

Equivalence of Growth Rate and Yield Methods

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Abstract

There are two approaches to modeling trihydrate alumina production in precipitation modeling. *Yield methods* relate the rate of change of plant measurable properties (typically Alumina concentration, A or A/C ratio) to key parameters such as temperature, supersaturation and caustic concentration; such methods have been tuned by plant operators to accurately represent plant performance. *Growth rate* methods such as White or Veessler-Boistelle determine an actual growth rate (either as a deposition rate or particle diametral growth), again as functions of a similar set of parameters. Yield methods are suitable for simplified precipitation circuit models and have been modified to include effects of additional observable parameters such as organics levels or free caustic. For full particle size balance simulation in circuits with recycle, a true growth rate method is necessary to determine the size distribution change through the precipitation row, but such methods are typically derived from laboratory experiments with synthetic liquors and may not incorporate parameters that plant operators have found to be important. We discuss how typical yield methods can be rewritten as true growth rate equations, allowing their use in full PSD circuit modeling.

Keywords: Precipitation circuit modeling, particle size distribution, growth rate.

1. Historical Overview

The analysis described here results from the historical development of the general-purpose process simulation SysCAD package. The original implementation of an alumina model precipitator was for a simple steady-state continuously stirred tank reactor (CSTR) based on the yield model and a simple empirical yield equation. The model required that the *Specific Surface Area* (SSA) and temperature be specified for each tank in a precipitation row — the model could then predict the solids concentration and composition for the inter-tank flows. Further refinements included adding reaction heats and various cooling and environmental heat loss options, so that energy balance could be included, and the row temperature profile predicted as well.

SysCAD incorporates general purpose programming capability, and the overall rate constant in the yield equation can be adjusted for the influence of other process parameters. At the request of various users, additional parameters were incorporated into the yield equation and users tuned these parameters to provide successful predictive yield models.

With increasing computing power, further development of the model into two areas became feasible. Various proprietary PSD models have been available, and SysCAD has always had PSD capability aimed at comminution and separation operations, so the underlying framework for incorporating full PSD into the precipitator model was available. Early implementations of PSD simulation in SysCAD had a separate precipitator unit operation which used a White growth model. Full PSD models can now predict the change in SSA between tanks in the precipitation row, and using cyclone and classifier models can close the circuit, something impossible to achieve with the SSA yield models.

At the same time, there was interest in dynamic simulation for purposes of operator training, commissioning optimization and upset recovery. Rather than having separate dynamic and PSD unit operations, we were aiming at a single unit operation that could operate with PSD and in either steady state or dynamic modes with the same process parameters. Such a model could be tuned for steady state yield conditions, then used in a dynamic or full PSD model, effectively maintaining compatibility with the original yield model.

To achieve this, it was necessary to recast the yield model as a true growth rate equation, allowing it to be used in these new areas. The key observation is that the SSA yield equation implies a growth rate — by distributing the precipitated material over available surface area. In section 2 we review the yield model and discuss some of the limitations to be overcome in moving to dynamic and full PSD modelling. Section 3 discusses briefly the standard growth models and various forms and shows the equivalence of growth and yield methods. We conclude with discussion some of the other parameters incorporated into yield models that imply influences on particle growth rates.

2. Yield Method Theory

Yield methods have been around for many years, and are useful in modelling single tank operation. They are easily derived from steady state operational plant data, since they are tuned by — and predict — readily observable plant parameters.

Looking at a single precipitation tank, we can measure the feed A_F and product A_P alumina concentrations in grams per liter (gpl), the difference $\Delta A = A_F - A_P$ is simply the solids yield, also in gpl. Since the volume flow is also measurable, we can determine the total solids Trihydrate Alumina (THA) production as

$$Q_v(A_F - A_P) = Q_v\Delta A = Q_v C \Delta AC$$

We work with AC since it is a dimensionless quantity and was the basis of the original SysCAD implementation. Subsequently, we will drop the product subscript; all the parameters influencing the yield equations are understood to be at the product (or tank) conditions.

