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® 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® 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® vessel. To this vessel, additional components (e.g. hydrate (Al_2O_3•$3H_2O$), Na_2CO_3, NaOH, and water) are added to a targeted liquor composition such that the final A/C = 0.72 ± 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 ± 5.0 g/L (as Al_2O_3)
C (Total caustic): 230 ± 5.0 g/L (as Na_2CO_3)
S (Total soda or alkali): 320 ± 5.0 g/L (as Na_2CO_3)
A/C: 0.72 ± 0.03
Chloride: 8.70 ± 0.02 g/L (as NaCl)

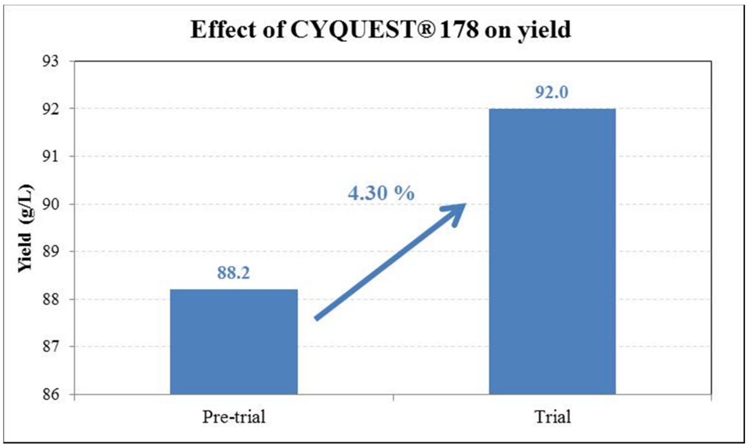

Figure 8. Average values for yield before and after the trial.

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.

8. References

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