Control of Product Size and Strength with Challenging Impurity Balance

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Abstract

Producing a good quality product depends on many refinery aspects. In several parts of the world, refineries have been designed and built for many decades. Bauxite chemical composition determines plant equipment and technology used in a refinery such as digestion design, precipitation design and impurity removal systems. Aughinish Alumina Ltd (AAL) was constructed for an oxalate free precipitation circuit and this is still a critical criteria to successfully control product size and product strength. Increase in production over the years from 800,000 tons in 1983 to approximately 2 million tons per annum in 2018 have led to an increase in the level of alumina, silica and oxalate scaling rate of the precipitation equipment and pipework. Opportunities to improve liquor productivity such as increased seed charge, increased surface area, liquor temperature and supersaturation control are covered in detail. The risks associated with generating solid phase oxalate and how it is controlled at AAL is also dealt with. This paper provides a summary of the general approach to control product size and strength at AAL to produce a good quality product.

Keywords: Product quality, precipitation, oxalate, product size, product strength.

1. Introduction

This paper reviews the evolution of the precipitation circuit in a refinery from its initial design and manufacturing capabilities of 800,000 tons in 1983 to approximately 2 million tons per annum in 2018. It looks at the requirements for strong nucleation, agglomeration and growth as well as the classification equipment as it pertains to product quality. The impact of Sodium Oxalate as a liquor impurity in a largely oxalate free circuit is examined.

2. Overview of Aughinish Alumina Precipitation Circuit

Aughinish runs an essentially oxalate free continuous circuit producing sandy alumina using Alcan design technology. It consists of three agglomerators and twelve precipitators in each of two chains with four in-tank precipitator coolers installed in each chain. The original design of three sets of primary and secondary gravity classifiers were supplemented by secondary hydrocyclones in 1994. Coarse seed filtration (CSF) on two filters was installed in 1997, with a third installed in 2006 to give 100% flexibility. Fine seed filtration (FSF) was installed in 2005. Four hydrate thickeners remain unchanged from the original design. The initial coarse seed charge has increased from 250 g/l to 420 g/l. The combination of coarse seed and fine seed filters increased liquor productivity by 5 g/l. Product quality design was for < 12% -45µ and < 20 % Attrition Index, the actual being achieved is < 10% for both parameters on average.

Figure 13 shows a block diagram of the Precipitation Circuit at Aughinish. Heat Inter-stage Department (HID) is the vacuum flash area where the pregnant liquor from the security filtration area is cooled under vacuum from 105 °C to 85 °C and where the spent liquor exchanges heat with the resultant vapour to heat up the spent liquor going back to the digestion area.

CSF is the area where the solids from the underflow of the secondary classifier is filtered and recycled in pregnant liquor to give increased residence time and a higher seed charge in the growth tanks. FSF represents the area where the underflow of the thickeners is filtered and recycled in a more supersaturated liquor to improve liquor productivity and quality of the agglomerates.

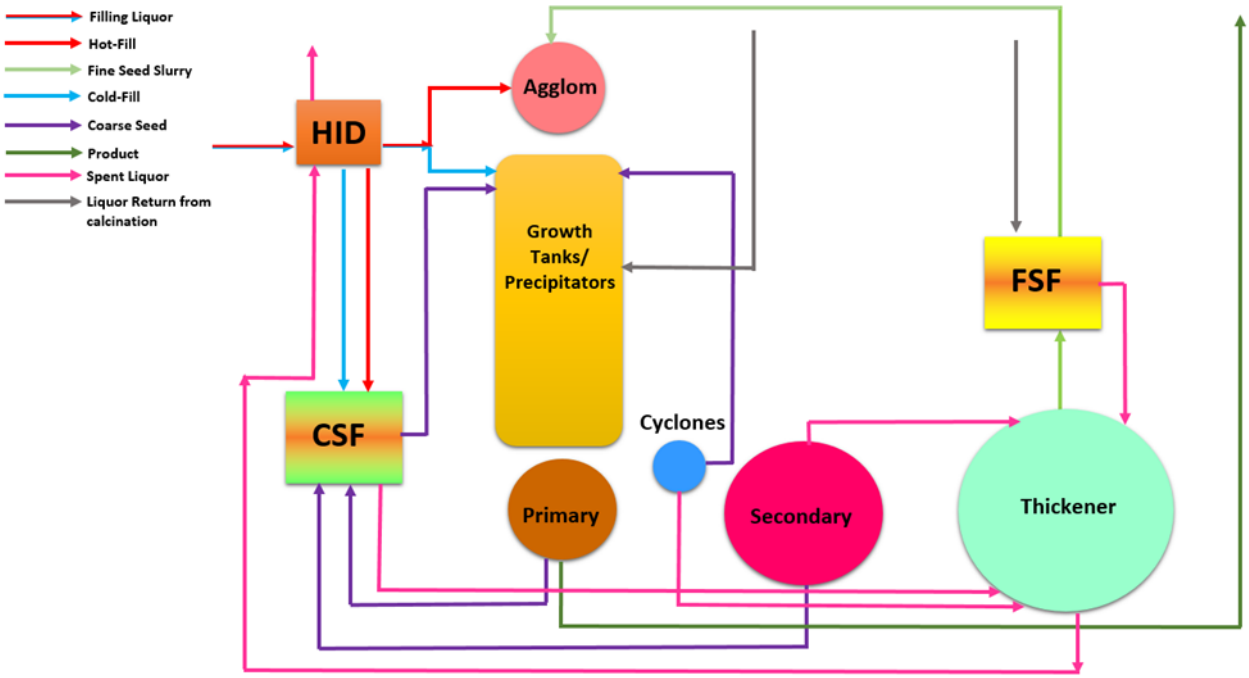

Figure 13. Block diagram of the precipitation circuit at Aughinish.

