75	3.05	23.25	54.64	99.84	0.16
+ 40 —63 μ Bogoslovsky Aluminium Plant	,,	24	37.5	4.94	9.83	76.44	99.95	0.05
		48	48.2	6.18	10.76	70.25	99.96	0.04
		72	53.3	7.91	12.19	69.78	99.96	0.04
+ 40 —63 μ (UAP)	Water	24	44.5	7.32	41.63	84.44	98.94	1.06
		48	52.1	5.47	51.26	90.56	99.82	0.18
		72	55.8	12.82	51.62	92.69	99.85	0.15
+40 —60 μ (BAP)	,,	24	40.75	0.65	6.82	81.42	98.78	1.22
		48	49.3	6.09	17.95	88.41	99.90	0.10
		72	54.7	7.26	13.42	68.24	99.87	0.13
+63 μ (UAP)	0.005 *M* solution $Na_4P_2O_7$	24	40.0	4.15	12.42	14.42	76.95	23.05
		48	46.5	4.06	9.79	11.07	73.01	26.99
		72	49.7	4.58	6.74	7.10	64.60	35.40
+63 μ (BAP)	,,	24	38.2	1.16	3.59	4.09	85.57	14.43
		48	47.5	8.05	10.40	16.26	99.65	0.35
		72	53.2	8.18	11.58	18.24	99.49	0.51
+63 μ (UAP)	Water	24	40.8	1.39	7.72	11.04	60.14	39.86
		48	49.7	7.55	11.53	15.15	74.26	25.74
		72	56.0	5.41	14.16	17.60	68.00	32.0
+63 μ (BAP)	,,	24	40.8	0.26	3.83	8.71	89.70	10.30
		48	49.4	8.43	10.58	17.57	99.72	0.28
		72	54.8	9.83	12.34	20.53	99.71	0.29
+63 μ * (BAP)	0.005 *M* solution $Na_4P_2O_7$	24	36.6	0.37	3.63	9.49	99.40	0.60
		48	42.2	2.30	3.90	7.63	99.70	0.30
		72	46.75	4.15	12.02	25.40	99.70	0.30
+63 μ * (BAP)	Water	24	37.0	0.44	5.46	9.02	99.09	0.91
		48	45.9	2.21	5.95	10.06	99.60	0.40
		72	47.3	5.24	7.74	19.24	99.56	0.44

* In these experiments temperature was kept constant, equal to 55°C. In all the others it was lowered from 55—37°C.

Comparing the above results with data obtained earlier[11], one may see that more careful washing of coarse grained seed hydroxide with water, as well as with $Na_4P_2O_7$ solution, to remove fine particles decreases the amount of fine fractions in the decomposition product. Sedimentation medium has no great influence on the particle size distribution of hydroxide obtained. However, the conclusion of S. Maričić about absolute passivity of coarse crystalline hydroxide in formation of new nuclei again is not confirmed.

In spite of exact reproducibility of conditions of washing of coarse grained seed recommended by S. Maričić, in all our experiments in decomposition we obtained hydroxide sediments which contained a great amount of fine particles (observations under microscope showed that the greatest amount of crystals of —40 μ fraction in sediments were in the range of 2 to 5 μ).

Thus, experiments show that coarse grained hydroxide is able to induce nucleation in the process of decomposition. New nuclei chipped off from large crystals are very small — less than 2—5 μ.

In the main they are fragments of fine dendrite branches which are formed on the surface of large crystals in the process of their growth.

During one decomposition cycle these nuclei cannot grow to 40—60 μ size, which fact is rightly mentioned by S. Maričić[4]. For that reason formation of particles of +40 —63 μ size in decomposition process with + 63 μ seed (Table I) cannot be explained by growth of dendrite particles.

Formation of such particles is most probably caused by breaking of individual +63 μ crystals due to internal stresses.

As demonstrated above, careful washing of coarse grained seed decreases the amount of fine particles in the decomposition product. This is partly due to more complete elimination of retained fine particles from coarse crystalline hydroxide. However, the main reason, in our opinion, is that dendrite branches on surfaces of large particles break when sedimentation is repeated many times.

Just for that reason coarse grained seed if washed carefully chips off fewer new nuclei during decomposition. The amount of seed is an important factor in nucleation.

