ADVANCES IN CONTROL OF TRIHYDRATE CLASSIFICATION USING HIGH PERFORMANCE FLOCCULATION

Aboagye A[1], Chester R[1*], Kildea J[1], O'Brien K[2], Phillips E[2] and Wang J[2]

[1]Nalco Australia Pty Ltd, 2 Richardson St, Kwinana, Western Australia, 6167
[2]Nalco Company, 1601 West Diehl Rd, Naperville, Illinois, USA, 60563-1198

Abstract:

Productivity in the Bayer process is often directly related to the efficient capture and classification of trihydrate particles into various size fractions. Efficient size classification can often be achieved using cyclones but in many plants a series of settling classifiers are still used. In such cases, the use of trihydrate flocculants can be advantageous in a number of ways. In addition to faster settling enabling higher throughput, flocculants can also capture solids that may otherwise be lost and recycled to digestion with spent liquor. However, a critical advantage that is often overlooked is the use of trihydrate flocculants to enhance underflow rheology, thus preventing premature tank failures due to excessive rake torques, "rat-holing" and scale formation in classification vessels. While a range of trihydrate flocculants have been accepted and used by the industry for more than a decade, recent work has resulted in the development of an enhanced range of trihydrate flocculants. These products provide a variety of properties that allow for further optimization and improvements in process productivity.

1. Introduction

Precipitation of alumina trihydrate is one of the key processes within any alumina refinery and is focused on achieving two key objectives. The first, and most often recognized, is the production of trihydrate crystals of appropriate quality that can be calcined to produce smelting grade alumina (SGA). The second objective is to crystallize a sufficient quantity of fine trihydrate particles for reuse as seed crystals within the process. These two objectives are somewhat opposed. One of the main parameters defining SGA quality is particle size; specifically the elimination or at the very least the minimization of fine particles within the product stream. On the other hand, seed crystals must necessarily be fine particles so as to enhance agglomeration and maximize surface area to increase the rate of precipitation, and therefore process efficiency.

Process operators are all too familiar with the conflicting nature of the two objectives with excursions to precipitation of particularly coarse particle size distribution resulting in a lack of seed for subsequent operation, while excessive production of fine material results in too much seed that cannot be effectively utilized. As a result, there is a constant quest to maintain the appropriate "seed balance" within the precipitation circuit which will enable both optimal production of trihydrate alumina of suitable size for calcination, as well as maintenance of an appropriate quantity and quality of seed crystals.

As a result, the outcome of the precipitation process is necessarily a mixture of particles of various sizes, both coarse and fine. This mixture requires separation into the appropriately sized material for use as either calciner feed or as seed crystals for further precipitation. This separation or classification of the precipitated trihydrate crystals is again, a critical process within refinery operations and a number of different methods are practiced throughout the industry.

Typically, the classification process is split into a series of steps involving conventional size separation technologies such as cyclones or thickeners with various streams delivering coarser or finer particles. Figure 1 is a schematic representation of a typical separation system involving three steps. These may be considered as primary, secondary and tertiary classification units. The initial cut separates out the coarse particles which can then be removed from the process and calcined. The next two steps involve the separation of the seed into a coarse and fine fraction. In some operations these two steps are combined so that there is only a single step for seed separation, but more often further classification into the two types of seed is undertaken. Typically, seed thickeners of some type are utilized for this purpose. The seed (as a single source or as individual coarse and fine streams) can then be used within the precipitation circuit to maximize throughput and productivity.

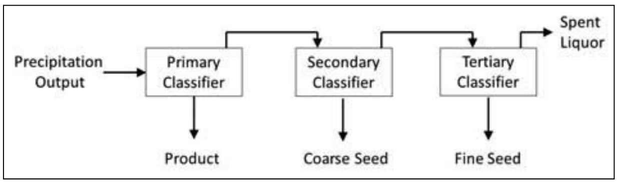

Figure 1. Schematic representation of a generic trihydrate classification system.

Within the first two steps of this generic classification system it is necessary to ensure the appropriate separation of particles of different sizes with the two output streams both being effectively utilized in further processing. Within the third step, solid material reporting to the underflow in a tertiary classification unit can be utilized within precipitation but overflow streams typically report as spent liquor and as such are eventually added back to digestion. Any solid material within the overflow liquor stream will eventually re-dissolve in the liquor. As a result, any solid material reporting to the overflow is clearly a reduction in process efficiency. To precipitate solid alumina trihydrate, only to re-dissolve it, is clearly both undesirable and inefficient.

