INCREASING THE EFFECTIVENESS AND SELECTIVITY OF CRYSTAL GROWTH MODIFIERS

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Abstract

Crystal growth modifiers (CGMs) are used extensively in Bayer plants to assist with particle size control within the precipitation circuit. In developing a range of more effective, second-generation CGMs, the primary aim has been to further enhance the coarsening potential of these products. Concurrent investigation of the mechanisms by which they function has also been part of the development and this has provided added insight into application optimization and provided direction for continued development. The result is a range of new Nalco products that are significantly more effective coarsening agents that cater more effectively to the particular requirements of individual plants.

Laboratory data presented here examines the coarsening effectiveness of these new chemistries. Additionally, data is presented assessing the optimum point of addition and the adsorption properties of these new products and this provides some insight into their mechanistic behaviour.

1. Introduction

Crystallisation of alumina trihydrate from supersaturated caustic aluminate liquors is the rate-determining step in the conversion of Bauxite ore into the final product of alumina, in the Bayer process. The majority of Bayer plants around the world have attempted to optimise this relatively slow process through sophisticated engineering designs. However there are a number of product quality parameters that restrict the full optimisation of any circuit.

Crystal growth modifiers (CGMs), developed by Nalco and widely used over a number of years, have added a powerful, independent option or "control lever" to Bayer circuits. CGM additives act as surface-active agents, which adhere to the surface of alumina trihydrate and induce a strong adhesive interaction force between particles and nuclei. This action consequently leads to effective trihydrate agglomeration and coarsening control, therefore making it possible for Bayer plants to further maximise product yield beyond their normal size control parameters.

Previous papers detailing the effectiveness of CGMs (Roe, *et al.*, 1988) and describing the mechanisms of CGMs (Counter *et al.*, 2005, Counter, 2006) have focused on these chemistries and their ability to coarsen particles. Further, the effectiveness of CGM at reducing occluded soda has been demonstrated (Esquerre, *et al.*, 2006) and more recently, emphasis has been placed on the effect of CGMs on the stability of oxalate and the morphology of oxalate crystals (Liu, *et al.*, 2007).

It is well known throughout the industry that Nalco's first generation CGM products work well with respect to coarsening. Therefore, these first generation products have served as a baseline from which improvement in coarsening performance was targeted for development. Previous publications (Kouznetsov, *et al.*, 2008) have detailed some initial results of this work.

Used in conjunction with further engineering and/or parameter optimisation, second-generation products have the potential to be significantly more productive than the original CGM family of chemistries. Results of testing are presented here for a variety of these new generation products. These tests include optimum point of addition and assessment of adsorption onto the seed surface. Results are discussed in terms of the mechanism of action and additional utilisation to enable enhanced process control.

2. Experimental

Precipitation Tests: General Conditions

Precipitation bottle tests (batch tests) were conducted for all precipitation experiments. Second generation CGM formulations were typically compared with equivalent doses of the most appropriate, commercially available, first generation CGM products. Un-dosed control samples were also included for comparison. For the batch tests, approximate first tank temperatures of the precipitation circuit from which plant liquors were sourced were typically used, together with estimated first tank holding times. Test times varied from 3-6 hours. This experimental regime allowed for comparison of coarsening behaviour for the different treatments.

Synthetic liquor or 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 test temperature. Seed samples (either deliquored or water washed and dried plant fine seed or standard seed – Alcoa C31 grade) were added to each bottle after the equilibration time, this marked the start time for the test.

After the appropriate time period the bottles were removed from the bath and sodium gluconate added to quench precipitation. The solid aluminium trihydrate was collected by filtration, washed with hot deionised water and dried in an oven (105 °C) overnight. Particle sizing on individual samples was conducted on a range of Laser based particle sizing instruments 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).

Data analysis was based on laser sizing (volume percent) techniques. No attempt to calibrate differences between the various instruments has been made. As such, comparison within individual tests is valid, however, comparison of results between particular tests is inappropriate. 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, undosed control samples were completed in triplicate whilst dosed treatments were run in duplicate. Single particle size analysis was completed on each sample and average data of treatments are reported.