The change in alumina to caustic ΔAC is then correlated against the supersaturation driving force to give us the *Yield Equation*:

$$\Delta AC = K(\mathbf{P}) \times \exp\left(\frac{-\Delta E}{RT}\right) \times C_S \times \sigma \times t_R \times (AC - AC^*)^2$$

Here K is an overall “constant” that depends on any number of observable tank parameters represented as \mathbf{P} ; different plant operators have found various quantities that may influence the yield, such as ionic strength, caustic concentration, and free caustic. The four other driving terms are the solids concentration C_S , the SSA σ , the residence time t_R , and the supersaturation. Empirically, more solids, higher SSA, and longer residence times translate proportionally to higher yield, while the effect of supersaturation (the primary driving force) is quadratic. All quantities are measured at tank (ie product) conditions. In practice, the contributions of the main terms may not be precisely linear, and the supersaturation dependence may not be quadratic, and additional exponents or functional forms may be introduced, but we will work with this form to illustrate the main points here.

For modelling a single tank we know the feed conditions and the tank volume, but we don't know the product conditions. It is straightforward to solve numerically, analytical solutions for simplified cases do exist, but in reality, internal or external cooling, reaction heats, and other complications in determining the steady state tank temperature make such analysis pointless.

In summary, the yield equations are straightforward to apply for single tank modelling, and have been developed by plant operators over many years to accurately represent tank precipitation. Use of this form does require knowledge of the SSA, which must be measured.

2.1 Limitations

With increased computer memory and power, process simulation moves beyond single tank modelling, and two key areas have emerged where we want to apply the theory. Full particle size distribution (PSD) models are available where the effects of agglomeration and nucleation as well as growth can be accounted. We can now model a series of tanks, starting with fine seed and agglomeration tanks through to the pump-off to see how the size distribution changes along the row. This can be extended to full circuit modelling, where we can track the change in PSD through a precipitation row, and determine (using cyclone or classifier models) the PSD of the fines feed, thus closing the circuit.

Dynamic simulation is now available as well, so we can model the response of a circuit to upsets, or simulate start-up conditions when tanks are filling for commissioning optimization. Batch processing is still used in a few plants around the world, and this is a variant on full dynamic where the overall cycle needs to be modelled dynamically because of changing conditions over the batch cycle, but the output can be represented as a steady state flow.

The yield methods are unsuitable for either dynamic or particle size distribution modelling. For dynamic modelling, the term T_R is clearly problematic. When a tank is filling with no overflow, there is no “residence time” per se, however precipitation will still be taking place and we want to be able to model transient conditions.

The issue with yield methods for size modelling is more subtle. We want to be able to model a precipitation row without having to specify all the parameters in the yield equation. In particular the SSA is one of the key parameters, so we would like to know how this changes from tank to tank. We could imagine a theory of how the SSA changes due to growth, and thus model a precipitation row, but it turns out that such a theory is impossible without invoking knowledge of the full PSD. If every particle has the same size initially and grows by the same amount we can show that the SSA must decrease. For a single particle of diameter δ the SSA is just

$$\sigma = \frac{\pi\delta^2}{\pi\rho\delta^3/6} = \frac{6}{\rho\delta}$$

so increasing the diameter via growth will reduce the SSA *for a single particle, or a group of particles of similar size.*

For size distributions however, it turns out to be possible that growth (even in the absence of agglomeration/nucleation) can *increase* the SSA, this in spite of the SSA *decreasing* for every individual particle. This seemingly paradoxical result is well documented in statistical theory. The reversal or amalgamation effect, or Simpson’s paradox is a phenomenon in which a trend appears in different groups of data, but reverses when the groups are combined.

2.2 Simpson’s Paradox

The amalgamation effect is often illustrated in sporting statistics by showing that one player performing better than another (in some statistical measure) in each of several games, but worse in the same measure over when the games are combined.

