THE DYNAMIC STABILITY OF PRECIPITATION CIRCUITS

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ABSTRACT

Bayer Process Precipitation circuits can undergo periodic variations in key operating and process parameters. Product size distribution in particular, can undergo significant change, and has implications for product quality and productivity. Causes of instability can be external to the circuit's process, such as changes in incoming pregnant liquor flow and quality, equipment performance changes and failures, mistuned plant controllers or non-ideal operator intervention, or from internal changes to process conditions. One example of an internal cause of circuit instability is a change in the oxalate related nucleation rate, destabilising circuit and product sizing. Over a period which is characteristic of the circuit, changes in the particle size distribution can result in gross and undesirable changes to seed and product size, demanding operational control responses. These control responses themselves may propagate instability. This work investigates the drivers of these variations using a detailed dynamic simulation circuit model. Simulations indicate that "unattended" circuits are surprisingly stable and will tend to a steady state (albeit not necessarily a desirable one). External control of the circuit using PID to achieve a particular target (such as pump-off solids concentration or overall yield) by controlling fine and coarse seed rates can lead to gain-driven instability. Interventions must necessarily account for the process sensitivities and timescales involved, if this is to be avoided. Overall, Dynamic Circuit Simulation provides key insights into the behaviour of a complex interconnected system and can be a powerful tool for optimizing process control strategies and responses, plant performance, assisting in upset recovery, and operator training.

1. INTRODUCTION

While there are numerous published works on the mechanisms underlying the behaviour of a Bayer precipitation circuit, and some on their dynamic[1] and cyclic[2,3] behaviour, there is little published analysing their dynamic behaviour (inherent stability or otherwise) by fundamentals using Dynamic particle balance models.

Based on observation of numerous Bayer precipitation circuits, it might seem that these circuits, without intervention or perturbation, tend to naturally oscillate in "size", a periodic variation in some measure of the product particle size distribution (PSD)[2].

Computational and theoretical modelling suggests that this is not the case. This work indicates that circuits are inherently stable if perturbations are not severe (in a sense discussed below) and intervention, by control action or direct operator intervention, is well calibrated and minimised.

Periodic variation in circuit size *is* observed in practice and this paper explores some of the probable causes of circuit size oscillation. The meaning of dynamical stability is discussed briefly and a simplified circuit model which serves as a model evolutionary dynamical system that encapsulates the behaviour of real circuits is examined. It is shown how under certain assumptions (continuous variation of PSD mechanisms), this simplified circuit is stable in a precise mathematical sense. Perturbations to the model near a steady state solution will die out exponentially, with the result applying to any circuit of a similar form with recirculation of seed from product.

Computer modelling does show that *discontinuous* rates, in particular of nucleation, can lead to periodic variation in size. We discuss nucleation driven instability in some detail since 'shower' events (discontinuous nucleation rates), are a familiar and unwelcome phenomenon in plant operation.

2. DYNAMIC SYTEMS AND STABILITY

A Dynamical System is any physical system that has an evolution rule; given the state of the system we can determine the state of the system at a short time in the future[4]. The evolution rule is, for physically continuous systems, a set of differential equations. In principal at least, we can then iteratively determine the future state of the system at any future time, the procedure being called "integrating the system".

Dynamical Systems Theory has its origin in Newtonian Mechanics and planetary orbits[5]. Newton solved the classical "Two Body Problem" which could predict the future evolution of a pair of orbiting bodies, thus validating Kepler's observations, but the "three body problem" proved intractable. Even in Newton's time, it was noticed that historical observations of planetary positions were different to Newton's predictions. He realized this was because interactive forces amongst the planets were affecting all their orbits, and this spurred development of Dynamical Systems Theory. Early on, the question of the stability of the solar system arose since Newtonian mechanics could have planets colliding or being ejected from orbit.