3. Results and Discussion

3.1 Effect of New CGM Products on Particle Sizing

Recent publications (Liu, *et al.*, 2007, Kouznetsov, *et al.*, 2008) have identified a range of new CGM products that can be used to further enhance alumina trihydrate particle sizing in Bayer plants. While coarsening potential is the primary criteria for development of the appropriate chemistry for new CGMs, secondary properties may also play some role in determining the most effective final product. As a result, products may also have "peripheral" properties such as enhanced oxalate stability, an effect on oxalate morphology, and on foam generation.

Once selected, the coarsening potential of an optimum formulation can be assessed across a range of doses. A typical dose response for a conventional CGM product and a second-generation product is shown in Figure 1. Both products are clearly very efficient coarsening agents, however the increased effectiveness of the new CGM product is obvious and substantial across the entire dose range.

Like other CGMs it has been noted that the new generation of CGMs typically display a dose response that increases significantly at lower doses before reaching a plateau, beyond which no further increase in coarsening is observed. The plateau effect, found for both types of product, is typical of surface-active agents and may well correspond to an effective saturation of the potential "active sites" on the trihydrate seed surface.

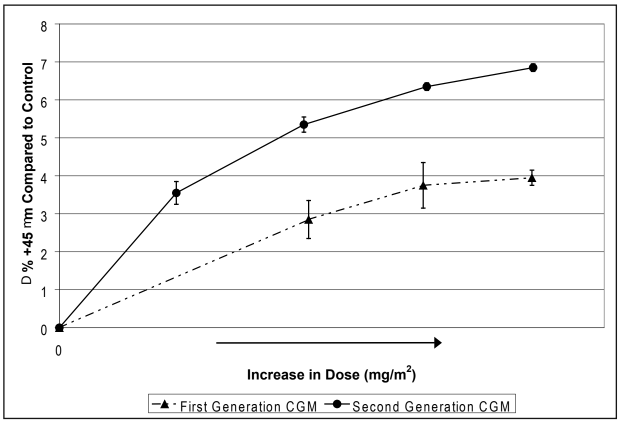

Figure 1. Dose response comparison (relative % +45μm) of a conventional CGM and a new, second-generation product.

Note that the dose is indicated as mg of CGM per square metre of seed surface area. This relates the amount of CGM to the surface area to which it is dosed. This measure is much more meaningful since the CGM is a surface-active product that attaches to the surface of the seed. A change in seed charge or significant change in seed surface area will significantly change the impact of the CGM, since it effectively changes the dose (mg/m^2) delivered.

In Figure 1 the x-axis is deliberately void of units since the measurement of surface area can vary significantly depending on the method of measurement. Commonly used laser sizing instruments typically report a "surface area". However, this number is a calculated figure based on a number of geometric assumptions and is significantly different to the surface area measured using other more sensitive methods commonly in use, such as BET. While the difference is important to note, the relative impact of the CGM is unchanged, regardless of surface area measurement. Plants can use whichever technique is commonly available to assess the appropriate dose of CGM. Typically plant operations use a dose about half way to the optimum point. This allows for a significant change in particle size distribution in the plant when changes in CGM dose are made.

The impact of CGM on the various size fractions typically used to assess particle size distribution can be seen in Figure 2. The percent change of each size fraction relative to an undosed control sample is plotted for precipitation tests using two CGM products, one conventional and the other a second generation product. Results are plotted as the delta (percentage change) in % < Xμm fraction where X equals the typical dimensions measured (e.g. change in % < 45μm). Because all fractions are reported in this case as "percent less than", a larger negative delta corresponds to a coarser product.

