

## **SOLVAY's CYQUEST® 170 Series: an Oil-Free and more Cost Effective Crystal Growth Modifier**

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### **Abstract**

Solvay has traditionally supplied Crystal Growth Modifiers (CGMs) to the alumina industry being CYQUEST® 120 Processing Aid one of its main products. Now, with the new CYQUEST® 170 series, Solvay offers a more robust and cost effective line of CGMs. The main features of these new CGMs include being an oil-free reagent, lower dosage required when compared to traditional CGMs, defoaming properties that vary across the product line and better dispersion into the substrate due to its addition in the form of an emulsion made in-situ. The performances of these products have been assessed in terms of particle size distribution (PSD), yield, defoaming level and dose reduction with various types of liquor and seed. This unique chemistry allows for the application of CYQUEST® 170 series without the use of organic carrier oil. When applied on the plant scale, a 77 % dosage reduction was measured compared to conventional CGMs, as well as a 24 % reduction of < 45 µm particles compared to the process without CGM. Additionally, the use of CYQUEST® 170 series CGMs allowed the plant to maintain a more stable process and with that to establish a better process control.

**Keywords:** Crystal Growth Modifiers (CGM), particle size distribution (PSD), oil-free, CYQUEST® 170 series.

### **1. Introduction**

Since 1897, the Bayer process has been used commercially for producing alumina from the caustic digested bauxite ores [1]. The crystallization of gibbsite from super saturated caustic aluminate solutions is the rate limiting step, taking up over half the residence time of the aluminum refinery [2]. The control of the particle size distribution (PSD), through the manipulation of solution conditions, is required to minimize the generation of fine particles. Due to the complexity of Bayer liquor, considerable research focusing on the mechanisms and kinetics of gibbsite precipitation conducted under industrially relevant conditions has improved product yield without sacrificing quality [1-10].

The precipitation of gibbsite does not take place under ideal conditions. While the digestion of bauxite ore in recycled Bayer liquor results in a solution that is supersaturated in aluminum, it also contains significant amounts of organic and inorganic impurities [3]. These impurities can interfere with the crystallization process [4]. The crystallization process is accelerated by the use of seed alumina trihydrate crystals. The seeded precipitation of gibbsite from caustic aluminate solutions is accomplished by a combination of three crystallization processes, secondary nucleation, agglomeration and ordered growth [5 - 9]. Secondary nucleation is the generation of new particles in the presence of seed material while agglomeration is the aggregation and cementation by growth of small particles. In the Bayer process, agglomeration and aggregation require a high aluminate supersaturation in the liquors. Ordered growth is the slow deposition of

new gibbsite on crystal faces so that it heals surface defects, resulting in a smoothing of surfaces [10, 11]. The three processes usually occur together during precipitation but the contribution of each process to the whole is dependent on precipitation conditions [8, 11].

The introduction of additives to inhibit nucleation and growth of crystalline materials is well established [3]. These CGMs can dramatically affect particle shape and size, inhibit nucleation and growth and may even increase the rate of crystallization [10]. The addition of CGMs to pregnant liquor is used to impose a deliberate modification of the product crystals. CGMs are known to enhance agglomeration by collecting and cementing smaller particles and can also influence secondary nucleation (generation of new particles on surfaces of existing particles) [11]. Improved PSD through the use of CGM can allow the user to use a lower fill temperature and higher seed charge. CGMs can also be used to affect the morphology of oxalate crystals that often co-precipitate in the hydrate precipitation circuit. Modifying crystal growth processes using additives is a well-established approach to solving problems in many processes.

Extensive efforts have been invested into finding chemical additives (e.g. CGMs) and methods to limit the factors negatively affecting particle size. Many of these solutions require significant amounts of ancillary oils or surfactants to aid in the dispersion of the CGM into the pregnant liquor. These additives do not provide a benefit to the plant, increase the impurity load in the liquor and may cause discoloration of the product hydrate, all of which is undesirable.

CYQUEST<sup>®</sup> 170 Series CGMs are surface active agents designed to improve agglomeration of hydrate particles and deliver a more consistent control of the product from precipitation. The CYQUEST<sup>®</sup> 170 Series CGMs also contain no ancillary diluents or surfactants that provide no benefit the Bayer process and as such, can deliver the same performance as conventional CGMs at a lower dose. Solvay CGMs also assist to stabilize dissolved sodium oxalate in the liquor, reducing the occasions of oxalate rain.

