A New Crystal Nucleation Theory for Continuous Precipitation of Silver Halides*

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A new steady state theory of crystallization in the continuous stirred tank reactor (CSTR), or mixed-suspension mixed-productremoval (MSMPR), system was developed based on a dynamic balance between growth and nucleation. The present model was (but is not) limited to nonseeded systems with homogeneous nucleation, diffusion controlled growth, and a nucleation model previously confirmed for such systems in controlled double-jet batch precipitations. No assumptions of size-dependent growth were needed. The model predicts the correlation of the average crystal size with residence time, solubility, and temperature of the system and enables calculation of the supersaturation ratio, the maximum growth rate, the ratio of nucleation to growth, the ratio of average to critical crystal size, and the size of the nasent nuclei. The model predicts that the average crystal size is independent of reactant addition rate and suspension density. The average crystal size is a nonlinear function of the residence time where the crystal size has a positive value at zero residence time (plug-flow condition). Results of continuous precipitations of silver chloride confirm the predictions of the model. The ratio of the fraction of the input stream used for nucleation and crystal growth was calculated from the experimental results to decrease from 4.79 to 0.12, and the size of the nascent crystals to increase from 0.194 to 0.221 µm between 0.5- and 5.0-min residence time. The ratio of average to critical crystal size was determined to 5.73*10³ (1.02 to1.09), the supersaturation ratio to 12.2 $(0.54, \text{ average crystal size } L= 0.5 \,\mu\text{m})$, the supersaturation to $8.2 \times 10^{-8} (12.7 \times 10^{-9} \text{ mol}/l, L = 0.5 \,\mu\text{m})$, and the maximum growth rate to 4.68 A/s (1.20 to 4.25). The data in the brackets are for equivalent batch precipitations. The experiments indicate that the width of the crystal size distribution increased with suspension density and was independent of reactant addition rate. While the present model was developed for homogeneous nucleation, diffusion limited growth, and unseeded systems, it may be modified to model seeded systems, systems containing ripening agents or growth restrainers, and systems where growth and nucleation are kinetically, heterogeneously, or otherwise controlled.

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Introduction

It is the object of this work to extend the previously reported model of crystal nucleation for precipitation of highly insoluble compounds in controlled double-jet precipitation batch processes^{1–5} to precipitations in continuous suspension crystallizers.

The present proposed new theory of crystallization in continuous mixed-suspension mixed-product-removal (MSMPR) crystallizers [here referred to as continuous stirred tank reactor (CSTR)] differs from the previous theory for continuous precipitation by Randolph and Larson^{6,7} in that it correlates the average crystal size of the crystal population with reaction conditions like residence time, temperature, and crystal solubilitity. It is thus intended to complement the Randolph–Larson theory which is concerned with the crystal population size distribution.

In addition, the new theory consists of three distinct parts that distinguish it from the Randolph–Larson theory:

- 1. The new model is based on a dynamic balance between crystal nucleation and crystal growth at steady state.
- 2. The new mathematical treatment of the model is based on mass and nucleation balance. It shares certain concepts of mass and nucleation balance with the Randolph-Larson theory. In addition, it introduces the concepts and equations of the crystal nucleation theory previously proposed and experimentally supported by the author and his coworkers. This leads to new mathematical equations that have no arbitrary adjustable parameters. These new equations are significantly different from those of the Randolph-Larson theory. Furthermore, the new theory and the equations make distinctly new predictions. Some of these were experimentally supported in the present work.
- 3. The new theory is supported by experimental results. As in any new endeavor, only few predictions could be tested. The theory and the equations give ample suggestions for further experimental and theoretical research.

The use of continuous precipitation systems for the precipitation of silver halide dispersions has been investigated previously.⁸⁻¹³ Continuous streams of reactants (silver nitrate and halide solutions) and a gelatin solution are fed to a well-stirred precipitation vessel and product is simultaneously removed while maintaining a constant reaction volume and reaction conditions (Fig.

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Figure 1. Schematic diagram of the continuous suspension crystallizer for silver chloride precipitations.

1). Initially, the precipitation vessel contains an aqueous solution of gelatin and halide salt. It may include silver halide seed crystals that would affect the transient period but would not affect the present results, which are based on spontaneous homogeneous nucleation. After a transient time period a steady state is reached after which the size distribution and morphology of silver halide crystals removed from the precipitation vessel remain unchanged. In Gutoff,^{8,9} Wey and Terwilliger,¹⁰ and Wey et al.^{11,12} the crystal size distribution was investigated using the formalisms derived by Randolph and Larson for the mixed-suspension, mixed-product-removal (MSMPR) system [Randolph and Larson^{6,7}].

Wey et al.¹² examined the crystal size distribution of AgBr using the population balance technique and included both McCabe's ΔL law (size-independent growth rate) and a size-dependent growth model. The crystal population distribution could not be satisfactorily modeled. Using the large grain population, nucleation and maximum growth rates were determined using the Randolph–Larson model. The rates were empirically related to temperature and supersaturation. Their data indicate that the nucleation of AgBr is homogeneous and that no significant secondary nucleation mechanism is involved in the precipitation of AgBr crystals.

Wey, et al.¹³ studied the transient behavior of unseeded silver bromide precipitations and determined that the steady state of crystal population distribution was achieved only at about 6 to 9 residence times (τ) after the start of the precipitations, much later than the steady state of suspension density (at about 4 residence times). Their results also showed that at steady state the crystal population is rather narrowly distributed around an average crystal size.