Clearly the second generation product is most effective at coarsening trihydrate across all particle size fractions. Initially, the large negative delta for the higher fractions (< 45μm, < 75μm, etc) can sometimes be interpreted as the CGM having most impact on the coarser particles. However, a reduction in the percentage of smaller sized particles results in a commensurate increase in the percentage of larger particles – a standard function of agglomeration and/or elimination and reduction of secondary nuclei as previously proposed (Counter, 2006). The impact of all CGMs has been consistently found to be a reduction of smaller particles – with commensurate changes in other fractions resulting. It should also be noted that this data is based on a volume distribution so smaller particles have little weight in the overall distribution. The impact of CGM on particle numbers more readily confirms the effect on small particles, and this has been verified in separate experiments.

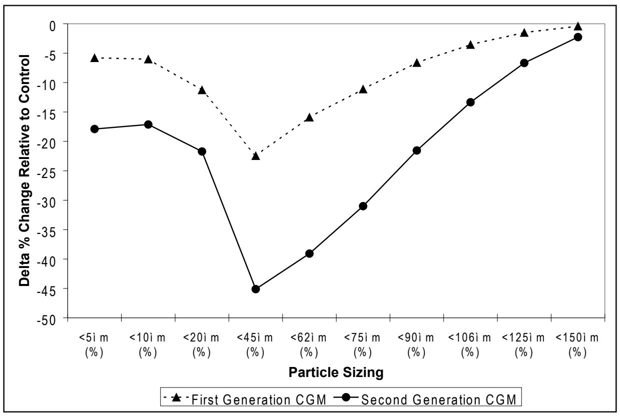

Figure 2. Percent change in size fraction relative to an undosed control.

2.2 Adsorption Measurements for New CGMs

Earlier studies (Counter, 2006) have shown that CGMs are surface-active materials that enhance the adhesive forces of two particles once they have collided. In terms of a plant precipitator, two treated trihydrate particles that collide are more likely to remain together, despite the fluid and particle shear forces present, which could potentially break them apart. The nature of the interaction of CGM's with the seed surface is therefore an important aspect of the mechanism.

An indirect measure of the adsorption of CGM onto seed surfaces was assessed in a series of "seed treatment" experiments. The general aspects of the experimental process are shown in Figure 3.

In these tests, seed (typically standard trihydrate seed (Alcoa C31)) was exposed to spent liquor containing CGM under a range of conditions. For all these experiments the liquor was subsequently removed via filtration and the resulting seed was used in standard precipitation tests. Comparison of the particle size distribution of seed treated in exactly the same manner, but in the absence of CGM, was the control for these experiments and gave an indirect indication of the adsorption efficiency of the CGM onto the seed.

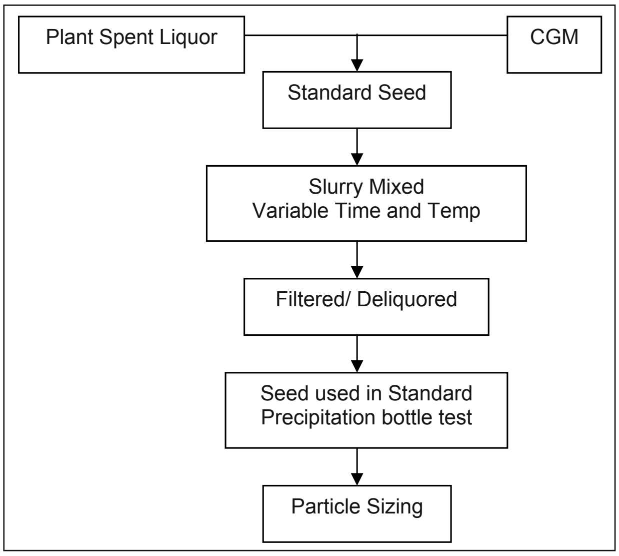

Figure 3. Experimental flow diagram of seed treatment tests.

