Light Metals 2014
Edited by: John Grandfield
TMS (The Minerals, Metals & Materials Society), 2014

New High-Performance Crystal Growth Modifiers to Improve Alumina Trihydrate Quality and Yield

Ryan Chester[1], John Kildea[1] and Everett Phillips[2]
1 Nalco Australia Pty Ltd, 2 Richardson St, Kwinana Western Australia
2 Nalco, an Ecolab company, 1601 West Diehl Road, Naperville, Illinois, USA

Keywords: Bayer Liquor, Precipitation, Crystallization, Alumina, Trihydrate, Crystal Growth Modifier

Abstract

Nalco first introduced its Crystal Growth Modifiers (CGM) technology to the alumina processing industry more than 25 years ago. Since then the use of CGM to enhance agglomeration, improve productivity and increase particle toughness has now been well established, with many plants using CGM dosage as a critical tool for process control in precipitation. Nalco continues to better understand the mechanisms and activity of CGMs, resulting in the development of a range of new CGM products with improved performance and with specific properties, for example, enhanced or reduced oxalate impact, or improved antifoam capacity. When compared to 'more conventional' CGMs, these new formulations are expected to 1) allow further increases in liquor productivity by improving agglomeration and coarsening, and 2) provide comparable or improved activity while adding less organics into the process. Together with existing Nalco CGM technologies, these new CGMs provide a broader selection of products to meet the wide and ever-changing producer needs.

Introduction

Crystal Growth Modifiers (CGMs) were first developed and implemented in Bayer process plants in the 1980s [1]. Since their initial deployment more than 25 years ago, the application and use of CGM technology has increased to the point where today more than 30 plants across the globe currently use a crystal growth modifier program.

The primary purpose of CGM addition is to enhance the particle size distribution of precipitated alumina trihydrate. Addition of CGM to the first stages of the precipitation process results in enhanced agglomeration, which ultimately leads to a reduction of fine particles and a shift to a larger particle size distribution of precipitated trihydrate.

This fundamental property of particle size improvement is common to all CGMs and forms the major, underlying reason why plants use a CGM within their process.

Many plants use CGM as a "remedial" measure to improve particle sizing when process conditions result in less than desirable quantities of fine particles. CGM can be added to help correct the situation and return the process to appropriate conditions more quickly than would otherwise be the case.

More commonly, CGM is used to improve productivity of plant precipitation circuits. Ensuring appropriate control of particle sizing through the use of CGM allows plants to manipulate other process parameters such as higher seed rate, lower fill temperature and increased liquor concentration to optimize yield. In the absence of CGM, changes in these process control parameters would typically result in a detrimental effect on particle sizing.

As a consequence, in the absence of CGM, plants can either choose operating conditions that improve yield or choose conditions that adequately control sizing. However, control of both yield and sizing requires some compromise on both counts. With addition of CGM, sizing control is independently determined by the appropriate dosage of CGM. This then enables changes in process conditions to be focused on enhancing liquor productivity or yield.

Fundamentally however, the primary function of size control of precipitated trihydrate is the key driver for both methods of CGM usage. As a consequence, the application of CGM under plant conditions is typically the same, regardless of the pattern of use. While some minor variation in performance has been observed when CGM is applied in different ways [2], the key to efficient application of a CGM is to ensure it is well mixed with the slurry in the first precipitation tanks. A convenient application point for many plants is often the suction side of a pregnant liquor pump. Alternatively, addition of CGM to seed slurry may be employed if this is logistically more favourable or practical.

In addition to application methods, a number of detailed studies have been undertaken to determine the precise mechanism of how CGMs function to enhance particle sizing [3]. These studies have determined that the mechanism is predominantly associated with enhancement of agglomeration as well as secondary nucleation. CGMs absorb onto the surface and change the surface energy of the alumina trihydrate seed. This induces stronger adhesive forces between the fine seed particles as well as small fractured particles and/or nuclei during secondary nucleation. Thus, under process conditions where trihydrate particles are colliding and continuously breaking off seed crystals, the CGM helps to keep particles together longer to allow cementation to occur. This results in increased coarsening and control of secondary nucleation. While a range of CGM products are available, the established mechanisms are considered to be common to all products.