In Fig. 2, electron micrographs of AgCl crystals (carbon replica) are shown that were obtained at steady state for CSTR precipitations at a residence time of 5.0 min. In Fig. 3, the crystal size distribution of AgCl at steady state is shown for precipitations varying in residence time from 0.5 to 5.0 min. It is apparent that the distribution is rather narrow and can be described by an average crystal size L, and a somewhat symmetrical crystal size distribution. In a log numbered size plot (R/L theory), the curves are not symmetrical in agreement with AgBr precipitations (Wey et al.¹²). Clearly, the steady state crystal size distribution predicted by the Randolph–Larson model (Ref. 7, p. 87).



Figure 2. Electron micrographs of silver chloride crystals (carbon replica) obtained at steady state. Residence time 5.0 min., 60°C, pAg 6.45, 2.4% gelatin, suspension density 0.1 mol/l.

An objective of this work is to derive a model that predicts the average crystal size of these precipitations and to support some of the model's predictions experimentally. This model is based on the previously derived nucleation model for batch double-jet precipitations, the maximum growth rate of the system, and the dynamic mass balance between nucleation and growth. The newly developed model explicitly describes the average crystal size as a function of experimental variables like solubility of the product, residence time, and temperature without the assumption of arbitrarily adjustable parameters. The fractions of the incoming reaction stream that are used for nucleation and growth can be determined. The average size of the nascent (newly formed) crystals at steady state also can be calculated. The new model also leads to the determination of the critical crystal size, which allows calculation of the supersaturation ratio in the precipitation system.

Theory

Review. Since its first publication, the model by Randolph and Larson^{6,7} has found wide application to describe the crystal size population in continuous MSMPR crystallizers (Eq. 1):

$$n = n^0 \exp(-L_x/G_m \tau), \tag{1}$$

where $n = \text{population density at size } L_x$, $n^0 = \text{nuclei population density, number/(volume-length)}$, $G_m = \text{maximum}$ growth rate, and $\tau = \text{residence time. Equation 1 describes}$ the expected number distribution of the crystal product at steady state. This equation is applicable where a straight line of a plot of the logarithm of population density n versus crystal size L_x describes the crystal size population. It was observed in precipitations of silver bromide¹² and AgCl (Fig. 3) that the crystal size distribution is not described by Eq. 1 but is given by¹³ a somewhat symmetrical distribution around an average crystal size L where only a small, large-sized part of the crystal population obeys Eq. 1. The Randolph–Larson theory (Eq. 1) also does not explicitly include other factors that affect the precipitation population



Figure 3. AgCl crystal size distribution for residence times varying from 0.5 to 5.0 min. (60°C, pAg 6.45, 2.4% gelatin).

such as reactant addition rate, solubility, or temperature effects. A new theory is presented that directly correlates the average crystal size L (cm) to the residence time τ (s), the solubility C_s (mol/cm³), and temperature T (K), and makes predictions about the effect on reactant addition rate and suspension density. This new model is derived from the nucleation theory for batch precipitation, which was developed by this author and coworkers.¹⁻³

New Model. In continuous MSMPR crystallizers, reactants, solvents, and other addenda are continuously added while the product is continuously removed (Fig. 1). In the following, this precipitation scheme will be referred to as a continuously stirred tank reactor (CSTR) system. For the present derivation, only the reaction-controlling reactant that leads to the crystal population will be considered. For instance, silver halides are generally precipitated with excess halide in the reactor, which is used to control the solubility. Thus the soluble silver salt, e.g., AgNO₃, is the reaction-controlling compound. The solubility of the resultant silver halides (chloride, bromide, iodide, and mixtures) is so low that their concentration in the reactor will be neglected for the mass balance. For other precipitations where the solubility of the reaction product is significant, the solubility will need to be retained as an explicit rate term on the right side of Eq. 2. Similarly, unreacted material needs to be added as a rate term on the right side of Eq. 2.

Flow rates of other necessary addenda for the precipitation, such as halide salt solutions, water, gelatin, etc., are included into the calculation of the residence time τ and suspension density M_i and are important to control the silver halide solubility. The present model is based on several premises. It is apparent that modifications of the present model can be obtained by changing some of these premises.

- The reactants react stoichiometrically to form the crystal population, and the solubility of the resultant product (in the present experiment, silver halide) is not significant with regard to the mass balance. It is straightforward to expand the model to include the effect of significant solubility of the reaction product.
- Homogeneous nucleation is assumed. For nonhomogeneous and other nucleation processes, the proper nucleation model must be substituted for the presently used nucleation model.
- The input reactant stream at steady state is consumed in a constant ratio for crystal nucleation and crystal growth (Fig. 4).



 R_0 = Reaction Addition Rate = Product Removal Rate

 R_n = Fraction of R_0 consumed for Crystal Nucleation R_i = Fraction of R_0 consumed for Crystal Growth

 $\label{eq:Figure 4. Dynamic mass balance model for the CSTR/MSMPR system.$

- Crystal nucleation in the CSTR system follows the same mechanism as in double-jet precipitation.
- Crystal growth is given by the maximum growth rate of the crystal population. In the present derivation, a single maximum growth rate G_m is assumed, which can be derived from the experimental results (see below). However, an analytical equation for G_m as a function of crystal size and reaction conditions may be substituted if it is known. This reduces the number of unknowns in the final equation to the ratio of average to critical crystal size L/L_c .
- For the present derivation it is assumed that the nucleation is by a diffusion-controlled mechanism.³

The following approach was successfully used previously to describe renucleation in batch precipitations quantitatively. 14

When a stream of reactant R_0 [addition rate of reactant, e.g., silver nitrate (mol/s)] is added to the reaction vessel at steady state, a fraction of the stream will be used to renucleate new crystals to replace crystals leaving in the product stream (R_n , addition rate fraction used for nucleation) and the remainder to sustain the maximum growth rate of the crystal population (R_i , addition rate fraction used for growth = crystal size increase) (Fig. 4). These assumptions are well met by the precipitation of highly insoluble materials such as the silver halides that perform at practically 100% conversion. The mass balance requires that

$$R_0 = R_n + R_i. \tag{2}$$

The addition rate R_0 is given by the concentration (mol/l) and flow rate (l/s) of the reactants. The product removal rate at steady state is by definition equal to the reactant addition rate. In the following, R_n and R_i will be derived and finally inserted in Eq. 2 to provide the new model for the crystal population at steady state.