With the advent of digital computers, most of the questions about planetary mechanics have been resolved and Dynamical Systems theory has developed in many ways: Chaos theory (the Butterfly Effect meme) is a familiar topic well-covered in the popular press[6]. From the modern perspective there are different approaches and definitions of stability in a Dynamical System.

A system characterized by a set of variables **X** is described by differential equations

$$\dot{\mathbf{X}} = \mathbf{f}(t, \mathbf{X})$$

A dynamical system has an equilibrium or steady state solution if there is a solution where the variables are unchanging, so that $d\mathbf{X}/dt = \mathbf{0}$. For our purposes, a system is stable if given a "kick" to move it away from an equilibrium point, the system will return to equilibrium. There are other forms of dynamic stability, for example Lyapunov stability implies that the system may not return to equilibrium but will continue to evolve near the equilibrium point[7]. Exponential stability is used with linear (or linearizable) systems to indicate that the disturbance will decay exponentially, and is important in control system design. Mathematically, circuit stability comes down to investigating whether the circuit is exponentially stable, so that periodic variations about some base state are impossible and perturbations will die out, returning the system to equilibrium.

3. DYNAMIC CIRCUIT MODELLING

A simplified circuit model is described here, and an informal mathematical analysis of the model stability is presented.

A circuit model incorporates a number of individual precipitation tanks (the precipitation row), which will be operating at different temperatures, liquor conditions and solids loading. Bayer precipitation circuits generally require progressive cooling to maintain supersaturation down the precipitation row (and gibbsite precipitation is exothermic). Tank cooling by heat exchangers and natural air convection controls the row temperature profile, which is also included in the model. At the final tank pump-off, liquor and solids are sent to classification, where solids are separated from the spent liquor. Part of the solids will be returned to provide seed in the precipitation row, and the remainder are further processed as product. Classification may also involve separating fine and coarse particles to give a better quality product, and fines can be dealt with in tanks set up for agglomeration, with coarse seed introduced further down the row.

A simplified circuit model with a number of precipitation tanks, a cyclone, and splitters is used. The cyclone splits the pump-off into fine and coarse solid (seed) components according to a specified d_{50} and sharpness. All the fine solids are returned to the beginning of the precipitation row, while a fixed fraction of the underflow (coarse) solids are removed as product, with the remainder returned to the third (growth) tank. The conclusions about stability will apply to any reasonable circuit configuration.

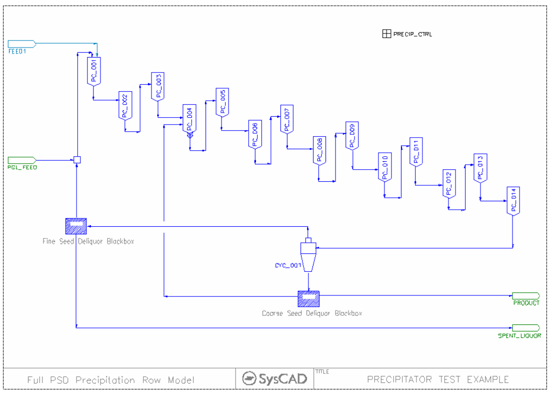

Figure 1. Simplified Circuit Model

For the purposes of validating the model's responses, simple boundary conditions were tested. Without nucleation, the average particle size will tend to increase; a coarsening circuit, leading to a decrease in specific surface area (SSA) and yield which over time increases the supersaturation (SSN). If product is continued to be removed the total solids in the circuit will fall to the point where there is little surface area and yield present, so the alumina concentration increases to that in the pregnant liquor. If the liquor is being cooled, the supersaturation will increase correspondingly.

With a low nucleation rate, the supersaturation will still tend to increase until there is a balance between removal of product and yield. We call this simplified model an "unattended" circuit, in that we do not attempt to control any of the variables such as the classification sharpness or coarse seed return. Computer simulations show that unattended dynamic circuits are stable. They will approach an equilibrium state which is equivalent to a solution found directly from a non-dynamic circuit model. The following analysis indicates why we expect an unattended circuit to be intrinsically stable in the presence of perturbations.