2. Value of recovering trihydrate from tertiary classification

Tertiary classification systems are generally designed to minimize the loss of solids in the overflow systems so solids content of overflow slurries, even without the use of a flocculant, are low (typically less than 5g/L as trihydrate). With such low solids content it is tempting to believe that the losses in efficiency are negligible, or at least minimal. Unfortunately, the exact opposite is the case since any increases in capture of trihydrate at this part of the circuit delivers substantial benefits to producers.

Any solids reporting with the spent liquor will potentially redissolve before digestion, most often in the heat exchangers, and as a result the spent liquor entering digestion effectively has a higher A/C ratio (or a higher alumina content) than it would otherwise have if all solids were captured in classification. This then restricts the extraction efficiency of the bauxite since less alumina is extracted in digestion to produce the target A/C ratio. Effectively this means that for every tonne of trihydrate recycled through the process, one tonne of alumina is NOT extracted from the bauxite. However, if less alumina is being extracted per tonne of bauxite, then to maintain a given production rate, more bauxite must be processed.

Effectively for each tonne of material "recycled" in the spent liquor from classification, a tonne of production is lost. Additionally, this loss must be recovered, not directly, but by processing more bauxite, and this entails additional energy, water, and chemical processing (e.g. caustic) costs.

Using a range of publicly available data [IAI, 2011, Henrickson, 2010] and making a number of general assumptions, the value of capturing and utilizing the solids from tertiary classifiers (or alternatively the cost of letting the solids report with the spent liquor to digestion) can be readily calculated.

For example, for a hypothetical plant operating with a flow of approximately 1800 m^3/hr, with a plant yield of 65 g/L and a production rate of 1 million tonnes per year, a 0.5 g/L reduction in overflow solids can result in an estimated increase of production by at least 5000 tonnes per annum. In addition to this direct production benefit, there are indirect yield benefits derived from increased seed surface area. This is particularly so because the solids that tend to overflow thickeners are the ultra-fine particles with the greatest surface area.

Additional savings in terms of energy, water usage, caustic and CO_2 emissions are also likely from the improvements in process efficiency afforded by the application of trihydrate flocculants and the consequent reduction in "recycling" of precipitated trihydrate solids. The costs associated with such actions can again be readily calculated using publicly available data [Henrickson, 2010; National Greenhouse Accounts Factors, 2008].

3. Use of Trihydrate Flocculants

In order to reduce the loss of trihydrate solids through classification, Nalco developed and implemented the use of trihydrate flocculants for the alumina industry (Malito, 1995). The application of these specialty flocculants has been optimized through extensive laboratory and in-plant testing (Malito, 1995) and their use throughout the industry is now well established.

The extensive use of these products has identified a variety of benefits which can enhance the operation of Bayer process plants. In addition to the traditional flocculant properties of reducing solids overflow and increasing particle settling rate, Nalco's trihydrate flocculants are known to deliver an enhancement of the flow characteristics of the flocculated trihydrate particles. Individually and in combination, these properties are highly desirable and have delivered clear benefits to process operators in each case.

3.1 Solids Capture – Overflow reduction

Like other flocculants, trihydrate flocculants capture and settle fine solid material in tertiary classifiers which results in a substantial reduction in overflow solids reporting to the spent liquor streams. Table 1 shows laboratory test data from cylinder tests in which plant tertiary classifier feed slurry was mixed with or without flocculant.

Table 1. Laboratory cylinder test results demonstrating the impact of conventional trihydrate flocculants on settling rate and solids capture. Treated Slurry = Conventional Trihydrate flocculant.

Parameter	Undosed slurry	Treated Slurry
Overflow solids* (g/L)	1.3	0.4
Settling rate** (m/hr)	0.7	3.1

* Slurry sampled after ~10 mins settling time. Data is relative - not indicative of plant values.
** Estimated from interface settling time.