Crystal Nucleation. The number of crystals nucleated Z_n must be equal to the number of crystals leaving in the reaction stream and is given by the mass balance:

$$Z_n = R_0 V_m / k_v L^3, \tag{3}$$

where V_m is the molar volume of the reaction product (to convert molar addition rate into volume cm³/mol) and k_v is the volume factor that converts from the characteristic average crystal size L to crystal volume (see glossary). This definition of nucleation rate is different from B^0 used in the Randolph–Larson theory, which is defined as the rate of formation of nuclei per unit volume in the crystallizer.⁷

As will be shown in the new theory and in the experimental section, the nucleation rate is independent of reactor volume for homogeneous nucleation conditions.

For homogeneous crystal nucleation under diffusion-controlled growth conditions, Eq. 4 was derived for double-jet precipitations¹⁻³:

$$Z_n = R_n R_g T/2 k_s \gamma D V_m C_s \Psi, \qquad (4)$$

where

$$\Psi = L/L_c - 1.0 \tag{5}$$

and R_g is the gas constant, T is the temperature (K), k_s is the crystal surface factor, γ is the surface energy, D is the diffusion coefficient of the reaction-controlling reactant, and C_s is the sum of the solubility with regard to the reaction-controlling reactant. The value L_c is the critical crystal size at which a crystal has equal probability to grow or to dissolve by Ostwald ripening. In previous papers,^{1-3,14} Eq. 4 was quoted for the specific case of spherical crystal morphology ($k_s = 4 \pi$). For batch processes Z_n equals the total number of stable crystals formed during nucleation. Here Z_n is equal to the nucleation rate (dZ/dt) at steady state. This extrapolation is in agreement^{1,3} with the underlying derivation of Eq. 4.

For the remainder of the derivation of the equations, the intermediate variable K is introduced:

$$K = R_{g}T/2k_{s}\gamma DV_{m}C_{s}\Psi.$$
 (6)

This leads to a simplified equation for Z_n :

$$Z_n = KR_n, \tag{7}$$

which is solved for R_n :

$$R_n = Z_n / K. \tag{8}$$

Substitution of Z_n from Eq. 3 into the equation for R_n (Eq. 8), leads to

$$R_n = R_0 V_m / K k_n L^3. \tag{9}$$

Thus, an analytical equation for R_n has been found, which below will be entered into Eq. 2. It remains now to develop an analytical equation for R_i , which is derived from the maximum growth rate of the crystal population.

Crystal Growth. The growth rate G is defined as the change in crystal diameter with time, dL/dt. The maximum growth rate G_m is given by the mass balance between the maximum growth of the system and the fraction of the reactant addition rate consumed for this growth R_i . The maximum growth rate is a function of crystal size, and thus the individual size classes will grow at different absolute maximum growth rates. The maximum growth rate of the whole crystal population is then given by an average maximum growth rate G_m , which is defined to be related to the average crystal size L.

If the crystal size is difficult to determine because of a complicated crystal structure, for instance, denditric crystals, the specific surface area S_m (e.g., surface area/mol of crystals) may be used to derive the maximum growth rate. This was not necessary under the present conditions. The use of S_m was discussed in Leubner,¹⁴ and may be transferred to the present model as desired.

Equation 10 results in solving this mass balance for G_m :

$$G_m = V_m R_i / 3.0 k_v L^2 Z_t.$$
(10)

Here, Z_t is the total number of crystals present in the reaction vessel during steady state. The value Z_t can be calculated from the average crystal size and the suspension density, which, in turn, is a function of reactant addition rate and residence time.

$$Z_t = R_0 V_m \tau / k_v L^3. \tag{11}$$

Inserting Eq. 11 into Eq. 10 and solving for R_i leads to the desired analytical equation for R_i :

$$R_i = 3G_m R_0 \tau / L. \tag{12}$$

At this point, both R_n and R_i have been expressed by analytical expressions that contain only fully defined parameters and variables. It is now possible to continue to the formulation of the new theory.

Crystal Growth and Nucleation in the Continuous Crystallizer. The foundation has now been laid to combine nucleation and growth at steady state. For this purpose the expressions of R_n (Eq. 9) and R_i (Eq. 12) are inserted into Eq. 2. After simplifying, Eq. 13 is obtained:

$$V_m/Kk_vL^3 + 3G_m\tau/L = 1.0.$$
 (13)

Reinserting K into this equation and solving for zero leads to:

$$k_{v}L^{3}R_{g}T - 2k_{s}\gamma DV_{m}^{2}C_{s}\Psi - 3k_{v}G_{m}R_{g}TL^{2}\tau = 0.$$
(14)

Solving for *L* results in a very complicated solution as a function of residence time which is of little immediate use. But solving for the residence time τ is relatively straightforward:

$$\tau = L/3 \ G_m - 2k_s \gamma D V_m^2 C_s \Psi/3k_v G_m R_g T L^2.$$
(15)

These equations can be used to determine G_m and Ψ from the experimental values of residence time τ and the average crystal size L obtained at crystal population steady state, and by entering the other parameters that are either known or can be experimentally determined. If G_m is known from other experiments (or an analytical equation of G_m is available that relates it to the crystal size and reaction conditions), this may be substituted in Eq. 15. This would reduce the number of unknowns to Ψ .