Even a single precipitation tank with fixed feed conditions can be considered a dynamical system. Indeed, the approach to solving the steady state of a single tank is to determine the evolution of mass/energy balance and particle size distribution and evolve the tank towards an equilibrium solution. For a single tank, the evolution is described by particle size balance mechanisms, which indirectly determine mass transfer and thus the change in liquor composition and solids production rate. At equilibrium, the various transfer and evolution rates provide a balance between the introduction of fresh liquor and solids and removal of product from the tank underflow. Thermal balance is also important in maintaining a suitable supersaturation profile.

For discrete bin PSD modelling[8], the evolution equation of a single tank can be written in matrix form - $\boldsymbol{n}$ is a column vector of the particle numbers in the different size bins; the superscript I denotes numbers in the feed and τ is the residence time:

$$\begin{aligned}\dot{\boldsymbol{n}} &= \boldsymbol{P}(\boldsymbol{n})\boldsymbol{n} + \frac{\boldsymbol{n}^I}{\tau} - \frac{\boldsymbol{n}}{\tau} \\ &= -\boldsymbol{Q}(\boldsymbol{n})\boldsymbol{n} + \frac{\boldsymbol{n}^I}{\tau}\end{aligned}$$

The term $\boldsymbol{P}(\boldsymbol{n})$ incorporates the various PSD rates. It can be shown that the term $\boldsymbol{Q}(\boldsymbol{n})=\mathbf{1}/\tau-\boldsymbol{P}(\boldsymbol{n})$ has positive eigenvalues if the PSD mechanisms (discussed further below) are in some mathematical sense "well behaved". Although this is not a true linear system, the coefficients will vary weakly with $\boldsymbol{n}$; by standard continuity arguments, the eigenvalues will remain positive near a fixed point, implying exponential stability for a single tank with fixed inputs.

We can then formulate a Dynamical model for a closed circuit by introducing classification operators for the coarse and fine seed:

$$\begin{aligned}\boldsymbol{n}_f &= \boldsymbol{C}_f\boldsymbol{n}_d \\ \boldsymbol{n}_c &= \boldsymbol{C}_c\boldsymbol{n}_d\end{aligned}$$

where $\boldsymbol{n}_d$ is the *pump-off* size distribution and the classification operators[11] are mappings from the feed to the overflow (fines) PSD. These act as sources for the feed for the first and fourth tanks. We assemble an overall response matrix having the individual tank entries as blocks.

$$\begin{pmatrix}\dot{\boldsymbol{n}}_1\\ \dot{\boldsymbol{n}}_2\\ \dot{\boldsymbol{n}}_3\\ \dot{\boldsymbol{n}}_4\\ \dots\\ \dot{\boldsymbol{n}}_d\end{pmatrix} = \begin{bmatrix}-\boldsymbol{Q}_1 & \mathbf{0} & & & \dots & \boldsymbol{C}_f/\tau\\ \mathbf{1}/\tau_1 & -\boldsymbol{Q}_2 & & & \dots & \mathbf{0}\\ \mathbf{0} & \mathbf{1}/\tau_2 & -\boldsymbol{Q}_3 & & & \dots\\ \mathbf{0} & \mathbf{0} & \mathbf{1}/\tau_3 & -\boldsymbol{Q}_4 & \dots & \boldsymbol{C}_c/\tau\\ \dots & \dots & \dots & \dots & \dots & \dots\\ \mathbf{0} & \dots & & & \mathbf{1}/\tau_d & -\boldsymbol{Q}_d\end{bmatrix}\begin{pmatrix}\boldsymbol{n}_1\\ \boldsymbol{n}_2\\ \boldsymbol{n}_3\\ \boldsymbol{n}_4\\ \dots\\ \boldsymbol{n}_d\end{pmatrix}$$

