

HYCLASS™ TECHNOLOGY FOR IMPROVEMENT OF TRIHYDRATE CLASSIFICATION IN THE BAYER PROCESS

Jing Wang¹, Jaqueline Herrera¹, Shawn Kostelak², Kody Frederic²
¹Nalco Company, 1601 West Diehl Road, Naperville, IL, 60563, U.S.A.

²Noranda Alumina LLC, 1111 Airline Highway, US 61, Gramercy, LA 70052, U.S.A.

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Abstract

The classification section in the Bayer plants is a critical part of the process. The final separation of the finest hydrate particles from the spent liquor takes place in the tertiary thickener vessels. Efficient capture of trihydrate particles in the classification circuit is essential to improve the productivity of the Bayer process. It is widely accepted that the efficiency of the classification circuit can be improved by the use of additives. Nalco is continually developing new polymer chemistries to improve the efficiency of trihydrate flocculation. A novel hydrate classification technology, HyClass™, was developed by Nalco and field evaluated in the tertiary thickener units of Noranda Alumina. HyClass technology significantly improves the flocculation performance against an industrial standard 85700 with respect to increased hydrate capture, improved settling dose-response, higher underflow densities and most importantly, further improved slurry rheology. The lab development and field evaluation work is summarized in this paper.

Introduction

In the Bayer process for the production of alumina, bauxite ore is pulverized, slurried in a caustic solution, and then digested at elevated temperatures and pressures. After removal of red mud impurities, the clarified green liquor is then cooled to a supersaturation condition and seeded with recirculated fine aluminum trihydrate crystals in precipitation tanks to induce the precipitation of alumina trihydrate from liquor. These trihydrate particles are then separated in the classification circuit according to Stokes law - coarse particles settle easily, and fine particles settle slowly. In particular, in the final classification step (tertiary thickener), the fine particles settle so slowly that it becomes very difficult to separate them from the spent liquor, potentially resulting in trihydrate production loss. In addition, the poor underflow rheology of densely compacted fine trihydrates can lead to premature tank failures due to excessive rake torques, scale formation in classification vessels and reduction in seed filtration efficiency. Therefore, within the settling steps of the classification system, trihydrate flocculants can be used to enhance particle capture, settling rate and improve underflow rheology. As a result, the efficiency of thickeners and the process can be improved.

The conventional flocculant technologies, synthetic water soluble polyacrylate flocculants and/or dextran flocculants, are used to improve the settling characteristics of the alumina trihydrate particles in the classification process and reduce the amount of solids in the spent liquor [1-4]. While various flocculants are often used in classification circuit of Bayer plants and have

demonstrated some capacity to reduce overflow solids and increase hydrate settling rate, there has been a clearly established need for further improvements in the classification and flocculation of trihydrate in Bayer process. The benefits of further reducing the overflow solids in the tertiary settlers include: (1) a direct net production increase, (2) a reduction in heat exchange scale and associated energy consumption [5], and (3) a reduction in the quantity of trihydrate that must later be redigested. In addition, the operational efficiency of the tertiary thickeners, seed dewatering and precipitation can be impacted significantly through (4) faster settling rates, (5) improved settling rate dose-response at higher feed solids and (6) marked improvement in settled hydrate underflow density and rheology.

Therefore, it is highly desirable to develop a novel polymer chemistry with superior performance for hydrate flocculation, which is the objective of this work. In current work, a new hydrate classification technology, HyClass, was developed by Nalco and field evaluated in the tertiary thickener units of Noranda Alumina. This paper summarizes the lab development and field evaluation work for HyClass technology as trihydrate flocculant in Bayer process.

Experimental

In the initial lab development, the flocculation performance of HyClass products was compared to 85700 benchmark using (1) cylinder settling test, (2) Imhoff cone method and (3) Focused Beam Reflectance Measurement (FBRM) [6]. Field evaluation was conducted in the tertiary thickener units at Noranda Alumina in Gramercy, LA.