With seed ratio decreasing the highly dispersed hydroxide content considerably increases. When organic admixtures are present in the original aluminate solution especially sharp reduction in size of particles was observed. Thus, for instance, with the aluminate solution which differed from the above mentioned only by the presence of organic admixtures — containing 1.0—1.5% O_2 expressed as weight percent of NaO_{total} — with small amount of +63 μ seed (seeding ratio — 0.135) at 55°C we obtained sediments in which —40 μ fraction was in the range of 20—30% after 48 and 72 hours of agitation.

It should be noted that when organic admixtures are present in solution coarse as well as fine hydroxide crystals chip off more new nuclei. The ability of coarse grained hydroxide crystals to induce nucleation is confirmed by industrial operation as well. When examining under the microscope periodic changes of hydroxide particle size distribution during decomposition the plant operators observed the following phenomenon. In the last stage of hydroxide coarsening fine particles (—10 μ) completely disappear. After some time, when the seed was coarse crystalline hydroxide with no fine crystals present, the latter again appear in the decomposition product. Since that moment hydroxide particles begin to become finer.

In the above observations one should pay attention to the fact that coarse grained hydroxide is not immediately able to chip off new nuclei. For a certain period of time coarse particles seem to be in the process of getting prepared to nucleation. Thus in certain cases coarse crystalline hydroxide in one decomposition cycle may not demonstrate its ability to induce nucleation. In fact, in certain decomposition experiments (at temperatures above 50°C), when the seed was coarse grained hydroxide (+63 μ) with fine particles not removed by sedimentation we got precipitates in which —40 μ fraction content was negligibly small — not more than 0.5%. With this hydroxide repeatedly used as seed, the above fraction content increased rapidly — to 17—20% (Fig. 3 demonstrating results of a series of laboratory decomposition experiments at 73—50°C). It is quite possible that it is the above property of hydroxide that caused the difference in results of S. Maričić's and our experiments. Thus observations both under laboratory, and plant conditions prove that coarse particles of hydroxide can chip off new nuclei which fact in the main depends on ability of such particles to form dendrites on their surfaces.

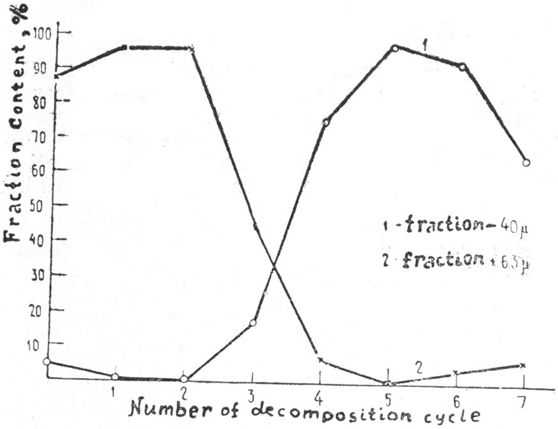

Fig. 3. Change of coarseness of aluminium hydroxide crystals in a series of succeeding cycles of decomposition of aluminate solution.

As noticed by P. S. Vadilo[13] and others, transformation of crystals to dendrites in the process of growth is the faster the larger the crystals. If the crystals are very small, central parts of their faces are near the edges and vertices. Supersaturation of solution near different parts of crystal surfaces is about the same. Thus small crystals grow uniformly even in well supersaturated solution. Vertices and edges of large crystals are in contact with greater volume of supersaturated solution, and thus are in more favourable condition for growth as compared with faces. Besides, these parts of crystals more quickly give up their heat of crystallization to the total amount of solution thus making the adjacent solution still more saturated than that near the faces. All the above mentioned facts contribute to formation of dendrites on surfaces of large crystals.

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IZVOD

O sposobnosti krupnozrnatog aluminijeva hidroksida da inducira nukleaciju u aluminatnim otopinama

S. I. Kuznetsov i V. A. Derevyankin

Opisani su pokusi, kojima je ustanovljena prisutnost novih sitnih kristalića, nakon što su aluminatne otopine bile cijepljene krupnozrnatim hidrargilitom. Taj se efekt pripisuje otcjepljenju dendrita, koji se formiraju na površini velikih kristala kako to pokazuju elektronmikroskopske slike. Do nastajanja čestica srednjih veličina dolazi zbog lomljenja velikih kristala uslijed unutrašnjih napona, koji se razvijaju rastom kristala. Ima slučajeva kada je potrebno izvjesno vrijeme, da bi krupne čestice mogle inducirati nukleaciju.

URALSKI POLITEHNIČKI INSTITUT
SVERDLOVSK, SSSR

Primljeno 19. studenoga 1959.