There will be additional secular terms relating to addition of liquor and removal of solids, but the overall form of the response is governed by an equation of this form. Since the eigenvalues of the diagonal blocks $\boldsymbol{Q}_i$ are positive, then for sufficiently large residence times the eigenvalues of this overall response matrix are also negative (in the limit at the residence times are large, all the off-diagonal terms vanish, by continuity the eigenvalues are positive for finite residence times). This implies the circuit as a whole is exponentially stable. Physically this means that any disturbance to the particle numbers near an equilibrium solution will tend to die out over time.

Note that nucleation (of the Misra form below) depends on *existing* surface area (no homogeneous nucleation). One solution of the equations is then for all particle numbers to be zero – with no solids present. This solution would be unstable, in that traces of solids would allow for eventual solids build-up (though on timescales that lead to the necessity of "seeding" a circuit during commissioning).

3.1 Discussion

Given that the simple circuit is stable, it is necessary to investigate further to find the possible sources of the instability seen in real circuits. One of the assumptions made in the previous derivation (and in simulations based

on this model) was that the PSD rates were constant (or at least only weakly dependent on process variables such as supersaturation or temperature). If this is not the case, then circuit instability becomes possible.

3.2 Particle Balance Mechanisms

There are three primary mechanisms influencing the overall PSD at different stages in the circuit: growth, whereby gibbsite is precipitated onto the surface of existing particles; agglomeration, where existing particles coalesce (and are subsequently cemented together by further growth) and nucleation. It is the latter that is of particular interest here, since nucleation can serve as a driver for circuit instability.

Growth is typically described by a growth rate equation (for example, Veesler-Boistell[9], White[10],) which relates the rate of deposition of gibbsite onto existing surface area to process conditions, particularly supersaturation and temperature. Agglomeration is modelled by a rate equation which gives an effective probability that particles of different sizes will interact, together with a correction based on process conditions, that the interaction will actually result in an agglomerated particle.

Nucleation provides only a small fraction of total overall yield, but is critical in renewing the supply of particles on which growth can occur. Without nucleation, the SSA will reduce over time along with the yield. We discuss nucleation in more detail later, since it introduces a mechanism which can yield periodic behaviour. Within each tank in the precipitation row, we can determine growth, agglomeration and nucleation rates from process conditions and use a population balance model to determine changes in the distribution, along with the precipitation yield and overall energy balance.

Growth and agglomeration both act to reduce the total SSA available in a tank (and hence coarsen the circuit), and by extension in the row, reducing the ability of the row to precipitate out further material. Without some mechanism to create new surface area, a precipitation circuit would ultimately tend to a very stable (but uninteresting) state where all the particles are large, and no further growth occurs. This can be demonstrated simply by disabling nucleation in the model. Since growth and agglomeration drive the system towards a more stable (but less desirable) state, it follows that nucleation might be the key to understanding circuit instability.

3.3 Discontinuous Nucleation Model and Shower events

The standard model nucleation rate is an equation of the Misra form[10].

$$N = K_N \left(\frac{A - A^*}{C}\right)^2 \sigma$$

Here N is the number of particles generated per unit time, supersaturation is the difference between A/C ratio and that at saturation (A/C^*) and σ is a measure of SSA (surface area per unit mass of slurry). Nucleation depends on supersaturation, but also on the actual surface area - larger average particles will have a lower nucleation rate. This suggests that at least one mechanism of nucleation is attrition from the surface of existing particles. A nucleation model of this form is quadratically dependent on supersaturation and linearly dependent on surface area, but if these do not vary significantly, neither will the overall nucleation rate. Even doubling the rate leads to little overall change in the circuit performance.

