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

IV. On the »Contact-intercrystallization«

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It is shown that agglomeration of fine particles takes place in this system by the contact of crystallites. This mechanism is very quick and does not involve any measurable separation of a new solid phase from the solution. The name »contact-intercry-

to be the most practical solution to our problem, at least at present. It does not imply any special kind of distribution function, and the surface as well as the number of particles can be easily determined. It has no »statistical parameters« defining the dispersed system, but these seem to become very questionable when trying to define »many-straight-lines« systems even by either of the two above mentioned methods.

By following Odén's idea^4 and taking into account the absolute amount of the dispersed material, one easily obtains the expression:

$$A = K_a W \int_{D_{\min}}^{D_{\max}} \frac{F(D)}{D} \, \mathrm{d}\, D = K_a W \int_{D_{\min}}^{D_{\max}} F(D) \, \mathrm{d} \ln D \qquad (1)$$

where A = absolute geometrical area; K_a = proportionality factor between a linear dimension and the surface of the particles (supposed to be constant for all particles in a given dispersed system); $F(D)$ = frequency distribution function (obtained from the cumulative curve by graphical differentiation), and D = an appropriate linear dimension (hereinafter refered to as diameter) of the particle. The integral defined by (1) and hereinafter refered to as I_a can be evaluated graphically whatever the form of the $F(D)$.

Starting from the total area we still have the difficulty of choosing a proper representative figure for a »mean« diameter. This is unavoidable if the equations (1) and (2) in loc. cit. 1 have to be used. The matter is dealt with later in the discussion of the results.

A more general way might be evolved by making use of the total number of the acting particles. Again, according to S. Odén one can write

$$N = K_n W \int_{D_{\min}}^{D_{\max}} \frac{F(D)}{D^3} \, \mathrm{d}\, D = K_n W I_n \qquad (2)$$

where N = the total number of the particles in the given weight (= W) of the dispersed material; K_n = an (assumed) constant including the volume-proportionality factor and the specific gravity of the material. I_n can also be graphically evaluated.

Supposing also that K_a and K_n remain in our experiments practically constant regardless of the mechanism by which the crystallization takes place, it is now possible to define the previous factor »F« (loc. cit. 1.) in this way:

$$F_n = \frac{W_f I_{nf}}{W_i I_{ni}} \qquad (3)$$

where indeces i and f refer to the initial and final state. The advant be shown later that such a state can be resolved by suitable design of experiments.

RESULTS AND DISCUSSION

Table I comprises all the data concerning particle-size distribution of the products obtained in the separate crystallization experiments lasting as indicated. Fig. 1 represents the rate of crystallization expressed in grams of the solid phase per litre of the aluminate solution at the end of each experiment.

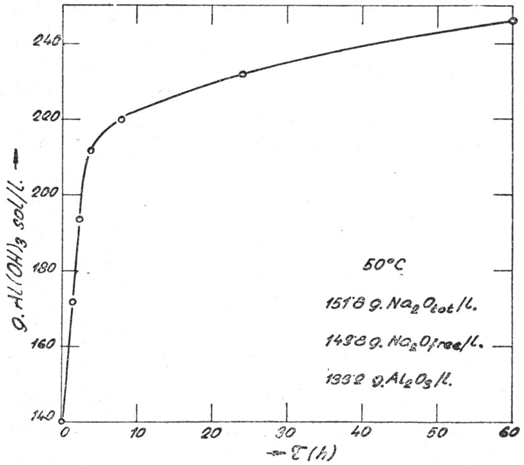

Fig. 1.

TABLE I

μ	W. — % undersize						
60	100.0	*****	*****	*****	*****	*****	*****
40	99.7	*****	*****	*****	*****	*****	*****
30	94.9	98.8	97.6	98.1	96.3	96.7	98.4
20	93.8	91.4	89.8	94.6	94.6	93.4	96.4
15	91.0	****	****	****	****	90.0	****
12	86.6	****	****	****	****	84.8	****
10	84.2	76.0	78.8	****	82.5	76.2	84.4
9	****	65.9	69.8	83.5	78.2	69.6	98.9
8	77.0	49.1	59.4	77.4	67.5	63.9	59.8
7	73.0	30.9	36.6	62.8	41.8	43.4	46.7
6	66.8	19.7	18.9	37.3	20.8	23.5	34.2
5	43.1	10.0	8.0	18.6	12.5	13.2	20.1
4	23.1	5.7	4.7	10.4	6.7	7.4	10.8
3	11.1	3.2	2.0	3.2	4.0	****	****
2	5.9	****	****	****	****	****	1.3
1	1.4	****	****	****	****	****	****
	0	1½	2½	4	8	24	60