3. Control of Precipitation at Aughinish

The precipitation circuit at Aughinish is divided into the following areas:

- Precipitation
- Classification
- Equipment essential for controlling productivity and quality

3.1. Process Flow through Precipitation

As shown in Figure the pregnant liquor flow from the security filtration area is cooled in HID, causing it to become supersaturated. This increases the driving force for the aluminate ion to precipitate out of solution as alumina trihydrate. Fine seed is added to the pregnant liquor to provide a large surface area for the hydrate to precipitate onto. A number of large vessels, three agglomerators of 1200 m^3 volume, followed by twelve precipitators of 4500 m^3 volume (See Table 1 and
Table 2), provide the residence time required for precipitation. Continuous agitation is provided to keep the solids in suspension and at the same time increase the number of sites on the seed for precipitation to take place. Temperature control (hotfill/coldfill) and the amount of seed added (coarse seed return/fine seed return) to the pregnant liquor determines the size and strength of the precipitated hydrate. Hotfill is filling liquor flow direct from HID. Coldfill is filling liquor flow from HID that has passed through the interstage heat exchangers. The different temperature flows are needed to effect temperature changes at various stages in precipitation to control alumina

crystal formation and liquor yield. The dimensions, feed and functions of the agglomerators and precipitators are shown in Table 1 and Table 2 respectively.

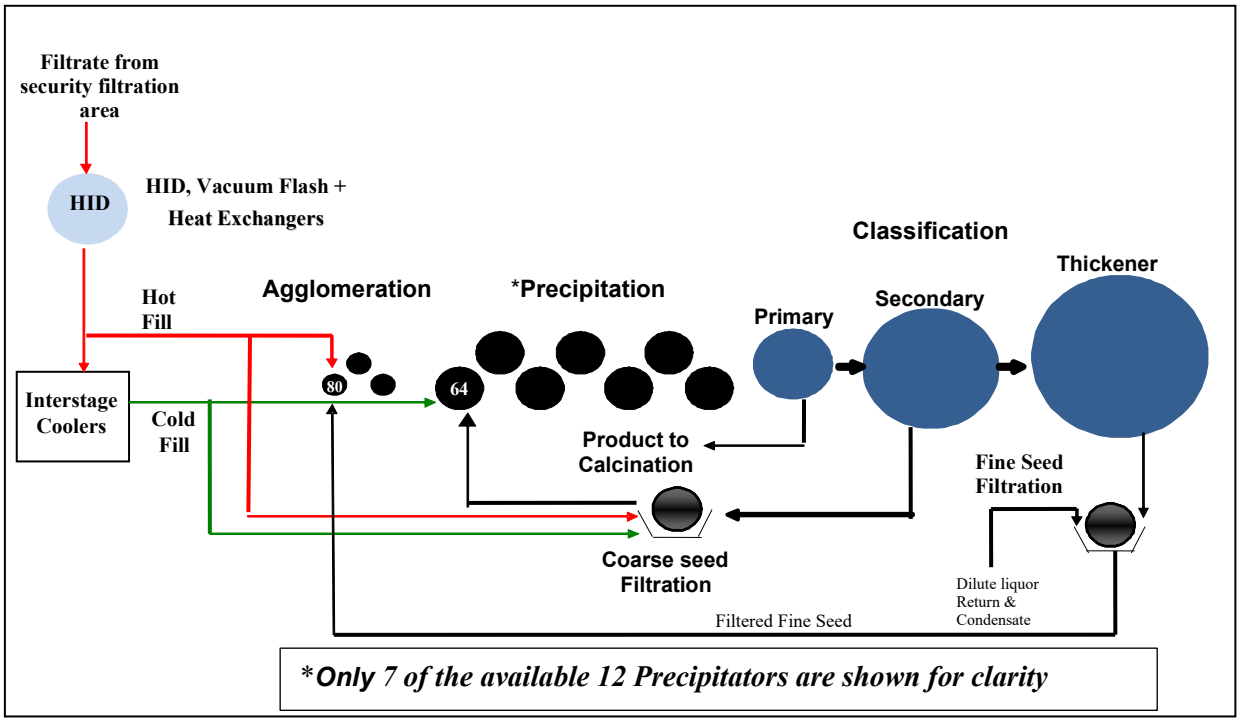

Figure 2. Precipitation process flow schematic.

Table 1. Dimensions, feed and function of Agglomerators.

Equipment	Agglomerators
Dimensions	1,200m^3, height 31m
Feed	The first agglomerator is fed with hot fill from HID and reslurried fine seed from FSF area.
Function	To provide the necessary conditions to enable the cementing together of fine seed particles to produce strong agglomerates. These conditions are: • moderate seed concentration, 175 – 275g/l • relatively high temperature, 79 -81°C • relatively high velocity for a residence time of 5 – 8 hours The medium which agglomerates the particles together is the gibbsite coming out of solution at the point that the crystals make contact.

Table 2. Dimensions, feed and function of Precipitators.

Equipment	Precipitators
Dimensions	Volume 4,500m^3, height 30m
Feed	The first precipitator is fed with agglomerator overflow, cold fill and reslurried coarse seed from CSF
Function	To provide the necessary conditions for crystal growth of particles and nucleation of fresh fine seed. These conditions are: • low supersaturation, 0.18 – 0.22 A/C • large seed surface area, 380 - 420g/l Crystal growth is the laying down of layers of precipitated gibbsite over particles until they reach product size. Secondary nucleation is the formation of fresh fine seed.

3.2. Classification

Classification segregates particles by size. The resultant segregation allows product size particles to be transferred to the calcination area; coarse seed to be transferred back to the precipitation circuit via CSF for further growth; and the fine seed particles to overflow to the hydrate thickening area to provide seed for agglomeration. As shown in Figure the overflow from the last precipitator on each chain is fed to a set of classifiers. Each set consists of a primary classifier and a secondary classifier. The primary classifier volume, feed and function is shown in Table 3 and the secondary in Table 4.

Table 3. Primary classifier volume, feed and function.

Equipment	Primary Classifier
Volume	2,100m^3
Feed	Flow from last precipitators
Function	To classify the mass flow of slurry exiting the last precipitator to achieve a mass underflow recovery of ~20% to next stage of classification, with a median size of 100±10µ and a cut size of 190µ

Table 4. Secondary classifier volume, feed and function.