Cylinder Test

In the cylinder test, 1-L bottles of Secondary Overflow slurry (containing about 50 g/L solids) were collected and stored in an oven at 75 °C. For a given test, a bottle was removed from the oven, shaken to re-suspend the hydrate solids, and, then dosed with a specific amount of flocculant solution. This bottle was then mixed by hand to allow the flocculant to contact the solids for 1.0 minute, prior to transferring the slurry into a 1L graduated cylinder. The settling hydrate interface was recorded at 1 minute intervals over 4 minutes to calculate the hydrate settling rate. The amount of solids in the overflow of each sample was determined after 4mins of settling by standard methods in the lab.

Imhoff Cone Method

In the Imhoff cone test, 1-L bottles of Secondary Overflow slurry (containing about 50-140 g/L solids) were collected and stored in an oven at 75 °C. For a given test, a bottle was removed from the oven, shaken to re-suspend the hydrate solids, then dosed with a specific amount of flocculant solution. This bottle was then mixed by hand to allow the flocculant to contact the solids for 1.0 minute, prior to transferring the slurry into a 1L Imhoff cone. The hydrate settling rate and overflow clarity were determined using a similar method as described in Cylinder settling test procedure. The flowability of the compacted hydrate solids was measured by determining the elution time needed for the hydrate to pass out of the Imhoff cone after 15 minutes of compaction.

Focused Beam Reflectance Measurement (FBRM)

Focused Beam Reflectance Measurement (FBRM) allows for in-situ measurement of particle (floc) size by insertion of a probe into the continually agitated slurry. The probe scans a highly focused laser beam at a fixed speed across the hydrate particles in the slurry and measures the back scattered light or the duration of the reflection of the beam from the particles. The backscattered light is expressed as chord length, which is related to the particle size. The unflocculated particles have short mean chord lengths. As flocculation occurs, the mean chord lengths increase and the total number of discrete particles decreases. In each test, 200mL of slurry was prepared comprising of 50g/L aluminum trihydrate solids and spent liquor (equilibrated at 60°C in 250ml Nalgene bottles for 1 hour). A commercially available fine standard aluminum trihydrate seed was added to each bottle and mixed for 30 seconds. The slurry was poured into a 250ml glass reactor connected to a hot water bath (60°C). The FBRM probe and stirrer were then placed in the reactor. After 1min of continuous agitation, data acquisition with FBRM started. After a certain point of time, a specific amount of flocculant solution was added. The information on the change in the mean chord length (which is proportional to the real particle size) was obtained over time.

Field Test

The trial was conducted in two of the three operating tray thickeners at Noranda Alumina during a five-week test period. The product was applied neat to each tray feed line (Figure 1). The current hydrate flocculant feeding system was used to run the test without any additional requirement of equipment, pumps or pipelines. During the trial, the feed slurry, tray overflow and underflow samples were collected three times per day. The solids (gpl) in each of the samples was determined by standard procedures in the plant quality Lab.