Duration of experiments in hours

Because we are mostly interested in the relative change of the values given by (1) and (2), all the figures in Table II have been obtained by using always the same method in all graphical calculations. Thus, the figures in Table II should be regarded as directly proportional to the specific ($I_a \rightarrow K_a m^2/g$) and absolute ($WI_a \rightarrow K_a m^2$) surfaces, and similarly proportional to the number of particles (I_n; WI_n). When two figures are given for one experiment, some uncertainty in the small-particles range of the size-distribution curves is indicated. It is obvious that the discrepancies are more pronounced for eq. (2) than for (1) because in the former case the final result is more affected by D, owing to the factor $1/D^3$, whereas the corresponding factor in eq. (1) is $1/D$. Actually, we may say that equation (3) yields a very sensitive method for distinguishing between various possible crystallization mechanisms providing the number-distribution function is estimated with good precision.

TABLE II

Hours	I_n	$W \cdot I_n$	I_a	$W \cdot I_a$	D_{infl}	$F_{n,o}$
0	4.011	561	0.669	93.6	5.2	****
1½	0.553 0.709	94.9 121.7	0.454 0.457	78.0 78.4	7.9	0.17 0.22
2½	0.346 0.374	67.0 72.3	0.417 0.409	80.7 79.2	7.4	0.12 0.13
4	0.739 0.944	199.6 156.3	0.505 0.511	106.8 108.0	6.5	0.35 0.28
8	0.750	165.0	0.472	104.0	7.1	0.29
24	0.442	102.5	0.449	104.2	7.0	0.18
60	0.694	170.5	0.499	123.0	7.2	0.30

It can be seen from the Table II that F_n is again always smaller than unity. Despite the discrepancies it may also be concluded that the intercrystallization occurs at the very beginning of the process. This is supported by the sudden fall in the values of both WI_a and WI_n during the first one and a half hour.

The F_n-value is a comulative one depending on the arbitrarily chosen starting reference figure (denominator in eq. 3). This fact was overlooked in our second paper and we consequently misconcluded that intercrystallization is a time-consuming process occuring simultaneousely with nucleation. The above results seem to lead to the conclusion that the agglomeration i. e. intercrystallization is at least a very quick process after which nucleation takes place (note the increase in WI_a or F_n, or even better the constant and pronounced decrease in D_{infl} after the first one and a half hour).

Another set of experiments was performed (with seed II.) to prove the correctness of the last conclusion. The final consequence of such an assumption must be that no consumption of new solid phase is needed, the intercrystallization taking place by mere contact of the crystallite surfaces. In this case the effect should only depend on a single critical distance between the particles. On the other hand, if the mechanism requires considerable time, the effect (expressed in terms of eq. 3) should be greater the larger is the concentration of the suspension.

In the first approximation it is possible to derive the equation connecting the concentration of the suspension and the distance between particles by supposing: a) monodispersity of the system; b) simple cubic lattice arrangement of the particles in the suspension (neglecting in this way the rheological conditions due to the mixing, or any other kind of random distribution); c) by taking the characteristic distance as the free distance (b) between the particles at the cube-edges; d) that the particles are spherical and e) that the probability for the intercrystallization is the same regardless of the size of the particle. The equation is then

$$b = D\,[(K\,C_s)^{-\frac{1}{3}} - 1] \qquad (4),$$

where $K = 1\,(\pi\,\rho\,/6)$.

A few preliminary experiments showed clearly that the duration of experiments could be cut down to 15 minutes (without any measurable decomposition of the aluminate solution). In this way it becomes possible to observe what might be called the »contact-intercrystallization«.