Equipment	Secondary Classifier
Volume	3,500m^3
Feed	Primary classifier overflow
Function	To classify the mass flow of slurry exiting the primary classifiers to achieve a mass underflow recovery of ~90%, with a median size of 97±10µ and a cut size of 45µ

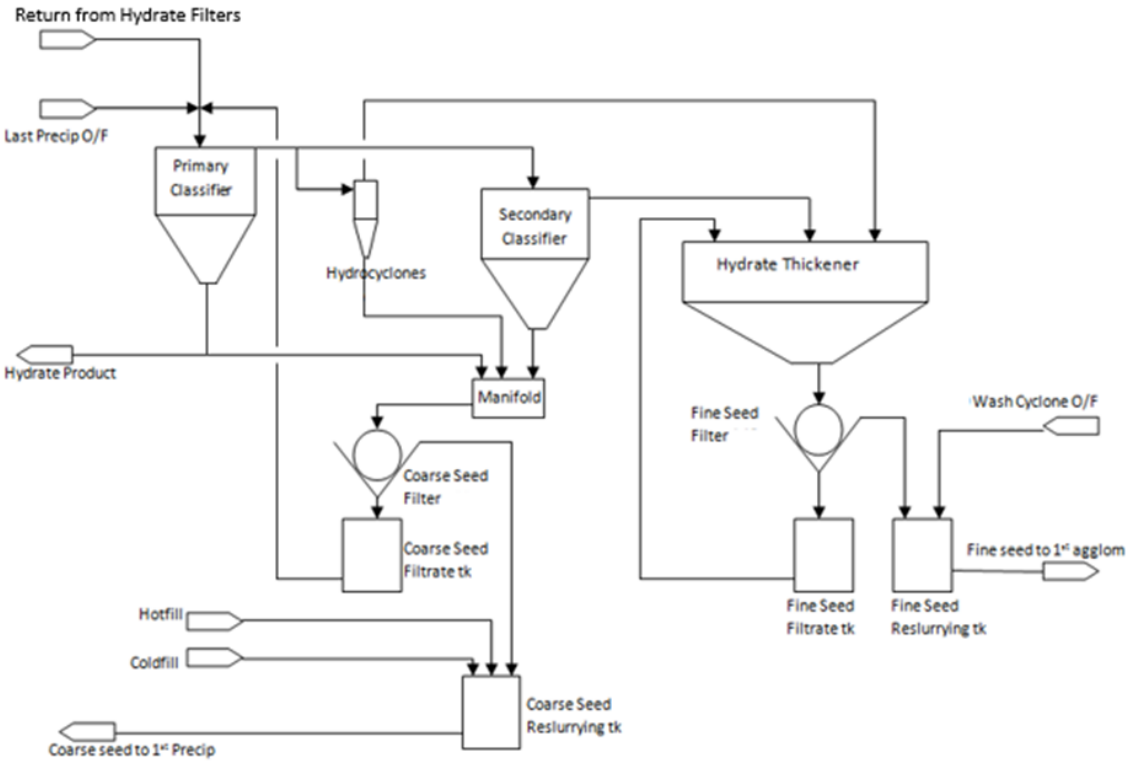

Figure 3. Schematic of Classification and filtration.

3.3. Equipment Essential for Controlling Productivity and Quality

A list of the other equipment areas in Precipitation is shown in Table 5 along with a brief description of their principles of operation. Table 6 lists equipment essential to controlling productivity and quality. A list of the actuators which control liquor yield and product quality is shown in Table 7. A list of the Key Process Indicators for Precipitation is shown in Table 8.

Table 5. Precipitation Supporting Equipment.

Area	Objectives	Principle of Operation
HID	Pregnant Liquor Cooling/Spent Liquor Heating.	Steam is flashed off the pregnant liquor in the HID flash tanks. This steam heats spent liquor from Hydrate Thickening Area (HTA) in shell & tube heat exchangers. The spent liquor returns to Digestion.
HTA	Hydrate thickening area/ minimising spent liquor solids.	Most of the hydrate (fine seed) remaining after classification is settled out in large settling tanks or thickeners, each 5340m3. The fine seed goes to FSF. The spent liquor overflow goes to spent liquor tanks and from there back to digestion, through Inter-stage cooling (ISC) and HID.
FSF	Fine seed filtration, collection and distribution.	Vertical disc filters collect the fine seed from the underflows of the hydrate thickeners in HTA. This fine seed is then reslurried to the desired density and pumped to the first agglomerators for pregnant liquor seeding.
CSF	Coarse seed filtration, collection and distribution.	Vertical disc filters collect the coarse seed from the underflows of the secondary classifiers. This coarse seed is then reslurried to the desired density and temperature and pumped to the first precipitators where the crystal growth continues.
ISC	To provide the cooling water used in the inter-stage heat exchangers and in-tank cooling systems.	Five evaporative cooling towers. The original six bay cooling tower incorporates the main pumping systems while a new cooling tower is used to supplement cooling capacity in inter-stage. Tower number three, four and five are used for three stages of in-tank cooling in precipitation.

Table 6. Cooling Equipment and Hydrocyclones.

Systems	Principle of Operation
Interstage cooling	Coldfill liquor must be produced for alumina crystal growth and quality control. Liquor from HID is cooled to 45-50 °C by heat exchange with spent liquor first and then cooling water.
In tank cooling	Cooling water flows through plate heat exchangers in Precipitators 6, 7, 8 and 10 to reduce pregnant liquor temperature and increase yield.
Hydrocyclones	The separation of the fine and coarse material in a 700 m^3/h stream from the top of the primary classifier, independent of the secondary classifier, is done using 6” Warman hydrocyclones.

Table 7. Productivity & Product Quality.