Plant use of trihdyrate flocculant is traditionally justified on the value of solids captured – that is, the reduction in the overflow solids in tertiary thickener vessels. While the dose rates of flocculant required can vary, generally the value of the captured solids is substantially greater than the cost of the treatment program – realising a positive benefit for producers. As outlined in the hypothetical example above, the value calculations for a reduction of 0.5g/L on a flow of 1800m^3/hr results in a net annual production benefit of 5000 tonnes. While the results shown in table 1 are not necessarily indicative of plant performance, a substantial benefit in overflow solids is likely in plant application and has been proven across a broad range of plant operations.

3.2 Settling Rate Enhancement

In addition to enhancing the solids capture, the use of trihydrate flocculants allows producers to increase flow through vessels while maintaining (or even enhancing) capture efficiency. Typically, an increase in the flow to a settling vessel can result in higher overflow solids due to potential "flaring" and/or increased upflow velocity in the tank. By adding flocculant to increase the settling rate of the particles, any increase in upflow velocity due to increased feed flow is unlikely to impact on solids capture. While often dependent on the capacity in other parts of the plant, the ability to increase flow in the classification system is a substantial process benefit that can eliminate potential bottlenecks and deliver significant production benefits to operators.

3.3 Underflow Rheology Impact

One of the key aspects of any settling vessel is not simply the capture and delivery of solids to the underflow outlet but specifically the nature of the settled solid slurry. Trihydrate particles that are allowed to settle naturally in the absence of flocculant can often form a slurry with poor flow characteristics, with the material being more solid in nature than fluid. Such densely packed material does not flow well and can often result in bogging of the underflow solids (requiring costly unscheduled maintenance), unacceptable rake torques (in vessels where rakes are used) or so called "rat-holing" of underflow beds where fluid flows through small, specific channels occurs while the majority of the bed remains immobile.

To avoid such undesirable outcomes plants often operate seed thickeners at less than desirable underflow densities. This results in less than optimum seed density and more spent liquor being returned with the seed – both highly undesirable and inefficient outcomes.

The application of trihydrate flocculant results in improved flow characteristics of the resulting underflow. Indeed, contrary to what might be expected in a flocculated slurry, the application of Nalco trihydrate flocculant results in a free flowing slurry that pumps more easily and enables increased solids density in operational use.

The change in rheology of settled trihydrate solids can be seen most apparently by settling the solids – with or without flocculant – in an Imhoff cone. In a test using tertiary classifier feed slurry, two separate one litre samples of slurry (one treated with conventional trihydrate flocculant and one untreated) were poured into separate Imhoff cones and left to settle for 20 minutes. The solids settled in both cases to approximately the same level. The bottom plug of each cone was removed and the time required for the entire contents of each cone to be expelled was recorded.

This test was completed in duplicate and average results are shown in table 2. The flocculated material flowed freely and quickly from the vessel while the untreated material showed very poor flow characteristics. While such testing is very basic in nature, it nonetheless gives a very clear and demonstrable assessment of the impact of conventional trihydrate flocculant on underflow rheological properties.

Table 2 Flow characteristics as measured by the time taken to flow through an Imhoff cone. Untreated trihydrate slurry and the same slurry flocculated with conventional trihydrate flocculant used. Average time of duplicate tests are shown. Settling time = 20 minutes. Dose rate ~ 80g/T.

Treatment	Untreated	Flocculated
Delivery Time (secs)	226	142

4. High Performance Trihydrate Flocculants

While conventional flocculants clearly deliver substantial benefits to operators of trihydrate classification systems, the need for continuous improvement beyond the existing technologies has resulted in the recent development by Nalco of a new range of high performance trihydrate flocculants.

This new range of products is the result of a comprehensive development program. The aim of this work was to maintain all the separate, desirable features of conventional trihydrate flocculants but specifically deliver greater capture of solids in the flocculation process.

Initial development of the new flocculant range monitored the flocculation performance of trihydrate slurries using Focused Beam Reflectance Measurement (FBRM). This technique allows for *in-situ* measurement of particle (floccule) size by insertion of a focused laser source (with detector) into the slurry. Back scattered light or the duration of the reflection of the beam is detected and expressed as a chord length of the particle since the amount of reflectance is related to the size of the particle. The unflocculated particles have short chord lengths and as flocculation occurs the chord lengths increase and the number of discrete particles decreases.