TABLE III

μ	W. — % undersize						
30	95.2	95.4	90.6	91.4	95.3	94.8	91.8
25	94.7	93.7	89.7	89.9	95.2	94.2	90.6
20	93.5	93.4	87.7	89.0	94.0	92.5	89.0
15	92.8	91.1	86.8	88.5	92.1	91.2	88.7
12	92.3	90.4	86.3	87.5	89.9	90.2	87.2
10	91.4	89.7	84.6	85.5	89.1	89.9	86.0
8	89.0	86.2	76.4	80.0	85.0	85.8	85.0
6	71.3	69.8	36.1	55.5	67.3	****	55.5
5	51.0	50.0	18.0	35.5	50.9	46.5	29.0
4	31.3	34.0	10.7	19.0	32.7	30,3	17.0
3	17.3	17.0	4.8	9.0	17.8	16.6	6.5
2,2	8.7	****	****	****	****	*****	****
2	7.1	****	****	****	****	****	****
1,5	****	****	****	****	4,2	****	****
1,2	1.9	****	****	****	****	****	****
	orig.	44.7	53.4	60.3	70,2	90.2	98.4
	seed	Concentrations of the seed-suspensions in g/l.					

Table III contains the suspension concentrations in each experiment and the resulting size-distributions. In Fig. 2 eq. (4) is represented graphically for $D = 5$ microns (according to the D_{infl} of the starting seed in Table III). The results of Table III expressed in terms of (3) (which now becomes $F_{\mathrm{n}} = I_{\mathrm{nf}}/I_{\mathrm{ni}}$) are also included in the same diagram.

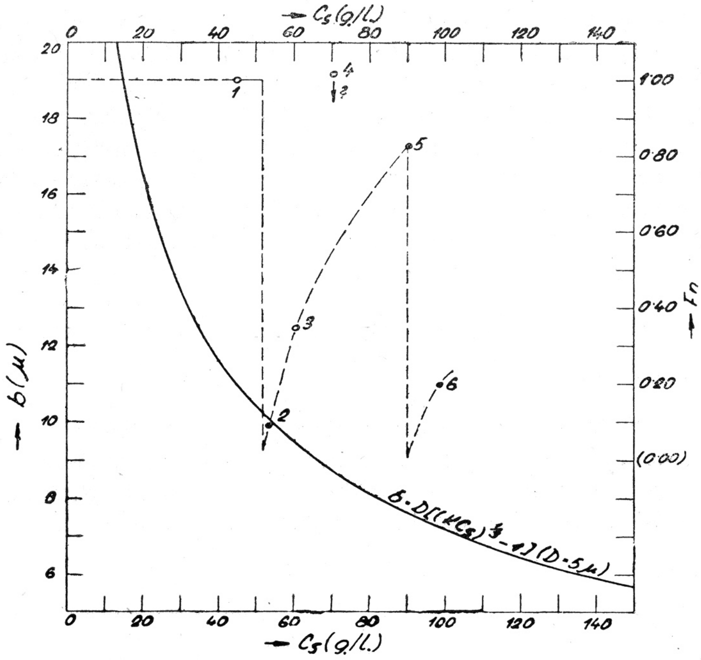

Fig. 2.

The explanation seems to be as follows. The experiments were performed by pouring a given amount of air-dried seed into the mixed aluminate solution (the composition of which was similar to that indicated in Fig. 1) at 50°C. If all the seed has been added and if the final suspension concentration is less than the critical one, the intercrystallization should not occur at all. This is the case in experiment No. 1 (Fig. 2). The first observed effect of contact-intercrystallization occured at a concentration of 53,4 g. seed/1. (No. 2) This concentration seems to be quite plausible in view of its coincidence with the region of eq. (4) in which a pronounced increase in b has to be expected when the suspension-concentration is lowered.

If the ammount of seed exceeds the critical concentration (hereinafter abbreviated as c. c.), then, because the intercrystallization occurs almost immediately after the c. c. is achieved by pouring the seed into the solution, the distances between the new agglomerates become much larger. Thus, the surplus of the seed poured in afterwards cannot change its state of dispersivity. This is the reason for the increase of F_{n} although, of course, it is still less than unity (No. 3, 5). An equal (maximum) change in F_{n} can occur again when the concentration of the suspension is (roughly) twice as large as the critical one (No. 6)