For the first experimental example the control sample conditions were standard seed, mixed with spent liquor at 60°C for a total of 20 minutes before filtering. This treated seed was then used in duplicate samples in the subsequent precipitation bottle test. Particle sizing data (% +45μm data) from the precipitation test is shown in Figure 4. The notation CGM (20) and CGM (1) indicates that the CGM was added and mixed with the slurry for either the full 20 minutes (CGM (20)) or for only 1 minute (CGM (1)). However, in all cases, including the control samples, the seed was exposed to spent liquor for 20 minutes. The separate seed samples designated as control, CGM (1) and CGM (20) were individually filtered and used in independent precipitation bottle tests with duplicate samples for each treatment.

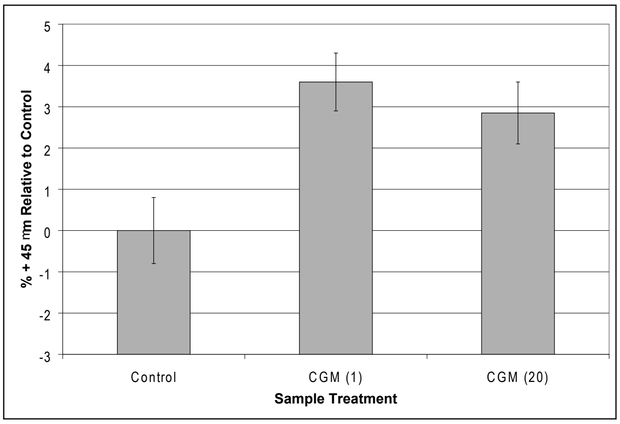

Figure 4. Relative % +45μm sizing data from precipitation bottle tests using seed pre-treated under various conditions as per Figure 3. All treatments had seed exposed to spent liquor for 20 minutes. Control = no CGM addition, CGM (1) had CGM added to spent liquor seed slurry after 19 minutes (1 minute exposure time), CGM (20) had CGM added to spent liquor at the start of the seed treatment (20 minute exposure time). Average of duplicates are shown together with standard deviation.

The data clearly indicates that, under such conditions, when seed is exposed to CGM even for a period of only 1 minute, significant coarsening of the particle size distribution occurs. Clearly this indicates that the adsorption of the CGM onto the seed surface is very rapid.

The extent and magnitude of the adsorption is further explored and graphically represented in Figure 5. In this test, seed and spent liquor were mixed for 45 minutes in all cases. In treatment A, the CGM was added to the spent liquor in the seed treatment step. For Treatment B the seed was exposed to CGM in the spent liquor during seed treatment (i.e. the same as treatment A) however, an additional dose of CGM was added to the "LTP" liquor in the precipitation step.

Despite some broad variation within the control sample, the treated samples both showed substantial coarsening of the resulting trihydrate product. The magnitude of the coarsening was approximately equivalent in both cases. If the adsorption of the CGM in treatment A were not comprehensive then it would be expected that additional dosing of CGM within the precipitation step might result in further particle coarsening. The fact that this is not the case indicates that exposure of CGM to the seed (treatment A) results in comprehensive, or at the very least, substantial adsorption.

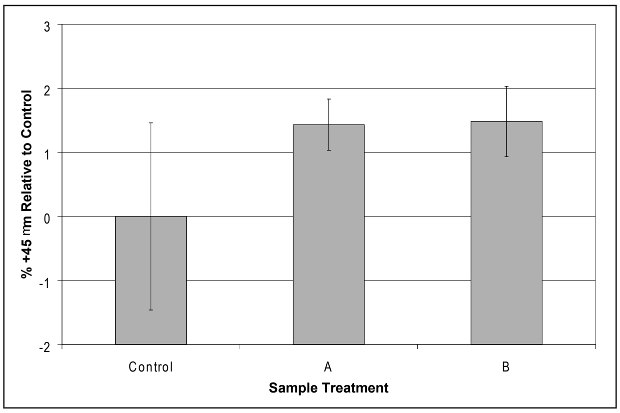

Figure 5. Relative % +45μm sizing data from precipitation bottle tests using seed pre-treated under various conditions as per Figure 3. All treatments had seed exposed to spent liquor for 45 minutes. Control = no CGM addition. Treatment A = CGM added to spent liquor seed slurry. Treatment B = CGM added to spent liquor seed slurry AND to precipitation bottle test liquor. Average of duplicates are shown together with standard deviation.