While the main focus of CGM use has typically been focused on the property of trihydrate particle size enhancement, there are a number of other effects of CGM usage that are known, demonstrated and documented. A number of these "side effects" are highly beneficial to the process. Published work by users of CGM has identified a number of these impacts. For instance, application of CGM has been separately associated with a reduction in occluded soda [4] and with an increase in particle toughness [5], both highly desirable outcomes in addition to the enhancement in trihydrate sizing.

Additionally, a number of CGM formulations are known to have an impact on oxalate in the process; both in terms of stability of oxalate in liquor, as well as the morphology of sodium oxalate crystals that are precipitated in the presence of CGM [6]. Depending on the nature of the process for a given plant, these properties can in some cases be desirable and can be used to further enhance process efficiency. However, under different processing conditions these properties can be undesirable. For instance, in plants that employ alternative oxalate control strategies such as side stream crystallization, use of a CGM that stabilizes oxalate in solution should be avoided.

In general terms, all CGM products are effective at enhancing particle sizing, however there may be variation in relative coarsening performance of one CGM product versus another based on both the formulations themselves and the liquor chemistry in which they are applied. It has been noted that the most effective product in one refinery may not necessarily be the optimum product in a different liquor and seed regime. Liquor chemistry appears to be particularly significant in terms of the impact of CGM on foam formation. A given CGM product when applied to one liquor can act as an antifoam and reduce foam generation on precipitation tanks. However, the same product applied in a different plant liquor may have an undesirable impact of generating unacceptable levels of foam. The presence of excessive foam on precipitation and classification tanks can interfere with classification, restrict temperature control by acting as an insulating “blanket” and can also be a safety hazard if the foam becomes airborne from the tops of the open vessels.

Since the original implementation of CGMs in the Bayer process more than 25 years ago, there has been a continuing advancement of CGM technology [2,3,6-9]. In addition to identifying and documenting both the mechanisms and the range of possible process impacts, a variety of formulations and products have been developed. Based upon the needs of a particular refinery, different formulations are designed to enhance those properties that may be desirable, while minimizing the impacts that are unwanted.

Through this development, the broad range of process conditions and operating methods can be matched by a range of products designed to address the criteria of plant operators. When selecting a CGM for use in a refinery, identification of the required and desired outcomes in terms of size control as well as the other potential properties such as soda, particle toughness, foam impacts, oxalate stability and oxalate morphology can be matched with the appropriate product for the conditions.

More recently, plant operators have identified the desire to reduce the input of organic materials to process liquors. Organic materials are known to be detrimental to process operations in a number of ways and any reduction in the input of organic material is therefore desirable. Traditionally, CGMs have been organic-based products and, while only a relatively small source of input to the process, they nonetheless add to the overall loading of carbon-based material in the liquor. Nalco has now developed a range of emulsion-based CGM formulations which substantially reduce the organic loading within the formulations while maintaining excellent trihydrate coarsening properties. These products provide a ready alternative to conventional CGMs for those plants where organic input needs to be reduced.

In this paper, the performance of these new, emulsion-based products is presented together with assessment of a low-foaming alternative formulation specifically designed for liquor chemistry where conventional CGM technology results in excess foam formation. Together with the existing, conventional range of CGM products these technologies make up the new CGMax^{TM} range of CGM products. This new, enhanced range is designed to address the full array of desired outcomes that Bayer process operators have when considering CGM use.

Experimental

Two newly developed formulations denoted CGMax (A) and CGMax (B) were used in laboratory-based tests. CGMax (A) is an emulsion-based formulation while CGMax (B) was developed as a low-foaming, non-emulsion-based product. Existing conventional, commercially available CGM formulations, denoted here as Conventional CGM 1 and Conventional CGM 2, were used for comparison in both precipitation bottle tests and foam assessment tests.

Precipitation Test Method:

Precipitation bottle tests (batch tests) were conducted to assess agglomeration performance. New CGMax formulations were typically compared with equivalent doses of the most appropriate, commercially available, conventional CGM product(s). Approximate first tank temperatures of the precipitation circuit from which plant liquors were sourced were typically used, together with estimated first tank holding times; thus test times varied from 3-6 hours. This experimental regime allowed for comparison of coarsening behaviour for the different treatments.