We can modify the overall rate constant K_N in this equation as a function of supersaturation, the idea being that above a critical level, the rate will increase rapidly:

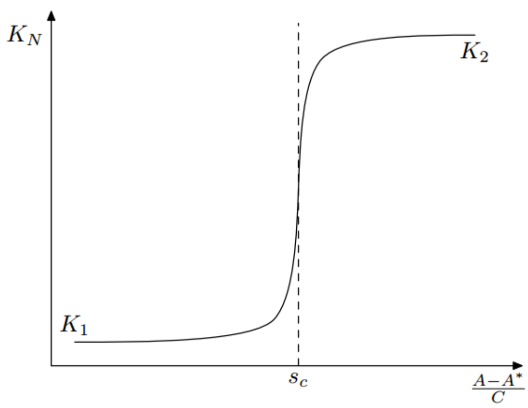

Figure 2. Discontinuous Nucleation Rate

Simulations with these modified nucleation rates still proved to be stable in some cases, however the stability depended on the critical supersaturation level. In some cases, even with sharp continuous transitions between the small and large rate constants, the numerical solution converges on an intermediate value and the overall circuit behaviour shows no long term oscillations. To guarantee instability in the circuit, a *discontinuous* nucleation rate is required. There is a critical value at which the rate has a jump. The continuity assumptions for the stability analysis no longer apply and the system can undergo a large excursion from equilibrium driven by the increase in nucleation.

A source of discontinuous nucleation would be an *oxalate precipitation event (or 'shower')* which yields large increase in the number of ultrafine oxalate particles that can serve as sites for gibbsite nucleation and subsequent growth[11]. Running a model with a discontinuous nucleation rate produces periodic variation in key process parameters – in particular the product d_{50}:

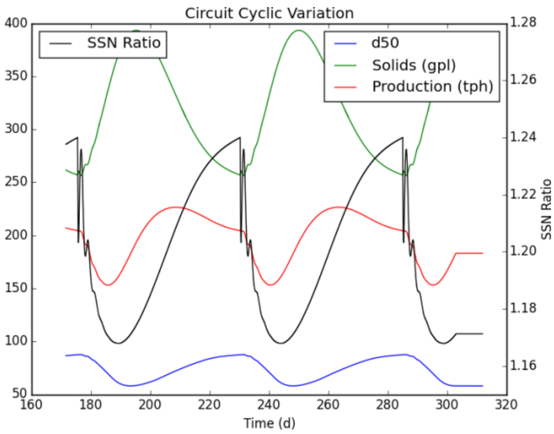

Figure 3. Nucleation-Driven Circuit Instability

Starting at 200 days, production is maximum and the circuit is coarsening. As the SSA decreases, the SSN ratio increases to the point where a shower event is triggered at around 230 days. The circuit fines rapidly, the product d_{50} drops and the solids level increases since more solids are returned. The increased solids (or primarily SSA) reduce the supersaturation until the cycle starts over; the figure shows three such events.

Supersaturation is used as a driver for a nucleation shower event, on the premise that high supersaturation will allow precipitation onto *any* existing ultrafine (submicron) particles. These are always present but have high surface energies that preclude precipitation except at high supersaturations. At a critical supersaturation, gibbsite precipitation onto existing ultra-fines rapidly increases the SSA, giving the appearance of a shower of new particles.

Other mechanisms could act as triggers for nucleation showers, for example oxalate concentration. Modelling indicates that the actual oxalate concentration does not change markedly, although in circuits which are kept free of solid phase oxalate, small increases in concentration past a "critical oxalate concentration" can result in oxalate precipitation and an associated spike in gibbsite nucleation rates.

4. EXTERNAL DRIVERS

The previous section examined internal mechanisms that may give rise to instability. This section now discusses externalities that can influence stability, in particular control action and operator intervention.

4.1 Control Actions

Our "unattended circuit" approaches steady operating conditions, but we may want to control conditions such as pump-off solids more closely. We can model control actions with a more realistic circuit simulation, where we include detailed classification, and look at the effects of control instability on the product quality.