## 2. Experimental

CGM laboratory tests are conducted by mixing pregnant liquor, alumina trihydrate seed and the CGM. The slurry is held at a reduced temperature overnight in a rotisserie water bath to facilitate the precipitation of trihydrate. The yield of trihydrate is determined both by weighing the final solids, and by measuring the change in liquor composition resulting from the alumina trihydrate precipitation via A/C titration. The particle size distribution of the trihydrate is also measured. A CGM material is found to be effective to the extent that it produces a coarsening of the particle size distribution that would otherwise occur during precipitation.

### 2.1. Laboratory Procedure

Pregnant liquor or liquor to precipitate (LTP) is prepared by reconstituting plant spent liquor. Spent liquor is the term used to describe the liquor after the final classification stage before it is returned to digestion. A calculated amount of spent liquor is added to a suitable sized stainless steel Parr<sup>®</sup> vessel. To this vessel, additional components (e.g. hydrate ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ),  $\text{Na}_2\text{CO}_3$ , NaOH, and water) are added to a targeted liquor composition such that the final A/C =  $0.72 \pm 0.03$ . The mixture is digested at 140 °C for one hour and cooled to ~ 90 °C for use. The typical LTP liquor prepared is:

A (Aluminum hydroxide):  $165 \pm 5.0$  g/L (as  $\text{Al}_2\text{O}_3$ )  
 C (Total caustic):  $230 \pm 5.0$  g/L (as  $\text{Na}_2\text{CO}_3$ )  
 S (Total soda or alkali):  $320 \pm 5.0$  g/L (as  $\text{Na}_2\text{CO}_3$ )  
 A/C:  $0.72 \pm 0.03$   
 Chloride:  $8.70 \pm 0.02$  g/L (as NaCl)

Sulfate:  $9.03 \pm 0.02$  g/L (as  $\text{Na}_2\text{SO}_4$ )  
 Oxalate:  $1.98 \pm 0.02$  g/L (as  $\text{Na}_2\text{C}_2\text{O}_4$ )  
 Total Organic Carbon (TOC):  $11.2 \pm 0.05$  g/L

The seed for laboratory experiments was obtained from R.J. Marshall (Southfield MI, USA), DF225 (average particle size  $45.4 \mu\text{m}$ , 63 % <  $45 \mu\text{m}$ , 20 % <  $20 \mu\text{m}$ ) and added at 50 - 100 g/L seed charge. CYQUEST® 170 Series CGMs are prepared as fresh emulsions using a laboratory blender or a hand-held homogenizer in deionized water adjusted to a pH of 10 with dilute sodium hydroxide. In addition to the new CYQUEST® 170 Series CGMs, two commercially available products (commercial product A, commercial product B) are used for comparison. A dose range of 1 – 50 ppm was used.

In a typical experiment, 200 mL of LTP liquor ( $90 \text{ }^\circ\text{C}$ ) is added to 250 mL Nalgene® sample bottles. Using a microliter syringe, the CGM is dosed onto the cap of the sample bottle; the bottle is tightly sealed and vigorously shaken. The bottles were then transferred to a carousel water-bath set at  $50 \text{ }^\circ\text{C}$ . The samples are allowed to equilibrate to the desired temperature for 30 minutes and removed from the bath to add the appropriate amount of seed, shaken vigorously to disperse the seed and returned to the water bath. The samples are rotated at 15 rpm for 18 hrs. After the 18 hrs are completed, the bottles are removed one at a time and a sample is removed for analysis. To prevent further precipitation of the sample, a few drops of 40% sodium gluconate solution is added. The remaining slurry is immediately vacuum filtered and washed with hot deionized water and then dried at  $105 \text{ }^\circ\text{C}$  overnight. The PSD is determined on a Horiba LA 920 light scattering instrument. The yield was determined both by mass and from A/C measurements using Equation (1).

$$Y = \Delta(A/C) * C \quad (1)$$

Y = Yield (g/L)

A = Liquor alumina concentration (g/L, expressed as  $\text{Al}_2\text{O}_3$ )

C = Liquor caustic concentration (g/L, expressed as  $\text{Na}_2\text{CO}_3$ )

$\Delta(A/C)$  = Change in liquor A/C ratio

Foam properties are tested by mixing pregnant liquor, fine seed, and the product under agitation at  $70 \text{ }^\circ\text{C}$ . The slurry is maintained in suspension by use of a magnetic stirrer and air bubbles are introduced by means of a gas diffusion (sparger) device. The height, of the foam generated is recorded over time. Performance is measured by the rate of foam formation when air is dispersed through the substrate.