Together with the rapid adsorption indicated in Figure 4, this data indicates that CGM adsorption onto trihydrate seed is both rapid and extensive. The nature of this adsorption has now been assessed using this "indirect" technique for both conventional, first generation CGMs as well as a range of second generation products. In both cases, a rapid, extensive adsorption onto the seed surface has been observed. While the exact magnitude of the adsorption of CGM onto the seed cannot be measured using this technique, it is clearly significant and as such, can be used as a useful indicator of the overall mechanism.

Figure 6 shows relative % +45μm data for a similar test using plant fine seed. Plant fine seed was exposed to spent liquor for one minute, vacuum filtered to approximately 10% moisture and used in a precipitation test (control). This was compared to equivalent tests where CGM was added to either the spent liquor used in the seed treatment (Seed Addition) or the pregnant liquor used in the precipitation test (Liquor Addition). All seeds were then used in precipitation tests. Again, in both cases of CGM treatment, substantial particle coarsening is evident in the test. There appears to be a slight advantage in seed addition in this test but the magnitude is small and the result is not supported in later tests (see below). In general terms, it can be concluded that the coarsening resulting from CGM treatment is similar regardless of the method of application.

To further explore the efficiency of the adsorption of the CGM onto the seed an experiment was designed to assess the application of the product via a seed washing step. Figure 7 shows data from a test where plant fine seed was collected then added to hot deionised water (60°C, 300g/L) and mixed for one minute before being vacuum filtered. A further 500mL of hot deionized water was used to wash the filter cake, which was then vacuum dried to approximately 10% moisture before being collected and used in a precipitation test.

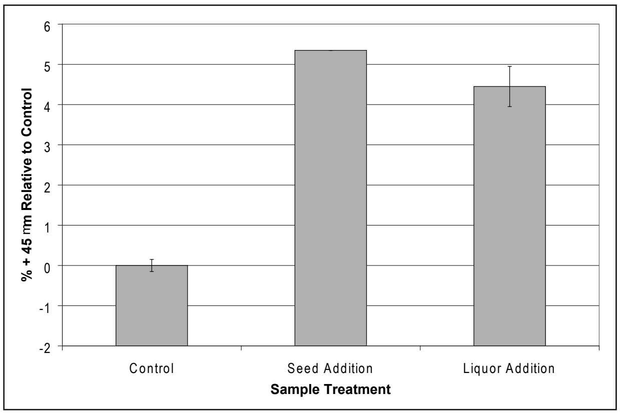

Figure 6. Relative % +45μm sizing data from precipitation bottle tests using seed pre-treated under various conditions. All treatments had seed exposed to spent liquor for 20 minutes. Control = no CGM addition. Seed Addition = CGM added to spent liquor seed slurry. Liquor Addition = CGM added to precipitation bottle test liquor. Average of duplicates are shown together with standard deviation.

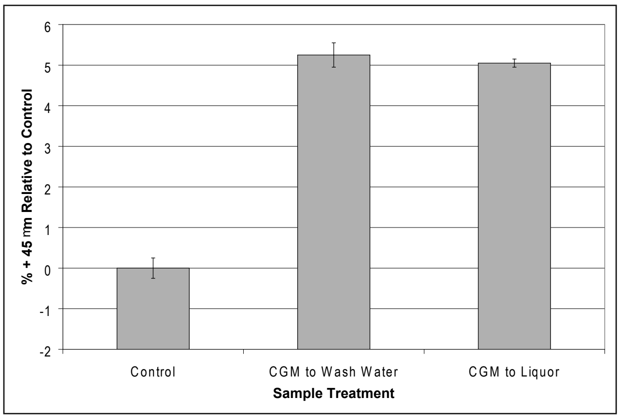

Figure 7. Relative % +45μm sizing data from precipitation bottle tests using seed pre-treated under various conditions. All treatments had seed washed in hot deionised water for 1 minute. Control = no CGM addition. CGM to Wash water = CGM added to water prior to seed addition. CGM to Liquor = CGM added to precipitation bottle test liquor. Average of duplicates are shown together with standard deviation.