For example, in football (as understood by most of the world, soccer to those in the colonies), we can compare the conversion rates of two players, defined as the number of goals scored per shot at goal. We follow two players A (Arsène) and B (Beckham). In the first game A gets a single goal from 14 shots, B gets two goals from 26 shots, so player B has a better conversion rate (1/13 compared to 1/14). In game 2 player A gets two goals from 13 shots, and player B get two goals from 12 shots, so B still has a better conversion rate. B has done better in converting shots at goal than A in both games. Overall though, A has converted three of 27 shots at goal, while B converted four of 38. So overall A has a better conversion rate, in spite of having worse stats in both games!

To illustrate Simpson's paradox in the context of PSD modelling, consider a bimodal distribution where most of the mass is in large particles, but most of the area is in large numbers of small particles. Such a distribution might arise in an upset event such as an oxalate shower. Considering only the large or small particles individually, growth will decrease the SSA of the group. However, considering both groups together, growth for each results in a large change in total area (since most of the area is associated with the small particles), with only a small change in total mass (since most of the mass is associated with the large particles).

The key point here is that predicting change in SSA, the amalgamation of a number of changes in individual surface areas, requires full knowledge of the area changes of particles in each individual size. We need a full PSD model to predict the SSA, which depending on the distribution, can increase or decrease.

If the bulk of the particles (represented as numbers rather than mass) are at a fairly uniform size then we can show the SSA will decrease by a factor $r^{1/3}$ where r is the average mass ratio increase.

3. Growth Rate Methods

The generic basis for these methods is an equation of the White form [4]

$$\dot{\delta} = k_G \exp\left(\frac{\Delta E}{RT}\right) (A - A^*)^2$$

This predicts particle diametral growth rate or deposition rate (different by a factor of 2). Many variants of this have been proposed [3]; we mention the Veessler-Boistelle method [5] which uses relative supersaturation defined as $r_\sigma = A/A^*$ as the driving force, along with a critical supersaturation $r_{\sigma c}$ below which no growth occurs:

From any of these growth equations, the THA yield can be calculated directly by;

$$M_{THA} = C_S V \sigma \rho_S \dot{\delta} \quad (3.1)$$

since $C_S V = S \rho_{SL} V$ is the total mass of solids in the tank. This form is independent of flow rates and can be used in dynamic or batch modelling. A tank may be filling with no outflow, but we can just set up a mass balance, with solids being increased by both inflow and precipitation.

More importantly, growth rate equations can be used in full PSD analysis, and we can determine how the size distribution changes, either in steady state from tank to tank, or in dynamic simulation over time. Since the SSA is now predicted by the model, we no longer need this as a parameter in the analysis. SysCAD implements the Hounslow [1] discrete bin method, which requires a suitable growth rate expression.

3.1 From Yield to Growth

There is a particular issue with the Yield growth model and how it predicts THA precipitation based on residence time. The total precipitation rate of THA in the tank (ie total yield in kg/s) \dot{M}_{THA} is calculated in a roundabout fashion involving the tank volume, residence time and discharge flow rates. In steady state, \dot{M}_{THA} is the difference in THA between the feed and product streams, but such an interpretation is invalid for dynamic models.

We can write the yield equation as a true rate just by dividing by the residence time, so we get an estimate

$$\frac{dAC}{dt} = K(\mathbf{P}) \times \exp\left(\frac{-\Delta E}{RT}\right) C_S \sigma (AC - AC^*)^2$$

Using this form we could implement a dynamic model for the precipitation tank where we calculate the solids precipitation at each timestep and adjust the composition and energy balance. To avoid having a separate implementation for the calculations for the yield method, our approach is to recast the yield equation as a growth rate equation which can be incorporated into both dynamic models and full PSD models.