For Increasing Yield	For a Coarse Circuit	For a Fine Circuit
Decreasing temperature	Relatively high temperature	Relatively low temperature
Increasing initial ratio	Relatively high initial ratio	Relatively low initial ratio

For Increasing Yield	For a Coarse Circuit	For a Fine Circuit
Increasing seed surface area	Moderate seed charges	High seed charges
Increasing residence time	Low caustic concentrations	High caustic concentration
Decreasing liquor impurities	Moderate liquor impurity levels	High impurity levels in liquor
	Little agitation and pumping	Violent agitation or pumping

Table 8. Key Process Indicators, (KPIs).

KPI	Target	Significance
Agglomeration, % -45µm particles exiting agglomeration	18 - 20% %-45µm size	Influenced by the quality of the fine seed. Target is dependent on fines balance and seed quality.
Precipitation Mid-stream Temperature	64 – 66 °C.	Controls supersaturation. Low for increased yield but there's a lower limit to prevent soda precipitation.
Particle Size Distribution (PSD) ex mid chain precipitators	0.8% %-20µm size	Required to maintain fines balance.
Classification, recoveries on hydrocyclones and secondary's	Target > 90%	Higher recoveries reduce pressure on tertiary classification.

3.4. Calcite Addition

Calcite ($CaCO_3$) has a limited solubility in Bayer liquor (~10 ppm). It functions however, as a very effective tool for inhibiting nucleation as the calcium ion will preferentially take up active sites on the hydrate crystal lattice, which would normally be taken up by aluminate ions. It is used to control nucleation, particularly in the coarse seed reslurry tanks where the formation of secondary nuclei in some circumstances can get out of control. While it will initially reduce gibbsite yield it soon becomes expended and the same equilibrium yield is obtained at the end of the precipitation chain as if it had played no part in the process. Refer to the Scanning Electron Microscope (SEM) images of hydrate crystals shown in figure 4.

No Calcite, 3 Hrs Precipitation 10ppm Calcite, 2 Hrs Precipitation 100ppm Calcite, 3 Hrs Precipitation

Figure 4. Images of Hydrate Crystals.

4. Gibbsite Crystallisation Theory

The processes which govern the crystal size distribution and crystal population, and hence liquor productivity in the Precipitation Circuit are; growth, nucleation and agglomeration. We shall examine each one in turn.

4.1. Growth

The growth of crystals in a crystallization process is effected by the existence of a driving force for growth. This driving force is the solute supersaturation. Supersaturation (ß) is defined as the difference between the actual aluminate concentration at time and the aluminate concentration at equilibrium. Figure shows the concentration versus temperature diagram for gibbsite crystallisation where C_{sol} is the aluminate solution concentration and C* is the aluminate equilibrium concentration. Below the solubility curve, the solution is stable and under-saturated. Here the liquor can still dissolve a given quantity of hydrate to reach equilibrium. It is only beyond the limit of the metastable zone illustrated by the supersaturation limit curve, that the solution will generate crystals by nucleation. In the metastable zone the solution is not in balance; however the probability of spontaneous nucleation in this region is practically zero.

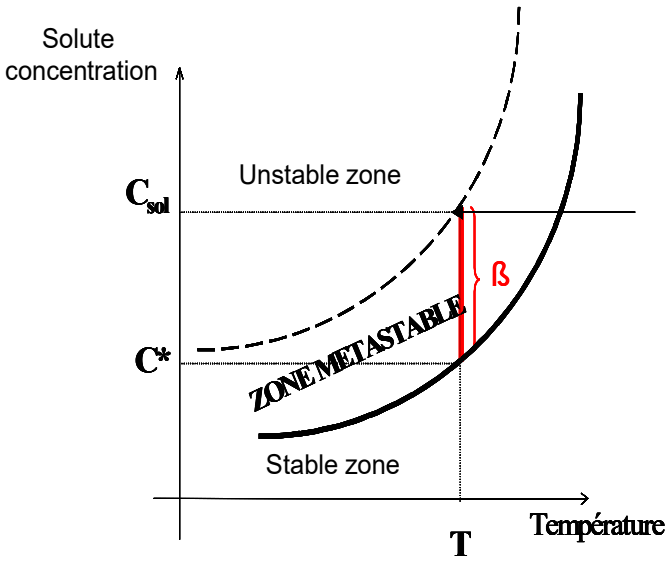

Figure 5. Concentration - temperature diagram for gibbsite crystallization.

The equilibrium aluminate solution concentration typically takes the form of that correlated by Misra and White (1971) [1]

$$A^* = C \exp\left(6.2106 - \frac{2486.7}{T} + \frac{1.0876C}{T}\right) \quad (1)$$

Where C and T are the caustic concentration in g/l Na_2O and the temperature in Kelvin respectively. The lower the temperature drops the lower the equilibrium drops.

Most of the growth correlations found in the literature are of the form shown below. [1][2][3][4][5]:

$$G = k_0 \exp\left(\frac{-\Delta E}{RT}\right)\left(\frac{A - A^*}{A^*}\right)C^n \quad (2)$$

Where;

G	Growth rate	m/s
k_0	Pre-exponential constant	(-)

ΔE	Activation energy	kJ/mol
R	Universal gas constant	J/mol K
T	Temperature	K
A	aluminate concentration	g/l
A*	Equilibrium alumina concentration	g/l
C	Caustic concentration	g/l

The reported values of n generally takes a value of 2 or 2.5.

So the growth rate of gibbsite crystals is very much a function of the Bayer process variables such as temperature, caustic concentration and the driving force provided by supersaturation.

A plot of Linear Growth Rate vs. Time will show that the two lines intersect after approximately 20 hours. The reason for this phenomenon is explained by the temperature and supersaturation dependence of the growth kinetics. At the higher temperature the supersaturation ratio in the system is lower than at low temperature. This would lead one to believe that the linear growth rate at the higher temperature would be lower. However the inverse negative exponential temperature dependence of growth is a far more dominant term in the equation. The result of this is that the linear growth rate at higher temperatures drops faster than that at lower temperatures.