### 3. Results and Discussion

#### 3.1. CGM

A series of laboratory experiments were conducted for the initial evaluation of the CYQUEST® 170 Series CGMs using the previous procedure outlined. The results are shown in Figure 1 below:

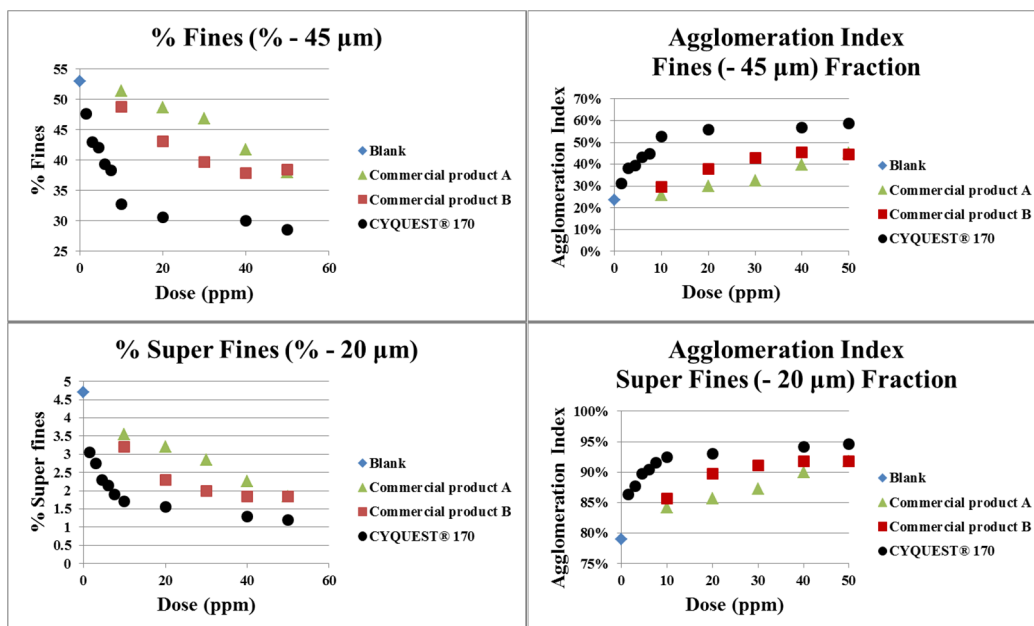


Figure 1. Dose response of CYQUEST® 170, Commercial product A, and Commercial product B in reconstituted plant liquor. (Time = 18 hrs, Temperature = 50 °C).

The results show a dramatic decrease in the amount of fines at a much lower dose for the new CYQUEST® 170 CGM resulting in a 70 - 80% reduction in dose.

### 3.2. Foam in Precipitation

Due to the organic content of Bayer liquor, it has a natural tendency to foam. The foaming of the liquor is aggravated by the mechanical processes throughout the Bayer process. Foaming is especially a problem after clarification, (after separation of the red mud) and into precipitation. Vessels that are filled with foam cannot be filled with the maximum amount of liquor, and therefore, cannot realize the maximum product yield and efficiency. Foam also poses a safety hazard in that the overflow of foam can expose workers to high levels of caustic, which can cause chemical burns. Foam is an insulator, and removing foam can improve heat transfer efficiency.

Because each individual Bayer process refinery has unique liquor chemistry, the foaming properties of the CYQUEST® 170 Series CGMs was evaluated in several plant liquors. Examples from two plant liquors are shown in Figure 2.