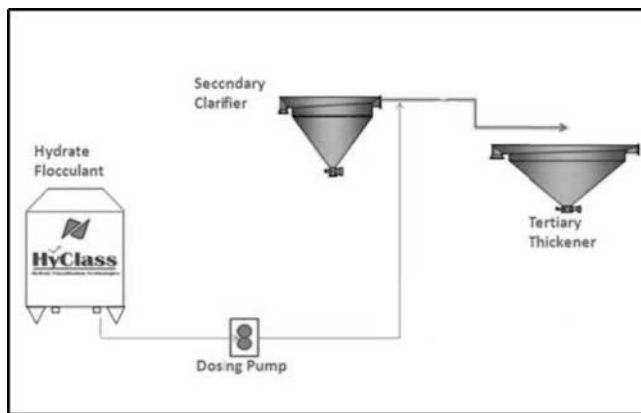


Figure 1. Diagram of HyClass flocculant application

Results and Discussion

Lab Development

Impact of HyClass on Trihydrate Capture and Settling Rate

Plant use of trihydrate flocculants is traditionally justified on the value of solids captured, which is the reduction of overflow solids in tertiary thickener vessels. Therefore, to evaluate the flocculation efficiency of HyClass flocculant against the 85700 benchmark, cylinder settling tests were conducted on seed secondary overflow. Figures 2 and 3 show the clarity and settling rate results of each flocculant versus dosage. It is apparent that the addition of HyClass flocculant significantly improves the overflow clarity and hydrate settling rate compared to 85700. In detail, with the treatment of 0.6ppm 85700, the overflow solid was 17g/l. However, with HyClass product at the same dosage, the overflow solid was only 5g/l. Furthermore, as shown in Figure 3, with the treatment of HyClass flocculant at 3ppm, a settling rate of over 14ft/hr was achieved. At the same dosage, with 85700, the hydrate settling rate was only about 7ft/hr. It should be noted that a plateau in the settling rate is observed with 85700, but with the HyClass product, settling rate increases linearly with dose.

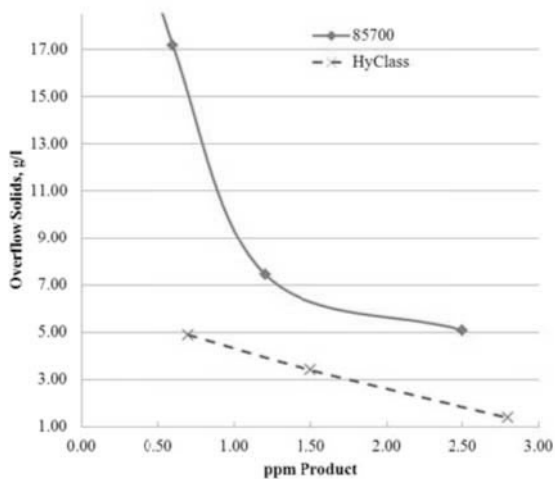


Figure 2. Overflow solids vs. HyClass and 85700 product dose (50g/l solids, 4 minutes settling)

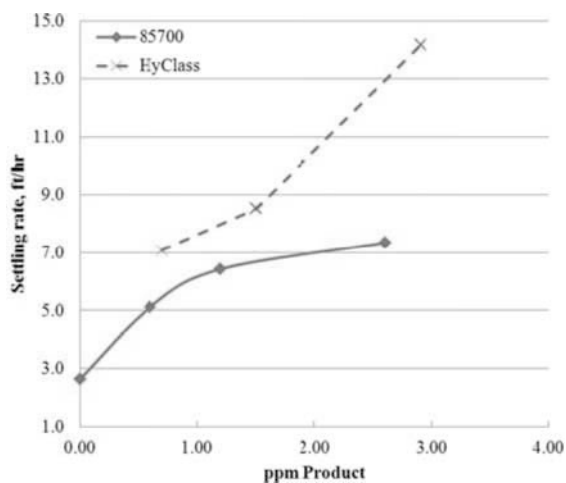


Figure 3. Trihydrate settling rate vs. HyClass and 85700 product dose (50g/l solids, 3 minutes settling average)

Impact of HyClass on Compacted Hydrate Flowability

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 often form a slurry with very poor flow characteristics. Such densely compacted trihydrate does not flow well and can often result in unacceptable rake torques or “rat-holing” within the underflow beds. 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. Therefore, improvement of underflow rheology would be a significant advancement. To study the impact of HyClass and conventional flocculant 85700 on settled hydrate flowability, the Imhoff cone method was employed.

As shown in Figure 4, compared to the blank and 85700, the settled hydrate flowability was increased significantly using the HyClass product. The flowability of settled trihydrate for the blank was very poor (only 0.1 L/min). With 85700, the flowability of flocculated material increased to 0.4 L/min, and reached a plateau. However, the addition of HyClass flocculant can increase the hydrate flowability dramatically to about 1.9 L/min at the same dose. As the product dose of HyClass is increased, underflow rheology was continually improved. This result clearly demonstrates the substantial impact of the new flocculant on the flow properties of settled trihydrate.