Fresh plant LTP liquor collected on the day of the test was filtered prior to use. Liquor samples were added to Nalgene® bottles, to which appropriate doses of CGM were added. Untreated bottles were also included for baseline comparison. All bottles were placed in a temperature-controlled rotating water bath and allowed to equilibrate at the desired test temperature. A standard, commercially available, DF225 fine seed sample (equivalent to historical C31 seed) was added at the desired seed charge to each bottle after the equilibration time. This marked the start time for the precipitation test.

After the appropriate time period the bottles were removed from the bath and sodium gluconate added to quench precipitation. The solid alumina trihydrate was collected by filtration, washed with hot deionized water and dried in an oven (~105°C) overnight. Particle sizing on individual samples was conducted on a laser-based particle sizing instrument typical of those routinely used for trihydrate particle size analysis. Particle sizing data is listed as percentage of the particles above or below (+/-) the listed particle size (e.g. % + 45µm).

While a broad range of particle size fractions were measured for individual samples, typically only key distribution parameters (% +45µm, and % -20µm) are reported. Unless otherwise stated, un-dosed control samples were completed in triplicate while dosed treatments were run in duplicate. Single particle size analysis was completed on each sample and average data of treatments are reported.

Foam Assessment Test Method:

Plant spent liquor samples were added to bottles, to which appropriate doses of CGM (typically 500ppm) were added. Untreated bottles were also included for baseline comparison. All bottles were placed in a temperature-controlled rotating water bath and allowed to equilibrate at test temperature. Seed samples were added to each bottle and the resulting slurries returned to the bath for further temperature equilibration. Samples were then removed from the bath and shaken vigorously to promote aeration and the formation of foam. Bottles were then placed on the bench and both the amount of foam generated and the stability of the foam was recorded by measurement of foam height above the liquor over a 5-minute period. Samples were also photographed after 5 minutes.

Note that in both precipitation tests and foam assessment tests dose rates of additives are typically well above typical usage rates for plant operations. These high doses are employed to enable differences in the performance of individual formulations to be discernible with appropriate significance.

Results

Precipitation Tests

Precipitation bottle tests were conducted to assess the coarsening performance of CGMax (A) compared to both an undosed control sample and a sample dosed with the same concentrations of a conventional CGM (CGM 2). The relative increase in percent of particles greater than 45μm (% +45μm) is shown in Figure 1. The % -20μm data is presented in the same way in Figure 2.

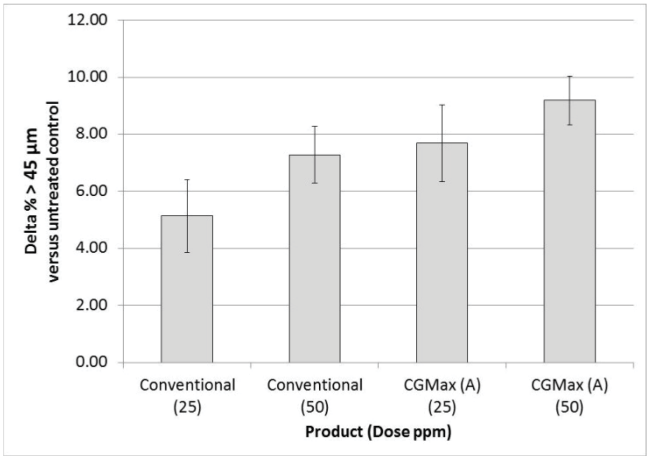

Figure 1. Results of a precipitation bottle test comparing the performance of conventional CGM 2 to the emulsion formula (CGMax (A)) at two doses. Sizing data is presented as the change in % +45μm relative to an undosed control sample. Error bars indicate standard deviation of duplicate samples.

Compared with the existing, conventional type CGM product, the new emulsion-based material is clearly much more effective as a coarsening agent. Typically, emulsion CGMax products have been found to be as effective as conventional CGM formulations and in many cases, as shown here, are much more effective.

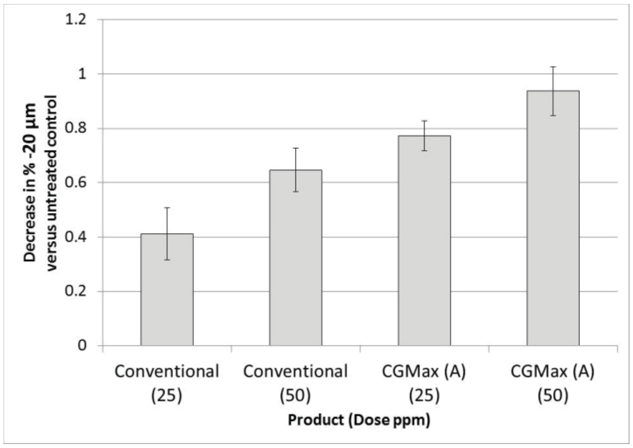

Figure 2. Sizing data from samples subjected to a precipitation bottle test presented as the decrease in % -20μm particles compared to an undosed control sample. Error bars indicate standard deviation of duplicate samples.