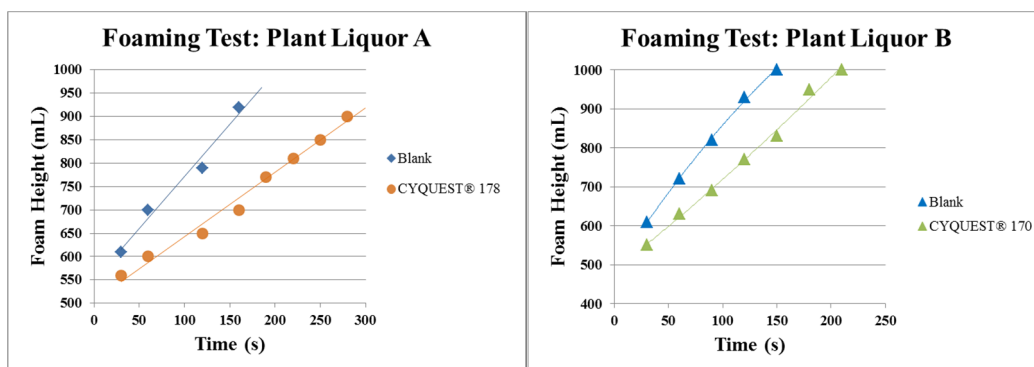
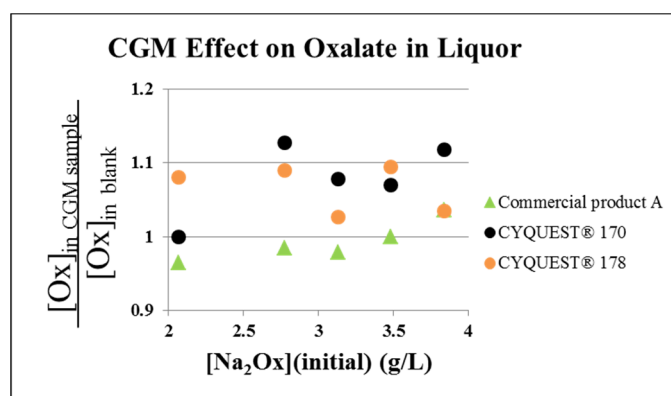


Figure 2. Foaming response of CYQUEST® 170 series CGMs in various plant liquors. Temperature = 70 °C, Seed charge = 100 g/L, CGM dose = 5 ppm.

The results demonstrate that the right CGM can be chosen for each plant to ensure the additive does not increase the normal rate of foam generation; CYQUEST® 178 for Plant A liquor and CYQUEST® 170 for Plant B liquor.

### 3.3. Oxalate

Oxalate is a small organic molecule that results from the breakdown of humates that enter the Bayer circuit primarily with the bauxite. There is no natural exit for oxalate and therefore the concentration increases until it reaches its solubility limit. As the concentration of oxalate increases, the conditions in the final stages of the precipitation circuit are ideal for oxalate precipitation to occur. Morphologically, sodium oxalate precipitates out as fine needles initially but can be influenced through the use of CGM to form dumbbell shaped crystals and eventually spheres or balls [12, 13]. Solid phase needle morphology is particularly detrimental to gibbsite precipitation. These needles act as seed for trihydrate precipitation causing an increase in fines generation, which leads to poor quality product, inefficient classification and insufficient agglomeration. Spherical morphologies are much more benign with respect to gibbsite precipitation and the detrimental effects are reduced or even eliminated. Therefore, it is important to know the effect any additive in the precipitation circuit will have on oxalate.



**Figure 3. Oxalate stabilization with various CGMs.**  
Temperature = 50 °C, Seed charge = 50 g/L, CGM dose = 4.5 ppm.

In Figure 3, the ratio plotted is the concentration of oxalate after precipitation in the CGM treated sample over the oxalate concentration in the blank sample. When this ratio is 1, there is no effect of the CGM on the oxalate concentration. When the ratio is > 1, oxalate is stabilized in the liquor, and when the ratio is < 1, oxalate is destabilized in the liquor. The results show that CYQUEST® 170 and CYQUEST® 178 stabilized the solution-phase oxalate, that is, there is more oxalate remaining in the liquor after precipitation with the use of the CGM than without.

The stabilization of oxalate in precipitation can be a benefit to producers who suffer from the negative effects of co-precipitation of oxalate in the circuit. Fine oxalate needles that normally precipitate and cause problems for the operators can be eliminated by this feature of increased stabilization. The effect can be reversed at high temperatures found in digestion.