All modern Bayer alumina refineries have some form of control system, and control of a precipitation circuit is a complex task. The general aim is to achieve a specified level of solids in the pump-off at the end of the precipitation row, and this is done by controlling the flow of coarse seed or fine seed to match the pregnant liquor influx. Product quality is also controlled (and productivity is influenced) by modifying the temperature profile of the precipitation row via coolers.

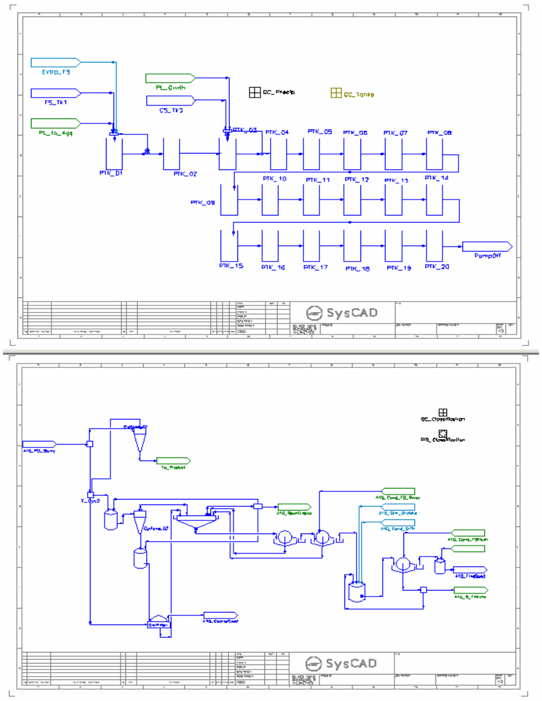

Figure 4. Detailed Classification Model

In practice, a circuit is controlled to achieve desirable product quality and production, both by feedback loops in the control system and periodic direct operator intervention. One key control target is the level of pump-off solids; this may be controlled by adjusting the

proportion of material removed from the circuit as product.

Any control intervention must be carefully tailored to the overall response time of the circuit. In this example, controlling the draw-off solids to a set-point using a naïve (Proportional Integral Derivative) PID approach acting on the proportion of solids taken to product can easily lead to large cyclic variations in total solids unless the actual range of action is limited. In this model, a simple PID is set to control the pump-off solids at 600gpl, but the high gain leads to instability in the solids and variations in the SSN ratio.

The question is whether control induced instability can lead to large variations in product size. This depends on the overall strategy: if we simply return all the fines to the circuit from the classifier, the actual d_{50} varies by only a couple of percent but production varies significantly. On the other hand, if *production* is to be maintained at a specified level then significant cyclic variations in size can occur. Bekker et al[3] indicates that varying process conditions lead to this is due to the effect on agglomeration. So, appropriate control strategies are important in maintaining levels of solids for agglomeration.

This particular model is complicated further by attempting to control both draw-off solids and production, and these controllers interact on different timescales. Using gravity classifiers with longer residence times rather than cyclones would change the outcome. There are complex interactions between controlled variables in a circuit, but dynamic simulation can clarify the relationship between these and assist in formulation of control strategies.