Foam Assessment Tests

In some particular liquors and when applied at very high doses (typically well above standard plant dose conditions) some CGM formulations may result in excessive foam formation. This property is shown in Figure 3 where a liquor sample was dosed with 500ppm of conventional product (denoted here as conventional CGM 1) which is known to promote foam in this particular liquor.

Contrast the amount of foam generated which remains on the surface with that found in the undosed control sample where no CGM was added. Addition of CGMax (B), at the same, high dose as the conventional CGM, results in much less foam formation. A second conventional CGM (Conventional CGM 2) also generates a low amount of foam.

Figure 3. Foam formation 5 minutes after agitation of slurries Left to right: Undosed slurry (no CGM treatment), CGMax (B), Conventional CGM 1, Conventional CGM 2.

Development and stability of the generated foam over time is shown in Table 1 where the foam height (mm) for each sample over the assessment period is given.

Table 1. Foam heights (mm) measure over time in the foam assessment test.

Time (min.)	Undosed Control	CGMax (B)	Conventional CGM 1	Conventional CGM 2
1	5	3	15	4
2	3	2	14	3
3	1	1	13	2
5	0	1	13	1

The relative performance of these products in terms of coarsening (versus an untreated control sample) is shown in the results of a precipitation bottle test plotted in Figure 4. As is typical, all three CGM products are effective in coarsening the trihydrate. Note however, that again the CGMax sample is most effective in coarsening the trihydrate in this liquor.

Comparison of the effectiveness of the conventional CGM products 1 and 2, indicates that the most effective coarsening agent is Conventional CGM 1. However, Figure 3 clearly shows the unwanted impact of foam generation from this material when applied to this particular liquor chemistry. The use of the CGMax (B) formulation, however, results in both appropriate foam control (Figure 3) together with the most effective coarsening (Figure 4).

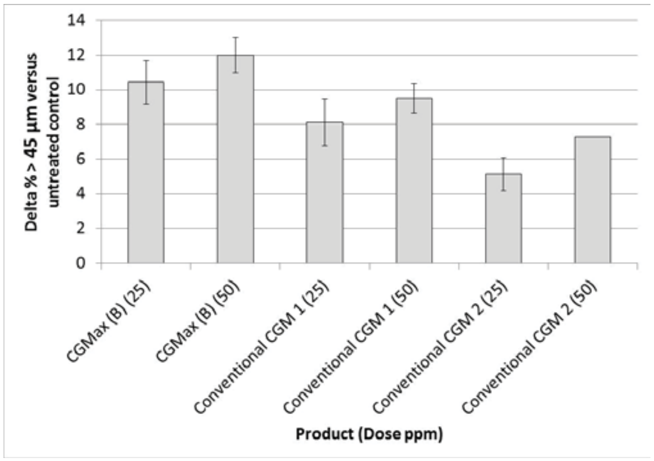

Figure 4. Results of a precipitation bottle test comparing the performance of CGM formulations used in the foam assessment test. Sizing data is presented as the change in % +45µm relative to an undosed control sample. Error bars indicate standard deviation of duplicate samples.

Discussion

While the use of CGMs across the alumina industry has now become widespread, in the time since their first introduction to the industry, development and improvement in product efficacy has continued. It has been recognized that, while in general terms, all CGM formulations are effective, the broad range of liquor chemistries presented across the different plants throughout the globe require a number of different formulation types to optimize the coarsening impact on trihydrate. Coupled with the subtle optimization of coarsening are the different requirements of plant operators in terms of the other impacts, both desirable and undesirable, which may result from implementation and use of CGM. Increasingly plants are seeking to enhance the properties that assist their operation, while minimizing any effects which may have a detrimental impact on plant efficiency.

The development of effective formulations that reduce the input of organic material to the process has now been added to the range of CGM products available. The new emulsion formulations can potentially reduce the organics input by more than 50%, while the coarsening impact is maintained or even substantially improved compared to conventional CGMs.