4.2. Nucleation

In Bayer liquor the mode of nucleation is widely accepted to be secondary in nature (Dirksen and Ring, 1991) [6]. Due to the presence of large amounts of impurities and solids typically found in the liquor the occurrence of primary nucleation can be disregarded. The equations used to describe the secondary nucleation generally take the form of:

$$B_0 = Ak_0 \exp\left(\frac{-\Delta E}{RT}\right)\sigma^n \tag{3}$$

where A, k_0, ΔE, σ and n are the active crystal surface area, pre-exponential factor, nucleation activation energy, alumina supersaturation ratio and nucleation order respectively.

The disadvantage of this equation is that is does not take into account the fluid properties or hydrodynamic conditions present in the system. Also, the effect of solids loading is not accounted for. An increase in solids loading results in an increase in the secondary nucleation rate. A correlation developed by Commonwealth Scientific and Industrial Research Organisation (CSIRO) takes account of the above and takes the form.

$$B_0 = k_B \exp\left(\frac{-\Delta E}{RT}\right)\sigma^a M^b m_2^e \gamma^n \left(\frac{C}{C_{ref}}\right) \tag{4}$$

B_0	Nucleation rate	#/s
$\mathbf{k_B}$	Nucleation pre-exponential constant	(-)
$\boldsymbol{\sigma}$	Supersaturation ratio	(-)
M	Solids loading	g/l
$\boldsymbol{m_2}$	Second moment	m^2
$\boldsymbol{\gamma}$	Fluid shear rate	/s
$\boldsymbol{C_{ref}}$	Reference alumina concentration	g/l

Where a, b, e, n, k_B, and ΔE are experimentally determined constants.

The effect of temperature on the kinetics of the system is quite significant. The reason for this is that the nucleation rate is significantly higher at lower temperatures resulting in an increase in the number of extremely small particles. The reason for the increased nucleation rate is that the supersaturation ratio is a lot higher and the exponential term in the nucleation governing equation is a lot higher at lower temperatures.

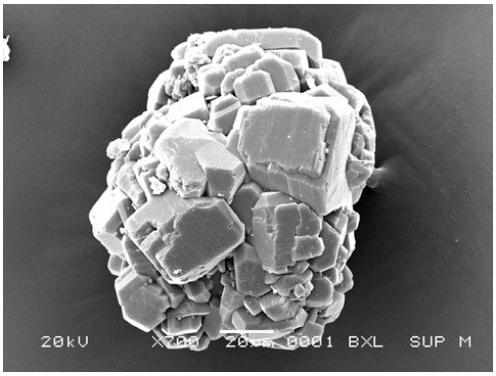

Figure 6. Agglomerate crystal showing good mosaic structure

4.3. Agglomeration

Agglomeration is the binding together through gibbsite cementation of fine particles of hydrate to form larger particles of a highly mosaic nature at high alumina supersaturation, relatively low seed charge or surface area and relatively high temperatures. These agglomerates then form the core of the product hydrate particles. The forces which bind particles together are believed to be weak van der Waals forces or hydrogen bonding. Figure shows an agglomerate. Figure shows the steps involved in the formation of a stable agglomerate.

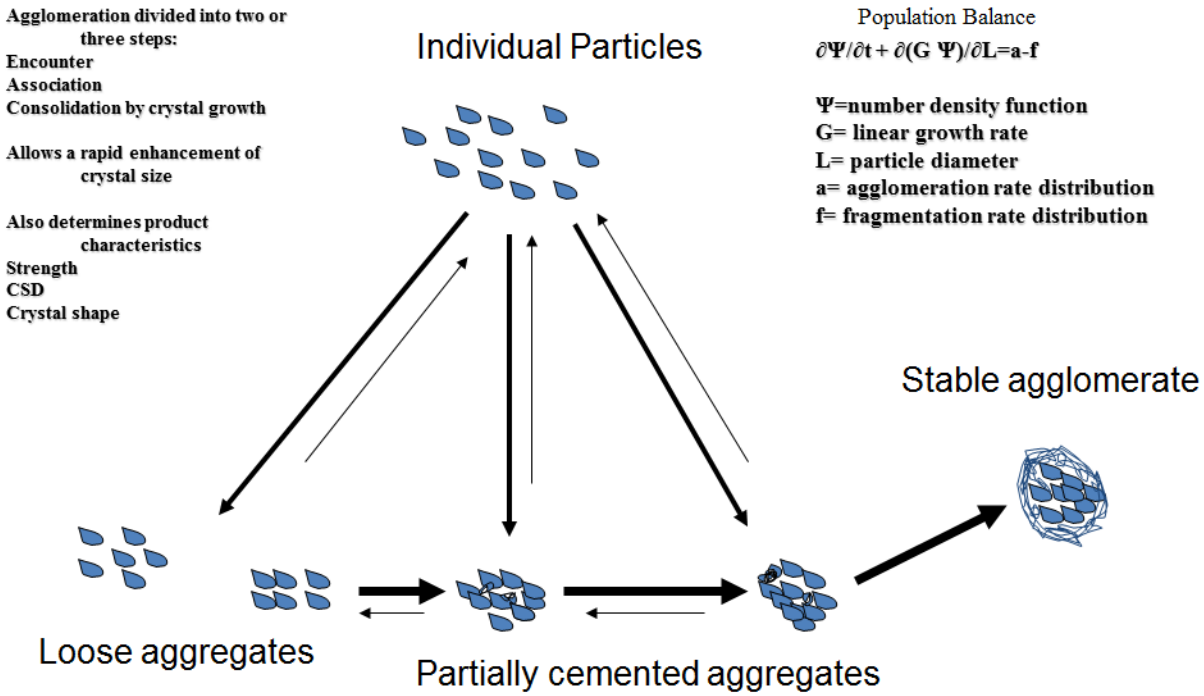

Figure 7. Steps in the formation of a stable agglomerate

The agglomeration process can play a significant role in the final crystal size distribution in the Bayer process. Agglomeration or adhesion is brought about by the impaction of two particles. The

probability of a three or more particle collision is so low that only two-particle interactions/collisions are considered in the literature.