## 4. Plant Application

CGMs are applied in different sections of the precipitation circuit depending on the type of benefit desired. To coarsen the hydrate via agglomeration enhancement, CGMs are applied to the agglomeration feed. To improve the growth and strengthening of the hydrate particles, CGMs are applied to the feed of the growth section. In both cases CGMs are added to the LTP (liquor to precipitation) before the seed tanks (fine and/or coarse seed) although the addition to

the top of the seed tank(s) is permissible when physical constraints are present. Additionally, CGMs are used to modify the morphology of the solid phase oxalate when co-precipitated with hydrate. The reagent can be added to the section of the precipitation circuit where solid phase oxalate precipitates to achieve morphological change.

Traditional CGMs are applied directly. However, the new CYQUEST® 170 Series is applied in the form of an oil-in-water emulsion made in-situ using any relatively clean process water (low content of Ca and Mg and no suspended solids) or cold condensate if available (at 50 °C or below).

The emulsion should be preferably prepared at concentrations 5 % or lower to ensure good physical stability and emulsion droplets  $\leq 30 \mu\text{m}$ . The emulsion is prepared by a dedicated emulsification unit where water and product are mixed at high shear rates by a high speed turbine pump. Optical micrographs of emulsions made with CYQUEST® 178 and condensate at 50 °C are shown in Figures 4 and 5 for concentrations of 5.0 % and 2.0 % respectively.

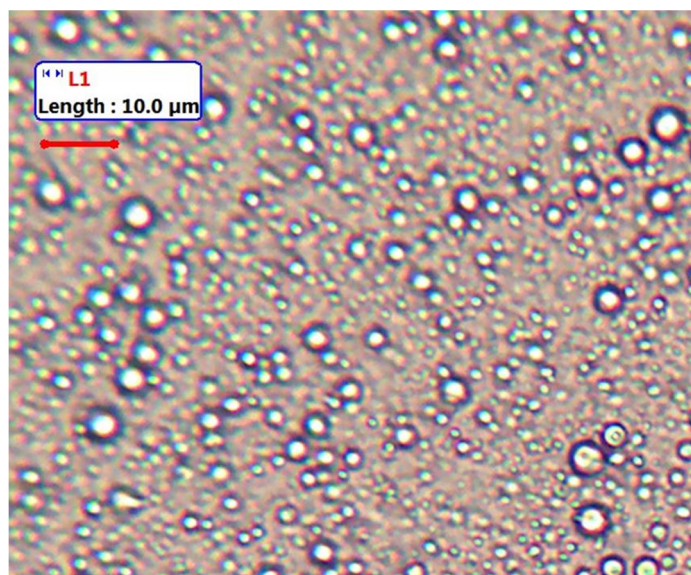


Figure 4. 400X micrograph of 5.0 % CYQUEST® 178 emulsion with condensate.

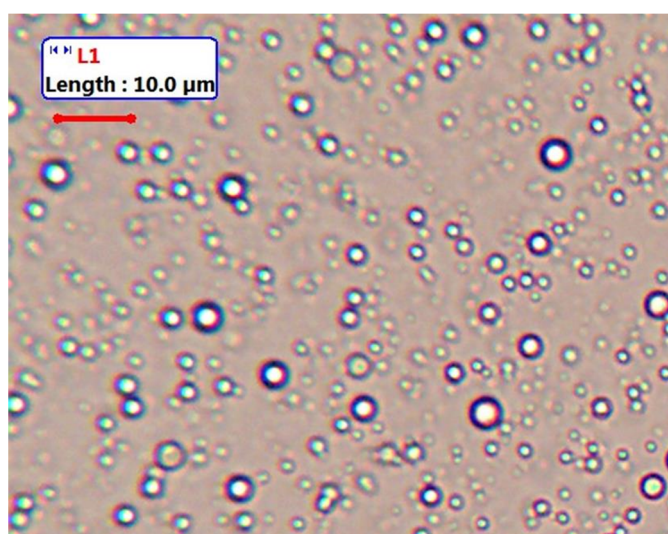


Figure 5. 400X micrograph of 2.0 % CYQUEST® 178 emulsion with condensate.