Invert (3.1) to obtain

$$\dot{\delta} = \dot{M}_{THA} / (\sigma \times V_T \times C_S \times \rho_S) \quad (3.2)$$

Here $V_T C_S$ is the total tank PSD solids in kg, multiply this by σ to get the total surface area of solids in the tank. \dot{M}_{THA} / ρ_S is the rate of increase in volume of solids, which is also $\dot{\delta} \times \sigma \times V_T \times C_S$.

This formulation has removed the dependence on the residence time and flow rates — and we may now remove the dependence on tank volume as well using the yield equation: we find the total yield as

$$\dot{M}_{THA} = C V_T K(\mathbf{P}) \times \exp\left(\frac{-\Delta E}{RT}\right) \times C_S \times \sigma \times (AC - AC^*)^2$$

Now this has been derived from the yield form for a tank of fixed volume at steady state conditions, but is clearly applicable for any volume of slurry. Combining this with (3.2) we have an expression for growth rate which is independent of the slurry volume.

$$\dot{\delta} = C K(\mathbf{P}) \exp\left(\frac{-\Delta E}{RT}\right) (AC - AC^*)^2$$

We see that the Yield model is equivalent to another variant of the White methods, with a number of additional tuning parameters. In terms of the alumina concentration A , we get the following variant of the White form:

$$\dot{\delta} = \frac{K(\mathbf{P})}{C} \exp\left(\frac{-\Delta E}{RT}\right) (A - A^*)^2$$

4. Other Factors Influencing Overall Rate

The rate constant K_G can be further tuned to include other factors. In implementing yield based methods, plant operators have observed effects from other plant parameters, and incorporated these into yield models. Such effects may not be independent, but the implementation of a generalized yield model allows any such effects to be modelled.

4.1 Organics

The presence of organic compounds, as measured for example by TOC, has been found to inhibit yield with a suggested correction

$$K_{\text{TOC}} = \exp(-n_{\text{TOC}} \times \text{TOC})$$

4.2 Caustic

The growth rate equation shows a C^{-1} dependence on caustic concentration, the White equation has no caustic dependence, a variant due to White and Bateman [6] has a dependence $C^{-3/2}$. The general yield method allows all these via a caustic rate correction $K_C = C^n$.

4.3 Free Caustic

Another White variant due to King [2] includes a factor for Free Caustic, so we can incorporate a further factor $K_{FC} = FC^n$

In implementing a precipitation model based on the generalized yield equation, we can include each of these factors; if the corresponding exponent is set to zero, then the parameter has no effect on the rate. These empirical factors from the yield methods indicate forms for generalized growth equations.

Our overall growth rate factor $K_G = K_{FC} \times K_{\text{TOC}} \times K_C$. We can add further corrections as needed — for example the supersaturation dependence may not be precisely quadratic, and the SSA dependence nonlinear.

5. Summary

We have shown how the empirically derived yield methods can be converted to true growth rate equations, allowing simulation software to incorporate such methods along with other standard previously available growth rate formulae. The resulting growth equation has a form similar to many others that have been proposed, but can be easily fitted to plant data — indeed a number of refinery operators have “tuned-up” variants of the yield equation available. These can then be used in full PSD and dynamic modelling, obtaining results consistent with previous models which only use SSA.

6. References

1. M.J. Hounslow, R.L. Ryall, and V.R. Marshall. A discretized population balance for nucleation, growth and aggregation. *AIChE. J.*, 11, 1988.
2. W.R. King. *Light Metals* 2, page 551, 1973.
3. Livk I Lee, T.S and D. Ilievski. Supersaturation and temperature dependency of gibbsite growth in laminar and turbulent flows. *J. Crystal Growth* 258, page 409, 2003.
4. C. Misra and E.T. White. *Chem. Eng. Prog. Symp. Ser. 67*, page 53, 1971.
5. S. Veessler and J. Boistelle. *J. Crystal Growth* 130, page 411, 1993.
6. E.T. White and S.H. Bateman. *Light Metals.*, page 157, 1988.