A correlation developed by CSIRO (2006) to describe the agglomeration kernel *B* is presented below:

$$B = k_a \exp\left(\frac{-\Delta E}{RT}\right)\sigma^a \mu^k \gamma^n \tag{5}$$

Where;
k_a is the agglomeration rate constant, σ is the relative supersaturation, μ the total crystal count and γ the shear rate. The order of a, k and n must be determined experimentally and are a function of the liquor concentration and seed charge. So the rate of agglomeration is a function of temperature, supersaturation, total crystal population and slurry agitation. Table 9 shows the %-45μm target for various parts of the circuit at Aughinish from fine seed to calcined product and the function of each.

Table 9. Showing typical %-45μm size targets for various parts of the circuit at Aughinish

Parameter	**Target %-45μm**	**Function of**
Fine Seed	25.6	Nucleation, Classification, population balance
Agglomeration Overflows	18.1	Temperature, surface area, seed charge, linear growth rate fine seed filtration
Coarse Seed	6.1	Cyclone and gravity filtration, coarse seed filtration
Latter Precipitator Overflows	6.6	Nucleation, growth, calcite addition, oxalate stabiliser
Primary Underflow	5.0	Gravity classification
Calciner feed	2.8	Two stages of cyclones
Calciner Product	7.2	Calciner conditions and breakdown/attrition

4.4. Liquor Yield

Applying the Veesler and Boistelle (1993) [4] equation below to describe liquor yield we find:

$$-\frac{dATC}{dt} = k_1 * Area * \exp\left(-k_2 \frac{\Delta E}{RT}\right) * (ATC_t - k_3 * \ ATC_e)^2 \tag{6}$$

where:

ATC	alumina to caustic ratio	(-)
ATC_t	alumina to caustic ratio at time t	(-)
ATC_e	alumina to caustic ratio at equilibrium for pure liquor and is a function of temperature and caustic concentration	(-)
Area	seed surface area	m^2
R	Universal gas constant	J/mol K
ΔE	Reaction activation energy	J/mol
T	Temperature	K
$k_{1, 2, 3}$	constants for a given seed and liquor	

The potential for yield increase is a function of ability to increase seed surface area, increase precipitation time, increase in-tank A/C ratio and finally decrease equilibrium A/C ratio.

Less obvious are the factors which influence the constants $k_{1,\,2,\,3.}$ These include liquor impurities which tend to stabilise the liquor with respect to alumina, thus increasing the value of k_3. Liquor impurities also tend to poison seed surface sites reducing the value of k_1. These impurities can seriously affect control of seed nucleation and agglomeration as well as liquor yield.

Temperature occurs twice in the equation, as part of the Arrhenius term ($-\Delta E/RT$) and as one of the determining variables for the equilibrium to caustic ratio term (ATC_e). Combining these two terms indicates there is an optimal temperature for each point of the reaction. This means that temperature should decrease continually as precipitation progresses, initially favouring the $-\Delta E/RT$ term, and later the ATC_e term.

4.5. The Optimum Temperature Profile

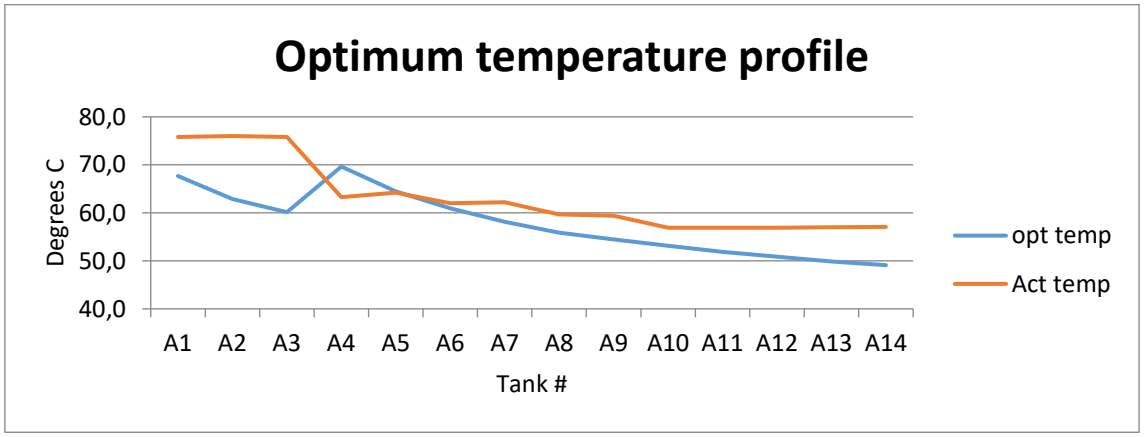

Figure 8. Calculated optimum temperature profile and actual at Aughinish

The optimum temperature profile shown in Figure shows both the calculated optimum and the actual temperatures achieved. The calculated temperatures are based on achieving optimum productivity at any stage in the precipitation process and do not take into account what the impact on quality would be, e.g. the optimum temperature in last tank would result in oxalate precipitation which would be detrimental for quality. The optimum temperature in agglomeration would not result in the formation of strong agglomerates and so would also be detrimental for quality. The actual drop in temperature achieved in Tanks 6, 8 and 10 are achieved through in-tank cooling in those tanks.

4.6. Options for Improving Productivity

A number of elements briefly discussed below:

- Seed Charge
- Seed surface area
- Temperature
- Super-saturation
- Equipment
- Liquor Chemistry

4.6.1. Increasing Seed Charge

Increasing seed charge can be accomplished by increasing the gram per litre solids in the crystallizers. Increasing seed residence time will inevitably lead to a higher seed charge, reducing spent or non-productive liquor recycle will increase seed charge and will effectively reduce volumetric flow, filtering seed will have the effect of removing non-productive liquor from the

growth circuit replacing it with more supersaturated liquor. To achieve this it is necessary to ensure that ancillary equipment such as agitators and classifiers have the capability to handle the extra solids loading.