An example of the results obtained in flocculated and unflocculated samples is shown in figure 2. As the material is flocculated the number of particles decreases and the size of particles increases. This technique was used as part of the screening process to develop and identify the most effective new products. A relative assessment of flocculation performance can be readily determined by addition of individual product samples into stirred slurry and monitoring the FBRM data over a relatively short length of time. As a screening technique for assessment of a broad range of chemistries, this was found to be most effective.

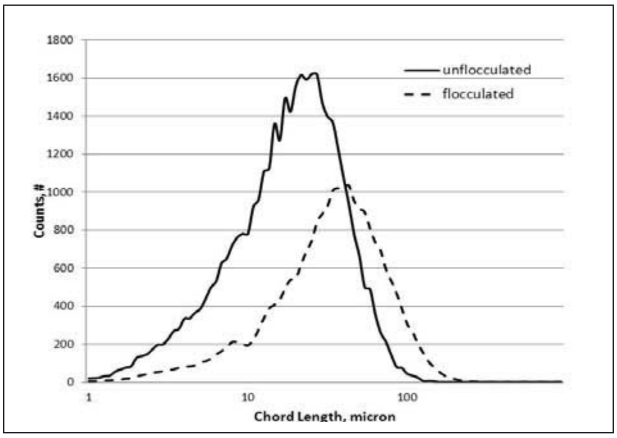

Figure 2. FBRM chord length and particle count data from flocculated and unflocculated slurry samples containing trihydrate

Comprehensive laboratory work by Nalcoa staff has now been completed comparing a new range of patent pending products to conventional trihydrate flocculants. Together with recently completed plant trials, the data have established that the new generation of products provide enhanced activity that allows operators to further optimize plant performance.

4.1 Solids Capture

Relative performance of the new flocculant versus conventional trihydrate flocculant and undosed slurry is shown in figure 3. This data was generated from laboratory work (cylinder tests) using plant slurries. While the data is only relative (lab data only) it is important to note that the reduction in overflow solids resulting from application of the new flocculant is highly significant.

In addition, further work has identified that, like conventional products, the new flocculants have a dose response which initially results in lower overflow solids with increasing dose. Although, this response eventually plateaux to a level where additional dosing of material results in little or no further benefit, use of the new product results in achievement of a much lower solids level (better solids capture) suggesting that use of the new products can deliver overflow solids concentrations substantially lower than that achievable using conventional trihydrate flocculant at any dose.

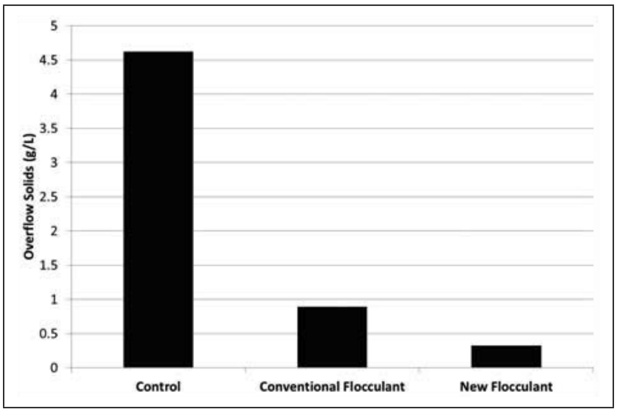

Figure 3 A plot of data from laboratory tests assessing the overflow solids from slurry treated with new flocculant and conventional trihydrate flocculant (same dose) versus undosed slurry. Overflow in g/L is indicative only.

4.2 Settling Rate

Figure 4 shows the settling rate data from cylinder tests using conventional and new flocculants. Again, the new flocculants clearly show superior settling rate on a dose for dose basis.

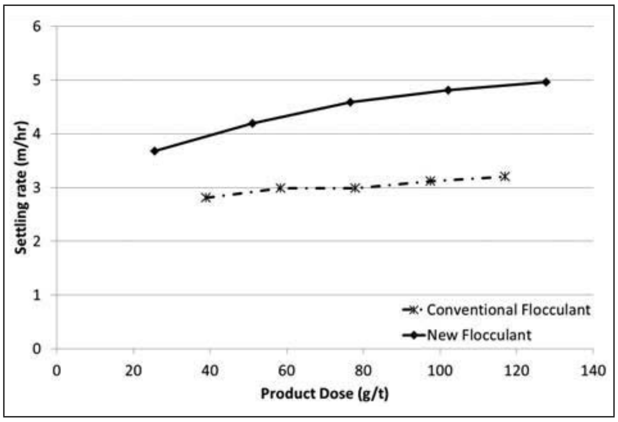

Figure 4. Dose versus settling rate curves from laboratory cylinder tests using slurry treated with conventional and new trihydrate flocculants.