From Ψ and the average crystal size L, the critical crystal size L_c can be calculated (Eq. 5), which is related to the supersaturation ratio by

$$S^* = 1.0 + 2\gamma V_m / R_g T L_c.$$
(16)

The supersaturation ratio S^* is defined by Eq. 17:

$$S^* = (C_{ss} - C_s) / C_s, \tag{17}$$

where $C_{\rm ss}$ is the actual (supersaturation) concentration and $C_{\rm s}$ is the equilibrium solubility as defined above.

Special Limiting Conditions for Continuous Crystallization. Two limiting cases of Eq. 15 are of special interest. For this purpose Eq. 15 is rewritten¹⁵:

$$\tau = L(1.0 - 2k_s\gamma DV_m^2 C_s \Psi/k_v L^3 R_g T)/3G_m.$$
(18)

Very Large Average Crystal Size *L*. If the average crystal size is very large as given by the definition in Eq. 19:

$$L^{3} \gg 2k_{s}\gamma DV_{m}^{2}C_{s}\Psi/k_{v}R_{\sigma}T, \qquad (19)$$

then the term inside the parenthsis of Eq. 18 can be set equal to one and simplified to

$$\tau = L/3G_m \tag{20}$$

or

$$L = 3G_m \tau. \tag{21}$$

This indicates that τ and L are linearly related and G_m the maximum growth rate can be determined from the linear part of the correlation at large crystal sizes. The growth rate G_m can then be resubstituted into the original Eq. 14, 15, or 18, and Ψ can be determined.

Continuous Precipitation in a Plug-Flow Reactor, τ

 \rightarrow **Zero**. The second limiting case of the above equation is when τ , the residence time, approaches zero. The above equation predicts that under this limiting condition, the average crystal size will not become zero but reach a limiting value.

Plug-flow reactors are characterized by a short residence time in the nucleation zone, $\tau \rightarrow 0$, followed by crystal growth and ripening processes. The present derivation allows us to predict the minimum crystal size for the condition where $\tau \rightarrow 0$:

$$L^{3} = 2k_{s}\gamma DV_{m}^{2}C_{s}\Psi/k_{v}R_{g}T.$$
 (22)

Substituting

$$V_{g} = k_{v}L^{3}, \qquad (23)$$

where V_{g} is the average crystal volume, leads to

$$V_{g} = 2 k_{s} \gamma D V_{m}^{2} C_{s} \Psi / R_{g} T. \qquad (24)$$

Thus, for residence times approaching zero, the average crystal volume V_g is only a function of solubility C_s and temperature T. The value Ψ , which can be calculated from Eqs. 22 or 24, may be a function of C_s and T. Note that without the $1/L^2$ term, Eq. 15 would predict zero crystal size for zero residence time.

Nucleation versus Growth, R_n/R_i . In the model used for these derivations, the reactant addition stream R_0 is separated in the reactor into a nucleation stream R_n and a growth stream, R_i (Fig. 4). It is now possible to derive the ratio of the reactant streams R_n/R_i by dividing Eqs. 9 and 12. After back-substituting for K (Eq. 6), Eq. 25 is obtained:

$$R_n/R_i = 2k_s \gamma D V_m^2 C_s \Psi/3k_v G_m R_\sigma T \tau L^2.$$
⁽²⁵⁾

Except for τ in the divisor this is equal to the second part on the right side of Eq. 15. If we simplify to Eq. 26, it becomes evident that the ratio R_n/R_i decreases with increasing residence time τ and with the square of the average crystal size at steady state.

$$R_n/R_i \sim 1/\tau L^2. \tag{26}$$

It appears intuitive that the nucleation should decrease relative to growth as the residence time and the surface area of the crystal population (proportional to L^2) increase.

The value of the ratio R_n/R_i was calculated from the experimental data. From the ratio R_n/R_i and the mass balance (Eq. 2), R_n and R_i were calculated as a fraction of the reactant addition rate R_0 .

Nascent Nuclei Size. For the present work, the term "nascent nuclei" is defined as the stable crystals that are newly formed during steady state, which continue to grow in the reactor and which are removed from the reactor. The size of these crystals is larger than that of the critical nuclei, which have equal probability to grow or dissolve in the reaction mixture. The nascent nuclei will have a crystal size distribution that is related to the critical crystal size. The nascent nuclei population may be represented by an average nascent nuclei size L_n . With the model that has been developed up to this point, it is possible to calculate L_n for the different precipitations.

For this purpose we define L_n by:

$$L_n^{3} = R_n V_m / k_v Z_n.$$
(27)

Here, Z_n can be calculated from Eq. 3 and R_n can be calculated from Eqs. 2 and 25. Back-substitution into Eq. 27 leads to Eq. 28:

$$L_n^3 = (R_n/R_0)L^3.$$
(28)

This equation was used to calculate L_n values for the different residence times.

It is now possible to back-substitute further from Eq. 25, and Eq. 29 is obtained that relates the nascent nuclei size to the precipitation conditions and the average crystals size at steady state:

$$L_{n}^{3} = 2k_{s}\gamma DV_{m}^{2}C_{s}\Psi L^{3}/(3k_{v}G_{m}R_{g}T\tau L^{2} + 2k_{s}\gamma DV_{m}^{2}C_{s}\Psi) \quad (29)$$

The terms in this equation have been defined above and are listed in the Nomenclature section. It is apparent that L_n is a complicated function of the reaction conditions and of the average crystals size, which in itself is a complicated function of the same reaction variables (Eq.14).