The resulting average particle size distribution from these samples (control) was compared to those found in tests using seed that was prepared in the same way, with the addition of CGM to the first washing step of the seed (CGM to wash water) or CGM added to the pregnant liquor used in the bottle test (CGM to Liquor). Again, the results indicate a rapid and extensive (almost comprehensive) adsorption of the CGM onto the seed surface when added to the washing step. It is also evident that the second washing step does not appear to remove any appreciable amount of the CGM product. It should be noted that this particular experiment used a second generation product not currently in commercial use.

Together, the results of the series of experiments described above, indicates the rapid and seemingly comprehensive adsorption of CGM onto the seed as measured (albeit indirectly) by use of the seed in subsequent precipitation tests.

Assessment of the adsorption of the CGM can also be indirectly assessed in a similar way by considering the coarsening impact of liquor exposed to seed. Based on the above results, liquor containing CGM that is rapidly exposed to seed would be expected to have little or no CGM remaining in solution. Precipitation bottle tests using LTP liquor treated in such a way could be expected to show little coarsening. This is indeed the case as shown in Figure 8.

In Figure 8, Treatment (T1) used LTP liquor exposed to standard Alcoa C31 seed (100g/L) at 80^{o}C for 2 minutes. The seed was removed from the liquor by filtration, and the resulting filtrate liquor was then used as "LTP" liquor in a subsequent standard precipitation bottle test. The sizing data from this precipitation test is shown in Figure 8.

Treatment T2 underwent the same procedure as T1 but CGM was added to the liquor immediately prior to seed addition. Treatment T3 was the same treatment as T2 but an additional dose of CGM was added to the liquor after filtering and prior to the precipitation bottle test. As expected, there is no evidence of an effect from "residual" CGM in the liquor (T2) in the form of significant coarsening in the agglomeration bottle test. However, the effect of the CGM is observed when it is directly added to the precipitation test (T3).

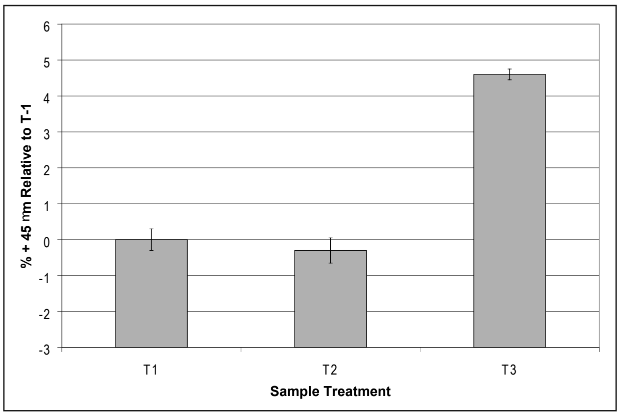

Figure 8. Relative % +45μm sizing data from precipitation bottle tests using LTP liquor exposed to various treatment regimes prior to use in standard precipitation bottle tests. Each liquor was exposed to standard seed for 2 minutes. T1 = no CGM addition. T2 = CGM added to liquor prior to exposure to seed. T3 = CGM added to liquor prior to and after exposure to seed. Average of duplicates are shown together with standard deviation.

It should be noted that, in this test, exposure of the highly supersaturated LTP liquor to a seed source may be expected to result in some precipitation. Analysis of the individual liquors prior to the precipitation bottle test (that is, after the exposure to seed and the filtration step) confirmed that all three samples had an equivalent A/C ratio (within experimental error.) The short exposure time (2 minutes) resulted in very little, if any precipitation from the liquor.