4.3 Underflow Rheology

The impact of the new flocculants on underflow properties was again assessed through a simple Imhoff cone test. Using two slurries, one dosed with conventional trihydrate flocculant and the other dosed with the new trihydrate flocculant at the same dose, a test as described above was completed in duplicate. Results are shown in table 3 and clearly demonstrate the substantial impact of the new flocculants on underflow rheology, indicating substantial improvement in the flow properties of trihydrate treated with the new flocculant.

Table 3. Flow characteristics of slurry treated with conventional trihydrate flocculant and the same slurry flocculated with new trihydrate flocculant. Flow characteristics as measured by the time taken to flow through an Imhoff cone. Average of duplicate results are shown. Settling time = 20 minutes. Dose rate ~ 80g/T.

Treatment	Conventional Flocculant	New Trihydrate Flocculant
Delivery Time (secs)	142	12

5. Potential for Operational Enhancement

Preliminary plant trials of the new flocculants have now been completed and results concur with laboratory assessments. Compared to conventional flocculants, the new product used in each case resulted in a substantial reduction in vessel overflow solids over a range of operating conditions. While settling rate and underflow rheological properties are more difficult to assess under plant conditions, evidence of enhanced performance has been observed. Importantly, as expected, no detrimental impacts of the use of the new flocculant were observed during these plant trials.

The ongoing use of the new range of products can deliver substantial savings and benefits to plant operators. By effectively reducing the losses of trihydrate to spent liquor through the reduction of classifier overflow solids, a direct production benefit is afforded. Interestingly, the benefits available from use of the new products are not achievable using conventional products. In particular, the reduction in overflow solids afforded by the use of the new products cannot be achieved using conventional trihydrate flocculants, regardless of the dosage.

While the enhanced capture of solids is a simple and easily discernable benefit that is available to operators through the use of the new flocculant range, the enhanced performance of these products results in the potential for other, less direct, but nonetheless substantial benefits.

In particular, the improved rheological properties of the settled solids may allow operators to target higher underflow densities in final classifiers while maintaining the "flowability" of the resultant high solids slurry. This can not only improve throughput but may also result in less spent liquor reporting with the slurry. It may also obviate the need for the injection of spent liquor into underflow streams – often done by operators to ensure flow characteristics – and thereby result in further efficiencies. While subtle, and often dependent on downstream processing steps that the fine seed may undergo, this reduction in spent liquor can be a significant advantage in both productivity and efficiency.

Additionally, improved flowability of underflow solids may reduce unscheduled outages and maintenance time associated with unplanned "bogging" of settling vessels.

It is also possible that the impact of these new flocculants on the rheology of trihydrate slurries may be utilized in improving the efficiency of hydrocyclone separation. While as yet unproven, the marked impact on slurry flow characteristics implies that application into cyclone feed slurries would result in differentiation of particle size cut. Additionally, with such improvements in flow properties, those plants that filter seed may observe some benefits in throughput and/or filter capacity through the use of the new flocculants.

Plant trial data also indicated a more steady operation of vessels dosed with the new flocculant, perhaps as a result of the higher settling rate. The reduction in variance in the overflow allows for more certainty in operation and potentially more efficient downstream processes.

6. Conclusions

Trihydrate flocculants can be applied to classification systems to assist in the capture of fine material that would otherwise be recycled within the process with the spent liquor through digestion. Such losses directly impact on production in Bayer plants and as a result, need to be minimized to enhance process efficiency.

Trihydrate flocculants have been extensively used throughout the industry to deliver benefits, not only in terms of solids capture but also in enhanced settling rate and underflow slurry rheological characteristics.

Further development by Nalco in this area has now resulted in a new range of trihydrate flocculants. These new products show enhanced activity beyond conventional trihydrate flocculants and consequently allow process operators to further enhance both the productivity and efficiency of their circuits.

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