Experimental

The present experiments were done before the present theory was developed. If the theory had been known at the time of the experiments, a wider range of experiments would have been performed to determine the present results to a greater degree. Unfortunately, the author is no longer in a position to provide additional experiments. However, the present experiments support several important predictions of the theory and might be the starting point for more extended work in the future. It should be remembered that the original paper by Randolph and Larson^{6a} did not supply any supporting experimental results to support their model.

Silver chloride, AgCl, was precipitated in a single-stage continuous stirred tank reactor (CSTR) system (Fig. 1). The residence time was varied from 0.5 to 5.0 min (Table I). For the residence time of 3.0 min the suspension density was varied from 0.05 to 0.40 mol/l (Table II). The temperature was held constant at 60°C. The reactor volume, flow rates, and reactant concentrations are given in Tables I and II. Bone-gelatin was used as the peptizing agent. The free silver ion activity $\{Ag^{*}\}$ was controlled in the reactor at pAg 6.45, where $pAg = -log \{Ag^{+}\}$. This corresponds¹⁶ to a solubility of 6.2×10^{-6} mol Ag/l. The exit stream had the same free Ag⁺ concentration as the reactor mixture. This solubility consists of the sum of concentrations of free silver ion plus complexes of silver ions with halide ions, $\operatorname{AgCl}_{n}^{1-n}(n)$ equals 1 to 4). The silver chloride precipitated in cubic morphology. A crystal growth restrainer was added to the output material to avoid Ostwald ripening and to preserve the crystal size distribution. The crystal size distribution

TABLE I. Effect of Residence	Time on the Average	Crystal Size of AgCl	Precipitated in the	CSTR System*
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Experiment	Residence time	Edge length	Size distribution	Crystal number	Reactor volume	Flow rate	Addition rate	Suspension density
No.	τ min	<i>L</i> μm	d.r.	$Z_{t} \times 10^{12}$	V ₀ ml	F ml/min	R ₀ mol/min	<i>M</i> _t mol/l
1	0.5	0.207	2.69	73	300	50	0.050	0.083
2	1.0	0.263	2.64	36	300	25	0.025	0.083
3	3.0	0.337	2.58	41	600	20	0.020	0.100
4	5.0	0.413	2.22	37	1000	20	0.020	0.100

* Reaction conditions: 60° C, AgNO₃, NaCl 1.0 mol/l, 2.4% bone gelatin τ residence time (min), V₀ reactor volume (l), *F* flow rate (ml/min, AgNO₃ and NaCl), R_0 molar addition rate (mol/min), M_t suspension density (mol AgCl/l), L (µm) cubic edgelength, d.r. decade ratio (measure of size distribution), Z_t total crystal number in reactor.

TABLE II. Effect of Susp	ension Density on Av	erage Crystal Size for	Precipitations of AqCI in	the CSTR System ¹

Experiment	Suspension density	Edge length	Size distribution	Crystal number	Reactant concentration	Addition rate
	M _t	L	d.r.	$Z_t \ge 10^{12}$	С	R_0
	mol/l	μm			mol/l	mol/min
1	0.05	0.327	2.45	11	0.5	0.005
2	0.10	0.350	2.59	18	1.0	0.010
3	0.10	0.337	2.58	41	1.0	0.020
4	0.20	0.331	2.79	43	2.0	0.020
5	0.30	0.333	(3.51) ^a	63	3.0	0.030
6	0.40	0.344	3.25	81	4.0	0.040

^{\dagger} Reaction conditions: 60°C, pAg 6.45, residence time τ 3.0 min; all experiments except No. 3: AgNO₃, NaCl 10 ml/min, gelatin (2.4%) 80 ml/min, V_0 300 ml. Experiment No. 3: AgNO₃, NaCl 20 ml/min, gel (2.4%) 160 ml/min, V_0 600 ml.

C is the concentration of reactants (AgNO₃ and NaCl), R_0 molar addition rate (mol/min), M_t suspension density (mol AgCl/l), L average crystal size (cubic edgelength, μ m), d.r. decade ratio (measure of crystal size distribution), Z_t total crystal number in reactor; (a) data not reliable.

of the crystal suspensions were determined using the Joyce–Loebl disk centrifuge.^{14,17} This analytical method determines the size distribution of the crystals by their sedimentation time using Stokes' law and the relative frequency of the crystal sizes by light scattering. This method determines the crystal size distribution of the material that represents the final product of the precipitation process. In situ determinations of the crystal size population were not done because the high concentrations did not allow precise light-scattering experiments. The original data were determined as equivalent circular diameter (ecd) and were converted to cubic edge length (cel), where

$$cel = 0.86 * ecd.$$
 (30)

The crystal size distribution curves are shown in the ecd scale. The crystal size distribution could be fitted to the sum of two Gaussian distributions, and thus the distribution cannot be described by a single standard deviation. Thus, the crystal size distribution is given by an empirical measure, the decade ratio (d.r.), which is defined by the ratio of the sizes at 90 to 10% of the experimentally determined crystal size population.

Electron micrographs (carbon replica) of AgCl crystals precipitated in the CSTR system (5-min residence time) are shown in Fig. 2. The results for the variation of crystal size with residence time are shown in Fig. 3 and Table I. The dependence of crystal size and crystal size distribution on suspension density was studied for the 3.0-min residence time (Table II). The constants used for the calculations are listed in Table III.

Results and Discussion

The new model makes a number of predictions that can be tested with the experimental results.

- The average crystal size is independent of addition rate and suspension density.
- The size dependence of the average crystal size on residence time can be modeled using the equations given.