The saw-like curve of $F_n = f(C_s)$ as in Fig. 2 is, in fact, what should be expected theoretically for the proposed mechanism. Quantitatively, it does not correspond to the theoretical one in that the slope of the increase of F_n must be smaller. In each next step it should become less and less pronounced until (it is to be expected) the much smaller surplus of the unagglomerated particles does not affect practically the primary state after contact-intercrystallization. Anyway, there is no doubt that this mechanism deserves the proposed name, being a very quick one and depending only on the critical concentration of the suspension (for a given seed). Let us add here, that the same effect (of intercrystallization) was also observed when immersing seed in an unsaturated aluminate solution. In view of this, it seems that the concentration of the Al-component of the aluminate solution does not play a deciding role. The problem remain still of solving to what extent both components of the solution contribute to the proposed mechanism. If neither of them were taking any part in the contact — intercrystallization, then he same effect could also happen during the washing (when much larger seed-concentrations are present), which was not the case.

CONCLUDING REMARKS

The ratio of the final to the initial number of particles ($= F_n$, see eq. 3) in a crystallization process yields very valuable information on predominance of enther simple-crystal-growth, or nucleation or contact-intercrystallization. As far as the present problem is concerned it is clear that further improvment in the crystallization experiments is very much desirable. But even using the present technique it is possible to resolve in doubtfull cases ($F_n \sim 1$) whether only simple-crystal growth occurs or a combination of the two other mechanisms is taking place. It can be done by following the change of F_n (or the absolute number of particles) with time. Generally, if in a certain period of time the decomposition of the liquid-phase takes place, but $dF_n/d\tau$ remains equal to zero, then simple-crystal-growth is the only mechanism involved in this period of crystallization. According to whether $dF_n/d\tau$ is larger or smaller than zero nucleation or contact-intercrystallization respectively predominates.

Because of the instantaneous character of the last mentioned mechanism one must, in fact, expect only discontinuous changes in the curve $F_n = f(\tau)$, namely, when the critical concentration of the suspension due to the nucleation (or a multiple of this) is achieved.

If, by chance, the concentration of the seed-suspension happens to be at the very beginning (as it was in the first set of experiments reported here) equal (or slightly greater) to the (multiple) critical concentration, contact intercrystallization will occur suddenly. After that the system is still able to create nucleation though to a smaller extent than before because of the smaller total (free) surface. The nucleation ceases to predominate after the supersaturation is lowered to such an extent that only simple-crystal-growth is possible (see Fig. 1 and Table I).

It seems that there is no further doubt about the existance of an agglomeration mechanism, which is also reported by T. G. Pearson[5]. Unfortunately, the results of this author have not yet been published in detail, so that it is difficult to discuss any possible explanation of the descrepancy between his results, which describe the agglomeration as a time-dependent process (measured in hours), and our conclusions here.

As for the practical applicability of the contact-intercrystallization it is too early to say anything definite. Anyhow, it seems that there is some potential possibility of solving the well known problem: to obtain not too fine-grained $Al(OH)_3$ in a reasonably short time. One can get a large ammount of the fine product in a very short time by seeding with an extremely active seed. It might be possible to obtain afterwards coarser product by allowing an increase of the suspension-concentration. Of course, many problems arise which must first be solved: 1) how many repeating steps in increasing the particle-diameter is it possible to attain at all; 2) the Na_2O-content in such a product; 3) the constructional problems and 4) the plant control.

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IZVOD

Kinetika stvaranja aluminijeva hidroksida cijepljenjem otopine natrijeva aluminata kristalima hidrargilita. IV. O »kontaktnoj interkristalizaciji«

P. Bogdanović, S. Maričić i M. Vidan

U ovom je radu podrobnije ispitan mehanizam aglomeracije finih čestica, na koji je bilo već upozoreno. Eksperimentalno je pokazano, da je taj mehanizam vrlo brz i da ne zahtijeva (mjerljive količine) nove čvrste faze iz otopine, koja bi služila kao vezivo. Aglomeracija nastaje čim se postigne kritična koncentracija suspenzije ili njezin (približno) višekratnik. Zbog tih je karakteristika predložen naziv iz naslova. Diskutiran je najprikladniji način za preračunavanje težinskih krivulja raspodjele veličine čestica u brojčane i upozoreno je na mogućnost razlikovanja između triju mogućih mehanizama u procesu kristalizacije.

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