4.6.2. Increasing Seed Surface Area

Increasing seed surface area can be achieved by increasing seed charge relative to unit slurry volume and reducing circuit size as finer particles will contain more surface area. This objective is in addition facilitated by increased residence time, less recycle of spent liquor, filtering of seed to remove spent liquor, and increasing slurry densities in conjunction with re-suspending the seed in a more active stream. The big question mark over reducing circuit size is what will be its impact on increasing fines in the calcined product, thus creating a potential environmental issue for customers due to the generation of dust in handling the product.

4.6.3. Reducing Circuit Temperatures

This can be achieved by operating at lower temperatures assuming there is sufficient cooling capacity available and by increasing seed residence time as the liquor will have longer exposure to ambient cooling. The installation of more and bigger tanks would have the effect of exposing the liquor to increased ambient cooling as well as offering an opportunity to get closer to the true equilibrium solubility which is only achieved close to infinite time. However the downsides of increased cooling are the high capital investment requirement on the installation of additional cooling towers and heat exchangers.

4.6.4. Increasing Alumina Super-Saturation

This can be achieved by operating at lower temperatures as per the kinetic rate equation for alumina solubility, increasing the alumina to caustic ratio in the mother liquor, dilution of the mother liquor with water to increase the alumina super-saturation, reducing contaminants in the liquor such as sodium carbonate which effectively reduces the liquors causticity, increasing seed residence time which increases driving force and reducing recycle of spent liquor. The recycle of spent liquor can be avoided by reslurring filtered seed in pregnant liquor.

4.6.5. Upgrade and/or Expansion Compromises

This effectively involves the installation of more and bigger tanks, pipes, pumps, valves, filtration apparatus, classification kit and cooling equipment with the objective to increase volumetric flow and hydraulic capacity. While the upgrade and/or expansion of equipment would undoubtedly increase production and maybe liquor yield, the capital cost could be prohibitive and needs to be assessed in advance.

4.6.6. Modify Liquor Chemistry

This can be achieved with varying degrees of risk by increasing liquor caustic, reducing contaminants, reducing scaling rates, chemical crystal growth modifier addition, and co-precipitation of alumina trihydrate with oxalate crystals or destabilization of the liquor organic stabilizers. All of these options are highly risky and so would require extensive research and development using reliable modelling and laboratory scale experiments before being considered.

4.6.7. Quality Compromise

A much finer circuit, which would result from the co-precipitation of solid phase sodium oxalate and destabilization of the humate organic stabilizers, would give a significant increase in liquor yield. This would result in a finer and weaker product.

5. Sodium Oxalate and its Impact on Precipitation Control

The detrimental effect of sodium oxalate in the Bayer process is both well-known and well-documented. Sodium oxalate represents one of the products generated in the Bayer process by degradation of higher molecular weight organic compounds in the digestion stage. The concentration of sodium oxalate in Bayer liquor depends on the level of organic carbon in the bauxite and digestion conditions. Under low temperature digestion conditions (125-150 °C) approximately 5% of the total organics are converted to oxalate, however this amount doubles under high temperature digestion conditions (225-250 °C). In the Bayer process the oxalate concentration builds up as the caustic liquor used for digestion is recycled. Due to its low solubility in concentrated caustic solution sodium oxalate readily precipitates as fine needles, once the critical oxalate concentration is reached, to form solid phase oxalate (SPO). This, above any of the other organic compounds present in Bayer liquor, has the most detrimental effect on the alumina trihydroxide precipitation process.

The presence of SPO in the gibbsite precipitation circuit at Aughinish has been observed to lead to:

- Reduced efficiency of gibbsite agglomeration (See Figure)
- Increased rate of gibbsite fines generation (See Figure)
- Increased scale formation rates in cooler parts of circuit
- Reduced efficiency of particle size classification due to poor settling
- Increased spent liquor solids in thickener overflows
- Material not settling in the thickeners
- Increased product breakdown rate in calcination
- Higher fines in product
- Increased residual soda

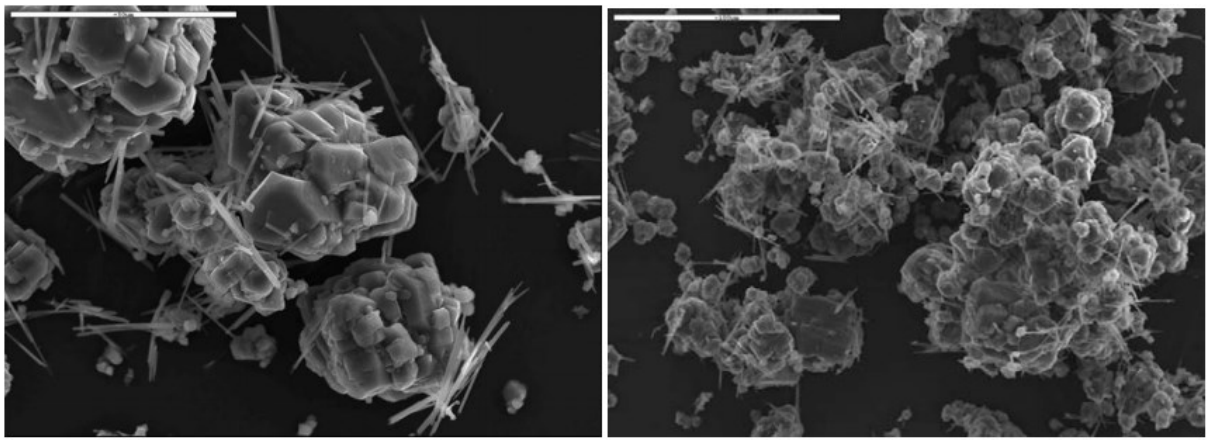

Figure 9. SEM images showing SPO needles attached onto gibbsite agglomerates, which interfere with gibbsite agglomeration.