TABLE III. AgCI Precipitations in the CSTR System. Constants Used in the Calculations

Constant	Value	Comment
k _v	1.0	cubic
k _s	6.0	cubic
γ	52.2	erg/cm ²
		(Ref. 16)
D	1.60*10 ⁻⁵	cm²/s
		(Ref. 16)
V _m	25.9	cm ³ /mol AgCl
C_s	6.2*10 ⁻⁹	mol/cm ³
		(Ref. 16)
R_q	8.3*10 ⁷	erg/deg mol
Ť	333 K/60°C	

- The average crystal size has a final value at zero residence time.
- The maximum growth rate, the critical crystal size, the supersaturation ratio and the supersaturation, and the ratio of nucleation to growth of the system can be determined at steady state.

Crystal Size, Addition Rate, and Suspension Density. The model predicts that the average crystal size is independent of the reactant addition rate and by implication of the suspension density. This is supported by the results in Table II, which show that over a range of addition rates from 0.005 to 0.04 mol/min and a suspension density of 0.05 to 0.40 mol/l the average crystal size did not significantly vary. At the same time, the total crystal number in the reactor, Z_{ι} , increased proportionally to the molar addition rate.

It is significant that for Experiments 2 and 3, which have the same suspension density but vary by a factor or two in molar addition rate, the average crystal size and the decade ratio are not significantly different. The doubling of the addition rate leads to a doubling in the total crystal number. Similarly, Experiments 3 and 4 have the same molar addition rate but vary in the suspension density by a factor of 2, while producing the same average crystal size and total crystal number. This supports the prediction of the theory that the crystal number is independent of suspension density and, by implication, independent of the population density.

The results in Table II show that the width of the crystal size distribution as measured by d.r. increased with increasing suspension density. This is indicated by Experiments 2 and 3 where for Experiment 3 the molar addition rate (and reactor volume V_0) was doubled while the suspension density was held constant. The value of d.r. is the same, indicating that the suspension density, not the molar addition rate affects the width of the crystal size distribution.

Experiments 3 and 4 have the same addition rate, but Experiment 4 has half the reactor volume and flow rate, so that it has twice the suspension density of Experiment 3. The experiment with the higher suspension density (Experiment 4) has the wider crystal size distribution which reinforces the direct relationship between suspension density and width of crystal size distribution. The unusually wide size distribution of Experiment 5 is probably due to some undetermined experimental deviation.

The crystal size distribution is governed by two different reactions:

For crystals larger than the stable crystal size, growth is dominated by the maximum growth rate. This part of the crystal population can probably be described by the Randolph–Larson model, which is based on the maximum growth rate of the crystals.

The crystals smaller than the stable crystal size also grow at maximum growth rate, but also disappear at some rate by Ostwald ripening. Ostwald ripening is the process by which larger crystals increase in size (ripen) at the expense of the dissolution of smaller ones. The critical crystal size at which a crystal has equal probability to grow or dissolve by Ostwald ripening can be determined by the present model and experiments.

In addition, it was determined that in controlled doublejet precipitations the maximum growth rate nonlinearly decreases with increasing crystal size.¹⁶

It was shown that the maximum growth rate increases under crowded conditions when the crystal population density is very high and where the diffusion layers of the crystals overlap.^{14,18,19} This effect may depend on the crystal size and the state of supersaturation in the reactor and thus may contribute to the increase in crystal size distribution with increasing suspension density.

Because two different reaction mechanisms, growth and the Ostwald ripening effect, are differently effective for the different fractions of the crystal size populations, it can be anticipated that the shape of the resultant crystal population might not be symmetrical. This idea is supported by the crystal size distributions shown in Fig. 3.

The result that the average crystal size is independent of molar addition rate and suspension density allows us to add the result from Table II to those of Table I for the correlation of crystal size with residence time.

Crystal Size and Residence Time. The results from Tables I and II were combined and plotted in Fig. 5. A linear least square evaluation using L and $1.0/L^2$ based on the size/t correlation predicted in Eq. 18 results in Eq. 31:

$$\tau = 11.88 * L - 0.1026/L^2, \tag{31}$$

where τ is in minutes and *L* in μ m.



Figure 5. Crystal size of silver chloride crystals (μ m cubic edge length) as a function of residence time (min), 60°C, pAg 6.45, 2.4% gelatin.

The standard error of estimate is 0.77 and 0.0214 for the first and second constant, respectively. The correlation coefficient is 0.9844.

In Fig. 5, the solid line is given by Eq. 31. The linear correlation (dashed line) represents the L/τ correlation for large crystal sizes as defined by Eq. 21.

Maximum Growth Rate, G_m . From Eqs. 31 and 18 the maximum growth rate was calculated to $G_m = 28.1 \times 10^{-3}$ µm/min, or 4.68 A/s. This is in good agreement with the results by Strong and Wey¹⁶ who determined the maximum growth rate of AgCl in controlled double-jet precipitations to between 4.25 to 1.20 A/s for grain sizes between 0.209 and 0.700 µm. This suggests that the growth rate G_m may be obtained independent from the continuous precipitations to be used for the calculations in the present theory. It was determined in the experiments by Strong and Wey¹⁶ that the maximum growth rate decreased with increasing crystal size. In the doublejet precipitations, G_m can be determined as a function of crystal size because the crystal size distribution is very narrow. In the present precipitations, G_m is the average of the maximum growth of a relatively wide crystal size distribution.

Minimum Crystal Size. This value is essentially the same as determined for $\tau = 0.5$ min, 0.207 µm. From the experimental results the crystal size for zero residence time was estimated to be 0.205 µm.