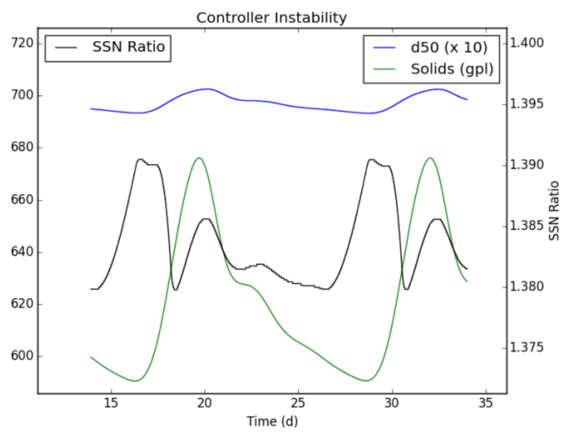

Figure 5. Controller Induced Instability

4.2 Operator Action

Those in charge of controlling a Bayer precipitation operational area are subjected to a hierarchy of imperatives, which vary from refinery to refinery. The ultimate requirement is to produce the maximum production at acceptable product size. At the next level however, deliverables include the performance of equipment maintenance and cleaning plans (including of other refinery areas), managing product inventory requirements (for shipping), product storage constraints (amongst others). All of this within limited human and financial resources, means operators have more and more complex operational variables and constraints than just maintaining optimal process settings and circuit stability.

As indicated previously, external factors may require adjustments to process settings in the precipitation area. A change in pregnant liquor flow and/or quality is a good example, where a key primary input is off-specification in a way that may require some comparatively large changes in process settings to minimise a major and protracted circuit size excursion. Under normal pregnant liquor conditions (when they are returned), such conditions may result in a significant shift in the circuit size balance. Such substantial interventions therefore need necessarily be of a well-considered size and duration.

Once, for whatever reason, a size excursion is initiated, the economic imperative to return the production rate and quality to optimum usually requires the operator to adjust process set-points aggressively to minimise the time that production is out-of-specification. The difficulty in these adjustments is firstly that typical Bayer circuits are slow to respond, and that key parameters that affect the stability of the circuit (such as the nucleation rate) are difficult to measure in the early stages of a change. This sometimes results in interventions that are longer and more extreme than ideal, and can result in overshoot of the set-point optimum. Typical responses in a real refinery are to increase or decrease agglomeration (where available and possible) using temperature or seed charge targets and/or nucleation rate manipulation using temperature and even oxalate chemistry. Once manifested in a production size excursion in the opposite direction to the initial concern, this overshoot can itself trigger an aggressive response and so an induced cycle might be propagated.

4.3 Maintenance Action

Different elements of refinery equipment have different cleaning and maintenance requirements to keep them operating within an optimum performance range. The availability of key human or financial resources, or the need to meet production plans, for example, might result in deferral or cancelling of key maintenance activities.

Should for some reason, maintenance of essential equipment be delayed or inadequately delivered, process parameter(s) supported by the equipment can trend away from target. In the precipitation area, cleaning (descaling) of liquor and slurry coolers and precipitator tanks are usually critical to maintaining circuit control and productivity. Maintenance and cleaning of seed filters are another critically important activity to maintain equilibrium product and seed flow targets.

The failure to deliver critical maintenance operations will often demand adjustments to process settings. Since it is usually difficult to quantify the magnitude and duration, these adjustments are largely based on trial and error, and can result in under/overshoots of process optima. Beyond short term instability, a state of prolonged sub-optimal maintenance of key equipment may result in a shift in optimum control points, making 'normal' process settings a source of instability.

5. CONCLUSIONS

This work has shown through theoretical analysis and computation modelling that observations of significant periodic variations in product size from a Bayer precipitation circuit necessarily depend on mechanisms that involve large variations in internal nucleation rates or production of substantial quantities of fine particles by some external mechanism.

Without these drivers, a circuit, at least in models based on accepted forms of nucleation, growth and agglomeration rates, is inherently stable. This study tends to counter any view that there is some sort of inherent instability in Bayer Precipitation circuit behaviour.

The precise trigger for instability is not always clear in every case. Certainly, excessive nucleation events do occur and can be related to oxalate management. Non-ideal control responses to size excursions may play a part, due to the difficulty in informing such responses.

This work is mainly interested in examining the effect of a nucleation shower event on overall circuit stability. In doing so, it highlights the value of Dynamical Circuit Simulation in understanding the optimum size and duration of control responses for controlling product size more directly.

Dynamical simulation of full circuits with PSD models provides a powerful tool for plant dynamic behaviour analysis.

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