In addition, for those liquors where use of conventional CGM formulations have a propensity to generate unwanted foam, new CGMax products are now available which can be used without this undesirable side effect. This issue has only been observed in a small number of refineries and appears to be an interaction of the particular liquor chemistry with specific CGM formulations. The development of alternative CGMax formulations which do not have such unfavorable interactions allows these refineries to take advantage of the benefits of CGM use which may have been previously unavailable to them.

Together with previously developed CGM products, these latest innovations provide a broad range of CGMax products with a variety of properties. Selection of the most effective product can now be based on both customer requirements as well as specific plant liquor chemistry. The properties and range of formulations can be categorized in general terms under a variety of headings as summarized in Table 2. While this table lists product types in distinct categories, clearly there is a spectrum of effects across the range of available products and combinations of effects, such as high coarsening performance with low organic input are possible.

Table 2. Summary of impacts and range of effects that can be addressed across the CGMax product range.

Low Oxalate Impact	High Coarsening Performance	Low Organic Input	Niche Applications
Effective coarsening performance with little or no downstream impact on oxalate	Very high coarsening performance to enhance trihydrate sizing	Emulsion-based products to reduce organic input to liquor	Low foam formation. Positive impact on oxalate morphology to make balls. Enhanced oxalate stability

Conclusion

Since the first deployment of Crystal Growth Modifiers in the Bayer process more than 25 years ago Nalco has embarked on a process of continuous improvement which has included both product development and a deeper understanding of mechanisms and potential downstream process impacts. This work has resulted in a range of CGM products which possess a variety of possible impacts in addition to the fundamental coarsening effect on trihydrate.

The latest step in this research has resulted in the development of additional formulations which enhance and broaden the range of CGM products now available. The inclusion of the new emulsion platform to the range, along with formulations with improved foam control, extends the choice of available properties. Together with the original CGM formulations, these new products constitute the full range of CGMax products.

This extended range now allows selection of the most effective and appropriate CGM products to specifically address the particular needs and desires of individual plant operators. Plants can now more effectively optimize both precipitation yield and particle sizing, while minimizing the potential for any undesirable downstream impacts. For plant operators, the broader CGMax range delivers greater flexibility in determining the most effective means to enhance and maintain plant productivity.

REFERENCES

1. W.J. Roe, D.O. Owen and J.A. Jankowski, "Crystal Growth Modifiers: Practical and Theoretical Considerations for the Bayer Process", *Proceedings of the First International Alumina Quality Workshop*, Gladstone, Australia, 1988.

2. R. Chester, J. Counter, J. Kildea and R. Plummer, "Increasing the Effectiveness and Selectivity of Crystal Growth Modifiers", *Proceedings of the 8th International Alumina Quality Workshop*, Darwin, Australia, 2008, 275

3. J.A. Counter, "Crystal Growth Modifying Reagents: Nucleation Control Additives or Agglomeration Aids", *Light Metals*, 2006, 131.

4. V. Esquerre, P. Clerin and B. Cristol, "Oxalate Removal by Occlusion in Hydrate", *Light Metals*, 2006, 65.

5. P.K. Narasimharaghavan, N.K. Kshatriya, S. Dasgupta, J.Ramaswami, "Study on the Precipitation Kinetics for Improving the Quality of Alumina with regard to fines and attrition properties", *Light Metals*, 2010, 193.

6. J. Liu, K. O'Brien, D. Kouznetsov and J. Counter, "Performance of New Crystal Growth Modifiers in the Bayer Process", *Light Metals*, 2007, 139.

7. J. Counter, J. Malito, J. Addai-Mensah and J. Li, "The Influence of Crystal Growth Modifying Reagents on Secondary Nucleation of Bayer Aluminium Hydroxide", P*roceedings of the 7th International Alumina Quality Workshop*, 2005, 97.

8. J. Liu, J. Counter, D. Kouznetsov, K. O'Brien and J. Kildea, "Application of Crystal Growth Modifiers in the Bayer Process", *Proceedings of 24th International Minerals Processing Congress*, Beijing, 2008, 3275.

9. D. Kouznetsov, J. Liu, K. O'Brien, J. Counter and J. Kildea, "New Crystal Growth Modifiers for Bayer Process", *Light Metals*, 2008, 226.