 Ψ , *L/L_c*, *S*^{*}, and *C*_{ss}. The parameters in Table III were used to calculate Ψ (5.73*10³), *L/L_c*(~5.73*10³, Eq. 5), the ratio of average to critical crystal size. The accuracy of the calculated results is affected by the constants in Table III, especially the values of surface energy γ , diffusion coefficient *D*,

TABLE IV. Critical Crystal Size	Supersaturation and - Ratio as a	a Function of Residence Time
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Residence time	Cubic edgelength	Critical crystal size	Supersaturation ratio	Supersaturation	
min	μm	<i>L_c</i> μm*10 ⁻⁵	<i>S</i> *	<i>C</i> _{ss} mol/cm ³ *10 ⁻⁸	
0.5	0.207	3.61	28.1	18.0	
1.0	0.263	4.59	22.3	14.5	
3.0	0.337	5.88	17.6	11.6	
5.0	0.413	7.21	14.6	9.65	

 $\Psi = 5.73 * 10^3$. For experimental conditions see Table I

TABLE V. Calculated Ex	perimental Constants an	d Variables CSTR a	and Batch Preci	pitations of Ac	ICI

Variable max. Growth Rate	CSTR 4.68	Batch 1.20-4.25	A/s	Variable G_m	Reference (<i>b</i>)	
Aver./Critical Size ratio	5.73*10 ³ 12 2	1.85		L/L _c	(a) (a b)	
Supersaturation	8.2*10 ⁻⁸	12.7*10 ⁻⁹	mol/cm ³	C _{ss}	(<i>a</i> , <i>b</i>)	

 Ψ = 5.73 * 10³. References for Batch Precipitations: (a) I. H. Leubner,² (b) R. W. Strong and J. S. Wey¹⁶

TABLE VI. AgCI Crystal Nucleation and Crystal Growth Reactant Rates and Nascent Nuclei Sizes

Residence time (min)	Cubic edgelength, <i>L</i> μm	R _n /R ₁	<i>R</i> _n % of <i>R</i> ₀	<i>R</i> , % of R ₀	L _n μm	% L _n % of L
0.5	0.207	4.79	82.7	17.3	0.194	93.9
1.0	0.263	1.48	59.7	40.3	0.221	84.2
3.0	0.337	0.30	23.1	76.9	0.207	61.4
5.0	0.413	0.12	10.7	89.3	0.196	47.5

 R_n = fraction of reactant input rate consumed for crystal nucleation, R_i fraction consumed for crystal growth at steady state.

The value $L_{\scriptscriptstyle n}$ size of nascent nuclei, $\% L_{\scriptscriptstyle n}$ = % of nascent nuclei sizes versus average size.

Reaction conditions: AgCl, 60°C, pAg 6.45, 2.4% gelatin.

and solubility C_s . The calculated results thus should be considered estimates and must be reevaluated when more reliable data become available for the constants used.

In Table IV, the critical crystal size L_c , the supersaturation ratio S^* , and the supersaturation C_{ss} during steady state were calculated as a function of residence time τ . The data indicate that the critical crystal sizes increase with residence time, while the supersaturation and supersaturation ratio decrease. A theoretical supersaturation ratio of $1.60*10^5$ is obtained if one adds 1.0 mol/l silver nitrate to a solution where the solubility is $6.2*10^{-6}$ mol/l as in the present experiments.³ In stop-flow experiments, Tanaka and Iwasaki²⁰ estimated that the size of the primary nuclei formed in AgCl precipitations were about (AgCl)₈. Thus, the difference between the theoretical $(1.60*10^5)$ and actual supersaturation ratio (14.6 to 28.1)in this system indicates that Ostwald ripening involving metastable nanoclusters may play a significant role in the nucleation/growth mechanism.

The values for the present CSTR system are substantially higher than those reported for controlled batch double-jet precipitations under the same conditions (Table V) as reported by Leubner² and Strong and Wey,¹⁶ who reported values of S^* of about approximately 1.02 and 1.09, and values for L/L_c of 1.85 and 4.2. For comparison of the systems, an average crystal size of 0.5 µm was used.

The higher values of L/L_c and S^* for the CSTR versus the batch system indicate that during steady state the balance between maximum growth and renucleation stabilizes much smaller critical crystal sizes than the batch double-jet precipitation. This is also supported by the wider crystal size distribution in the CSTR system. However, the absence of very small crystals in the product suggests that upon removal of the high supersaturation in the product stream, the small initial crystals rapidly dissolve by Ostwald ripening to produce the observed crystal size distributions. This is in agreement with simulations of the effect of Ostwald ripening on the crystal size distribution in batch precipitations by Tavare.²¹ Unfortunately, Tavare did not provide experimental evidence for his simulations. The effect of Ostwald ripening and growth restraining agents on the crystal nucleation in batch precipitations was modeled and experimentally supported by this author.^{22,23}

Nucleation versus Growth, R_n/R_i . Using Eqs. 2 and 25, R_n/R_i and R_n and R_i (as a percent of R_0) were calculated as a function of residence time τ and average crystal size L. The results are listed in Table VI. The data show that at short residence times, nucleation (high R_n) is dominant, while at long residence times, growth (high R_i) dominates the reaction.

Nascent Nuclei Size. The size of the nascent nuclei L_n were calculated using Eq. 28. The results are shown in Table VI. Note that the size of the nascent nuclei is relatively independent of residence time and of the final crystal size, ranging between 0.194 and 0.221 µm. Interestingly, this size range is of the same order of magnitude as calculated for the limiting crystal size for the plug–flow reactor, 0.205 µm. As a consequence of the relatively stable size of the nascent nuclei, their size relative to the steady state average crystal sizes decreases with increasing residence time.