Most recently, experimental techniques have been in development to try and directly measure the concentration of CGM in synthetic liquor by UV-Vis spectroscopy (Li, 2008). While only preliminary data is available, to date this work appears to be consistent with the hypothesis of rapid and comprehensive adsorption of CGM onto seed.

2.3 Application of CGM

Practical application of CGM within plant operations is an important aspect of ensuring that appropriate coarsening of particles is optimized. Earlier, unpublished work by Nalco using first generation products (Counter and Malito, 2004) has indicated that addition of CGM to either the seed slurry line, or the LTP liquor stream, resulted in equivalent coarsening performance. This outcome corresponds with the data above that indicates a rapid and seemingly comprehensive adsorption of CGM onto seed surfaces across a variety of test conditions. Whether the mixing and adsorption occurs in the seed slurry line or in the first few minutes of residence time in the precipitation tank, the distribution of the CGM across the seed surface is rapid and extensive.

Assessment of performance of second generation CGMs under a variety of dosing regimes has also now been completed. Figure 9 shows relative sizing data (% -20μm) from a precipitation test comparing simulated addition of CGM to the seed slurry (S) or to the LTP liquor (L). In this test, seed slurry was prepared and added to LTP liquor at the start of the standard precipitation test. Unlike the results shown in Figure 6, this test indicates a very slight (and likely insignificant) benefit in dosing to the liquor rather than the seed slurry. Taken together the conclusion is that, like first generation CGMs, no significant difference in performance is observed between using the next generation CGMs in either method of application.

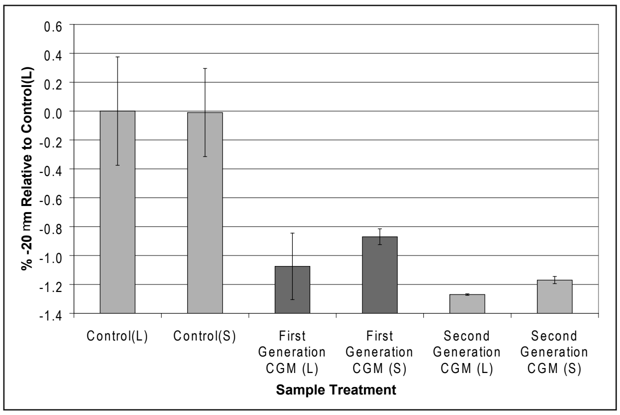

Figure 9. Relative % -20μm sizing data from precipitation bottle tests using seed slurry addition to LTP liquor. Different treatments were defined by addition of CGM to the liquor (L) or the seed slurry (S) prior to mixing of both components. Average of duplicates are shown together with standard deviation.

4. Conclusions

A range of new CGMs is currently being finalised for use within the Bayer process. This range of products could be used to significantly enhance the coarsening of trihydrate particles under precipitation conditions over and above the performance of existing, first generation CGMs. The performance of the new CGM products can vary significantly depending on the liquor in which they are used, however, appropriate chemistries can be employed to optimise performance across a range of desired properties.

The key property for all Crystal Growth Modifiers is the effect on trihydrate particle coarsening. The activity of the new, second generation products is clearly superior. The mechanism of action of the new CGMs appears to be similar in nature to that of the first generation products. Both types of product are surface-active agents that rapidly and seemingly comprehensively, adsorb onto trihydrate seed surfaces, where their function is to enhance the success of particle collisions by substantially increasing the adhesive forces between the two colliding particles. Like first generation products, the application point of the new CGM formulations does not impact performance, provided sufficient mixing and contact with the seed or liquor slurry is achieved.

Overall, the key to developing the most effective CGM for a given operation is to match the most effective coarsening agent with the most appropriate properties that are desired by the particular plant operation.

New CGMs currently being developed are clearly more effective as coarsening agents. However, despite the changes in both chemistry and performance versus the first generation products, the mechanism of action and the most effective application methods of these new products appear to be very similar.

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