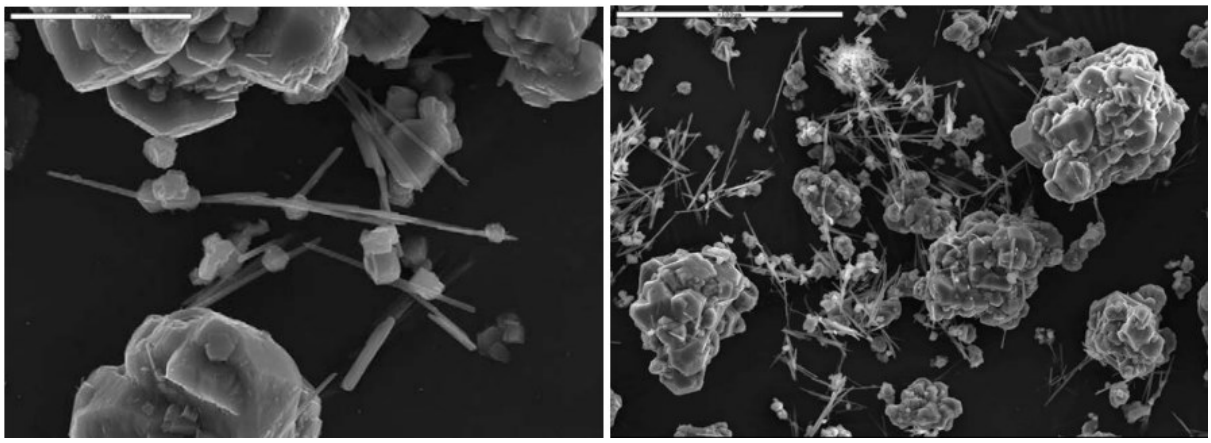

Figure 10. SEM images showing gibbsite nuclei formed on oxalate needles during gibbsite precipitation in oxalate-aluminate liquors.

5.1. Control of Organics and Sodium Carbonate

5.1.1. Deep Evaporation

Deep Evaporation is achieved through evaporation of part of the spent liquor stream to precipitate oxalate, long chain organics and Na_2CO_3. The process also precipitates NaF, Na_2SO_4 and V_2O_5 as sodium sulphate and sodium flourovanidate. The solids are separated and discarded as salt cake. This is the method practiced at Aughinish.

Precipitation yield is dependent on:

- Temperature: the lower the temperature the higher the yield
- Presence of seed: seed provides surface area for growth of new oxalate crystals
- Caustic concentration: oxalate is less soluble at higher caustics
- Time: the longer the residence time the higher the yield
- Quality of seed: seed which is coated with organics (poisoned) is inactive

5.1.2. External Causticisation

Carbonate formed by the breakdown of organics, or any other source (air carbonation, pond return, scrubber solution from smelters) may be controlled by lime in an outside causticisation circuit to produce largely insoluble calcium carbonate. The process consists of liming a dilute mud and washing solution (first or second stage mud washer overflow).

5.1.3. Control of Oxalate Concentration

While not many plants make an effort to control the total organics level in their liquors, they are forced to do something about the oxalate concentration. There are two approaches to the oxalate problem:

- The first is to allow the oxalate to reach the critical solubility level and precipitate somewhere in the hydrate precipitation - classification circuit. The oxalate-bearing hydrate product (Shimizu) or fine seed (Kaiser) is water washed to dissolve the oxalate for treatment or disposal as insoluble calcium oxalate in a process similar to external causticisation.
- The second is to precipitate the oxalate as $Na_2C_2O_4$ in a side circuit for treatment or disposal and thereby prevent the oxalate from precipitating with hydrate. This is the approach favoured by Aughinish through its deep evaporation process.

5.2. Oxalate Control of the Precipitation Circuit at Aughinish

Oxalate precipitation can lead to excessive nucleation, poor agglomeration, poor classification, high thickener overflows and high residual sodas. These can ultimately result in poor product quality. Oxalate supersaturation therefore is controlled to within a limit such that oxalate precipitation is not likely to occur. Oxalate supersaturation depends mainly on oxalate concentration, caustic concentration and temperature. The oxalate in the plant liquor is determined by the amount of organic material in the bauxite and the rate of removal in the deep evaporator unit area.

The following parameters are monitored carefully to minimize the risk of oxalate precipitation

- Oxalate in spent liquor
- Spent liquor oxalate supersaturation
- Oxalate on unwashed fine seed
- Oxalate on washed fine seed
- Spent liquor caustic concentrations
- Backend temperatures
- Blinding of the fine seed and coarse seed filters
- Poor classification

The prevention of the generation of solid phase oxalate is controlled by using the following actuators:

- Oxalate stabilizer addition to the 1st agglomerator
- Spent liquor temperature control
- Spent liquor caustic control
- Test tank caustic control

Prolonged high spent liquor oxalate supersaturation is an indication that the plant test tank caustic target needs to be reviewed downwards.

6. Conclusions

Producing a high quality alumina depends on many refinery aspects, not just the precipitation area but also on the upstream areas of digestion and decantation as well as the quality of the bauxite or combination of bauxites being refined.

The precipitation circuit at Aughinish has evolved over the years since it first went into production back in September of 1983. Over the years plant production has almost trebled and plant productivity has increased with the introduction of improved classification, fine and coarse seed filtration, more efficient cooling equipment and optimised process control.

Interrogation of the kinetic rate equations which govern alumina crystallisation provides information on where the potential for improving quality and increasing liquor productivity opportunities lie.

The three precipitation mechanisms of agglomeration, growth and nucleation are all detailed in depth in the body of this report with the opportunities and risks that each mechanism carries.
Central to achieving high quality alumina is having sufficient cooling capacity to control alumina supersaturation at the defined targets in each stage of the precipitation process.

It is critical to maintain a manageable and well defined fines balance through good control of nucleation and seed classification to produce a strong agglomerate which will not breakdown in calcination.

Opportunities to improve liquor productivity include increasing seed charge, increasing seed surface area, reducing circuit temperatures, increasing alumina supersaturation or upgrading plan equipment but all of these need to be carefully assessed for their impact on product quality and cost effectiveness.

The impact of sodium oxalate needs to be carefully assessed when deciding the most appropriate mode of operation for any particular plant based on bauxite quality and equipment availability.

7. References

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