Thus, at the 0.5-min residence time, the size of the nascent nuclei is about 93.9% of the final crystal size, while for 5.0-min residence time it is only about 47.5% of the final crystal size.

Conclusions

A new theory of crystallization is proposed for the CSTR or MSMPR system. The model is based on nonseeded systems with homogeneous nucleation, diffusion controlled growth, and the nucleation model previously derived for such systems in controlled double-jet batch precipitations. It does not need any assumptions about size-dependent growth (McCabe's law).

The model predicts the correlation between the average crystal size and the residence time, solubility, and temperature of the reaction system and allows determination of useful factors that are experimentally hard to determine such as L/L_c the ratio of average to critical crystal size; the supersaturation ratio S^* ; the supersaturation C_{ss} , the maximum growth rate G_m , and the ratio of nucleation to growth R_n/R_i .

Results of continuous precipitations of silver chloride were chosen to support the predictions of the model. Silver chloride precipitations in batch double-jet precipitations indicate that the crystal growth is mainly determined by a diffusion-controlled mechanism.^{2,16}

The model predicts that the average crystal size is independent of reactant addition rate and suspension density, which was supported with experiments where the molar addition rate was varied from 0.005 to 0.04 mol/min and the suspension density from 0.05 to 0.40 mol/l. The width of the crystal size distribution (given by the decade ratio) increased with suspension density from 2.45 to 3.25 and was independent of reactant addition rate. The crystal size distribution is a factor of maximum growth rate (small and large crystals), Ostwald ripening (small crystals), and possibly of crowded growth conditions. These insights may be applied to modify the Randolph-Larson model to describe the size distribution of the crystal population.

The model also predicts that the average crystal size and residence time are linearly related when the average crystal size is significantly larger than a certain limiting size is, which can be derived from the experimental correlations. At smaller crystal sizes, the average crystal size is larger than predicted by the linear part of the correlation. These predictions were confirmed by the experimental results.

The model further predicts that when the residence time approaches zero, the average crystal size approaches a limiting value larger than zero. For the present AgCl precipitations the limiting value was calculated to about $0.205 \,\mu m$, while the average crystal size varied from 0.207 to 0.413 µm between residence times from 0.5 to 5.0 min. The condition where the residence time approaches zero is similar to that obtained during nucleation in plug-flow reactors and thus predicts a lower limit of average crystal size for the CSTR and plug–flow systems of about 0.205 μm.

The model also allowed us to calculate the part of the input reactant stream R_0 is used for nucleation R_n and for growth R_i . The ratio R_n/R_i decreased with increasing residence time from 4.79 to 0.12.

The average crystal size of the nascent (newly formed) crystals L_n was determined for the different residence times to vary between 0.194 to 0.221 µm. This size range is in the range calculated for the plug–flow condition ($\tau \rightarrow$ 0), 0.205 µm.

Experiments are needed to confirm the model as a function of solubility and temperature where care has to be taken to consider that $\Psi (= L/L_c - 1.0)$ may be a function of solubility and temperature as shown for AgBr, AgCl $^{\rm 1-4}$ and addition rate.⁵

The present model may be expanded to include the effect of Ostwald ripening agents and growth restrainers using the formalism previously applied to precipitations in batch precipitations.^{22,23}

While the present model was developed for homogeneous nucleation under diffusion-limited growth conditions and unseeded systems, it may be easily modified to model seeded systems and systems where growth and nucleation are kinetically, hetrogeneous, or otherwise controlled. The present work also suggests many additional experiments and new approaches to the evaluation of the results of continuous precipitations.

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Nomenclature:

- cel = cubic edge length
- Cconcentration (mol/l) =
- C_{ss} = supersaturation (mol/cm³)
- C_s = solubility (mol/cm³)
- \mathbf{ecd} = equivalent circular diameter
- Ψ = $L/L_{c} - 1.0$
- D diffusion constant (cm²/s) =
- F = flow rate (ml/min)
- F_t = total flow rate (l/min)
 - = surface energy (erg/cm²)
- $\stackrel{\gamma}{G}_m$ = maximum growth rate of crystal population (cm/ $s, A/s, \mu m/s)$
- L= average crystal size (µm, cm)
- L_c = critical crystal size (µm, cm)
- L_n = nascent (newly formed) crystal size (µm, cm)
- L_x = crystal size (cm)
- k_{v} = volume shape factor, (if L is the edge length of a cubic crystal, $k_v = 1.0$; if L is the radius of a spherical crystal, $k_v = 4\pi/3$)
- surface shape factor, (if L is the edge length of a k_s = cubic crystal, $k_s = 6.0$; if L is the radius of a spherical crystal, $k_s = 4\pi$)
- Ν = population density, number/(volume-length)
- n^0 = nuclei population density, number/(volume-length)
- M_{t} = suspension density (mol/l)
- gas constant $(8.3 \times 10^7 \text{ erg/deg mol})$ R_{g} =
- R_0^- = addition rate of reactants (mol/s)
- R_n addition rate fraction used for nucleation =
- R_i addition rate fraction used for growth (crystal size = increase)
- S_m characteristic surface (e.g., area/mol silver halide) =
- residence time, (s, min) =
- $egin{array}{c} {\mathfrak T} & & \ T & V_0 & V_g & \ V_m & Z_n & \ Z_r & \ Z_r & \end{array}$ = temperature (K)
 - reaction volume =
 - average crystal volume (cm³) =
 - = molar volume, (cm³/mol, crystals)
 - number of crystals nucleated at steady state =
 - number of crystals/ml in the reactor during steady = state
- Z_{t} total number of crystals in reactor during steady = state

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