## 5. Plant Trial Application of CYQUEST® 178

A plant trial was conducted at a customer site where CYQUEST® 178 was applied to one of the precipitation lines. The trial lasted three months.

This customer already uses CYQUEST® 120 and the main objectives of the trial were:

1. Demonstrate the ability of CYQUEST® 178 to replace CYQUEST® 120.
2. Improve and maintain process stability mainly in terms of PSD.
3. Achieve at least 75% of dose reduction with respect to current dosage ranging between 20 ppm and 40 ppm, which will translate in significant cost savings.

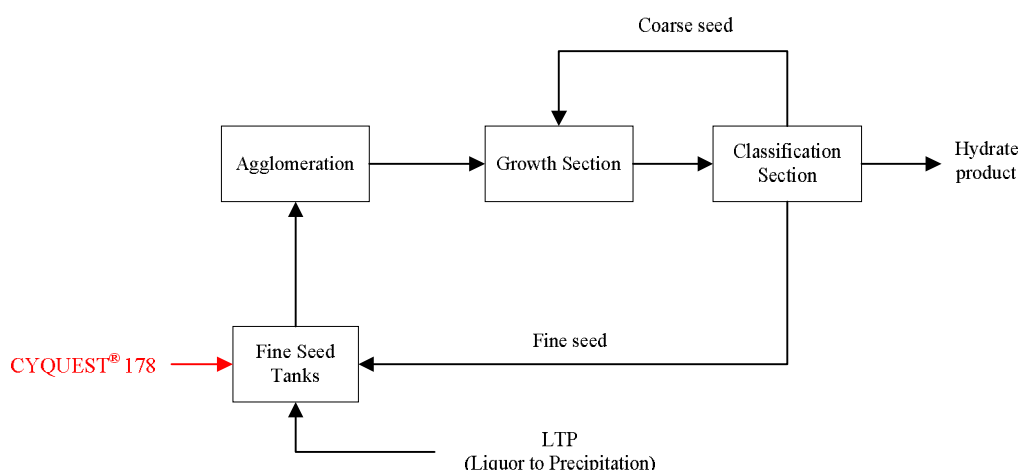
### 5.1. Injection Points for CYQUEST® 178

The precipitation line was composed by two fine seed tanks, two agglomerators operating in series whose discharge splits and feeds two parallel lines of growth tanks. A simple classification system composed of a battery of cyclones and seed filters to distribute fine seed to the seed tanks and coarse seed to the first growth tank while cooled pregnant liquor or LTP is fed to the fine seed tanks too.

As the main objective for the application of CYQUEST® 178 was to maintain or improve the hydrate PSD, the best injection point for the new CGM emulsion was in the feed to the fine seed tanks. In this case, due to physical constrains it was not possible to add the emulsion to the LTP line but to the top of the seed tanks.

An emulsification unit was installed and set to operate with cooled condensate at 50 °C to continuously produce emulsion at 5.0 % concentration that was split and distributed to the two slurry seed tanks.

A general schematic of the precipitation line is shown in Figure 6.



**Figure 6. Schematic of the precipitation line indicating the injection points.**

## 6. Plant Trial Results and Discussion

### 6.1. Dose Strategy for Plant Trial

The level of fine particles obtained from the last precipitation tank pump-off follows a cyclical trend, passing from periods of high content of fines to low content of fines. This customer

applied CYQUEST® 120 and followed an on-and-off dose strategy in synchronization with the fines cycle. In other words, it initiated the CGM addition when hydrate particles started to get finer so that the peak of the cycle (maximum content of fines) can be controlled and reduced and it stopped it when they began to turn coarse.

Based on this dose strategy, CYQUEST® 120 was usually applied with doses between 20 ppm and 40 ppm. However, during the trial, CYQUEST® 178 was applied with doses between 4.8 ppm and 8.9 ppm translating to a dose reduction between 76 % and 78 %.

## 6.2. Control of Fines – Hydrate PSD

The data collected during the trial was compared against historical data collected during approximately four months before the trial while no CGM was being used on the precipitation circuit. Therefore, the comparison was really made against no CGM addition.

The results indicate that the < 45 µm and < 20 µm fractions from the last tank pump-off were reduced by 24.2 % and 13.6 % respectively during the application of CYQUEST® 178 as shown in Figure 7.

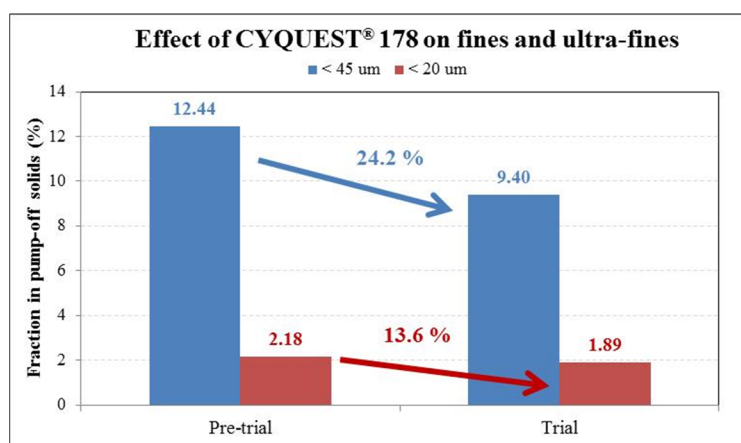


Figure 7. Average values for < 45 µm and < 20 µm fraction before and during the trial.

## 6.3. Productivity – Yield

Figure 8 shows the productivity or yield observed before and during the trial. During the trial the yield was higher with an average value of 92.0 (g/L) compared to an average of 88.2 (g/L) before the trial, representing an increase of 4.3 %.

However, the observed yield in a precipitation circuit is the result of the level of liquor supersaturation at a given seed charge. The supersaturation is determined by liquor chemistry (A/C and C level) and filling temperature. The higher the liquor supersaturation, the higher achieved yield will be. This, however, may negatively impact particle size distribution.

During CYQUEST® 178 trial periods the customer was able to operate at a higher supersaturation levels without compromising the product quality. The supersaturation was mainly increased by raising the A/C ratio of LTP from 0.660 to 0.700. At the same time, the first growth tank temperature decreased from 62 °C to 60 °C. The observed yield increase was a result of these stressed fill conditions.

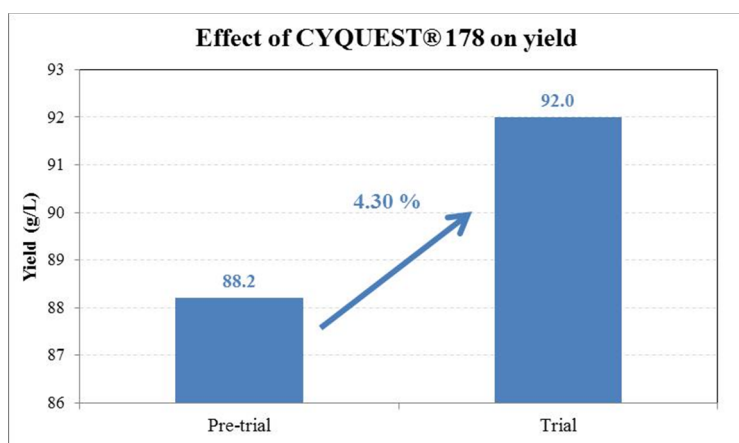


Figure 8. Average values for yield before and after the trial.

## 7. Conclusions

CYQUEST® 170 series CGMs offers a more robust and cost effective line of Crystal Growth Modifiers. The main features of these new products include a significant reduction in required dosage relative to current CGMs, improved dispersion into the liquor due to addition as an emulsion and the absence of oil from the product building in the liquor.

When applied on the plant scale CYQUEST® 178 is effective in controlling fines allowing for a more stable operation of the precipitation circuit. The < 45 µm and < 20 µm fractions were reduced by 24.2 % and 13.6 % respectively when compared to no CGM treatment. CYQUEST® 178's ability to control fines allows for running the precipitation circuit at lower filling temperatures and higher liquor A/C ratios promoting higher yields. By manipulating these factors the circuit had a yield increase of 4.3 % from 88.2 g/L to 92.0 g/L during the trial. CYQUEST® 178's effectiveness allowed for dose reduction of at least 75 % with respect to CYQUEST® 120 which ensures significant cost savings.

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