Similar tests were subsequently conducted with various feed slurry solids from 50 to 140g/l. From Figure 5, it is apparent that the flowability of untreated settled hydrate diminishes as the feed solid loading is increased from 50 to 140g/l. Treatment with 85700, improved the hydrate flowability to some extent. However, with addition of HyClass flocculant, a dramatic increase in hydrate flowability was achieved. In detail, for the Blank and 85700 treated hydrate, the hydrate flowability is less than 1 and 2 L/min respectively at a solid loading of 50g/l. However, with HyClass product, even at a much higher solid loading of 140g/l, the same hydrate flowability of 2L/min was maintained. Therefore, HyClass technology shows great promise in allowing plants to operate thickeners at a more desirable condition of higher underflow density without the risk of unacceptable rake torques or “rat-holing”.

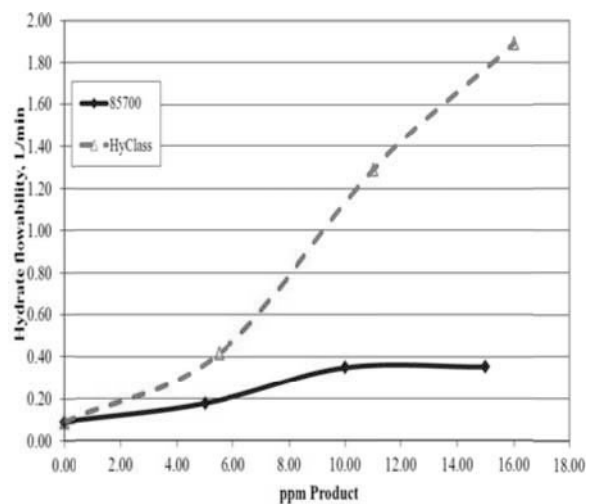


Figure 4. Flowability of settled hydrate treated with HyClass or 85700 at different dosages (compaction time: 15 minutes, 140g/l solids)

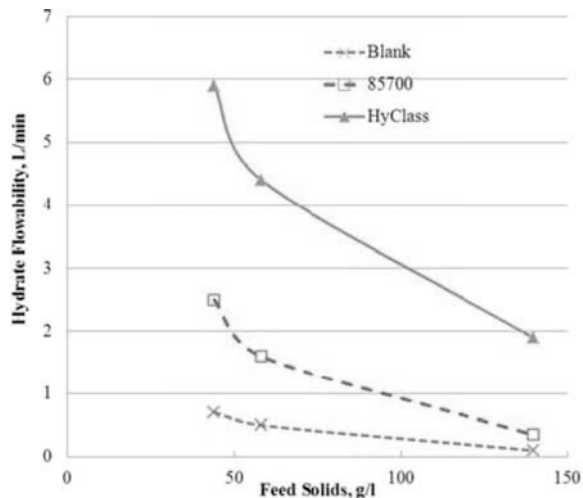


Figure 5. Flowability of settled hydrate untreated or treated with HyClass/85700 at different solid loadings (compaction time: 15 minutes)

FBRM Study of Flocc Formation

To further evaluate the flocculation performance of the new flocculants, Focused Beam Reflectance Measurement (FBRM) was also used to in-situ monitor the flocculation rate, floc size and shear resistance of trihydrate floccules formed with treatment of different products. As shown in Figure 6, the mean chord length of untreated alumina trihydrate solid particles is 20 μm . Under slow mixing condition, with the addition of 85700 or HyClass product, the mean chord length starts to increase, which indicates floccule formation. For 85700 treated trihydrate particles, the maximum mean chord length is only about 22 μm . However with the addition of HyClass product, the mean chord length of aggregates continually increases to over 34 μm , which means larger floccules formed. To study the shear resistance of the floccules formed, once stable aggregates have formed, the mixing rate was increased from 250 to 400rpm. As a result, the floccules start to breakdown, and the aggregates formed with 85700 breakdown completely. However, the floccules formed with HyClass flocculant only breakdown partially. Note that although the mean chord length of flocs decreased considerably during periods of high mixing, upon lowering the shear to the original mixing speed, the flocs quickly reform to their original size.

In conclusion, the trihydrate particles treated with HyClass flocculant form larger floccules compared to 85700. In addition, significantly better shear resistance was observed with treatment of HyClass product.

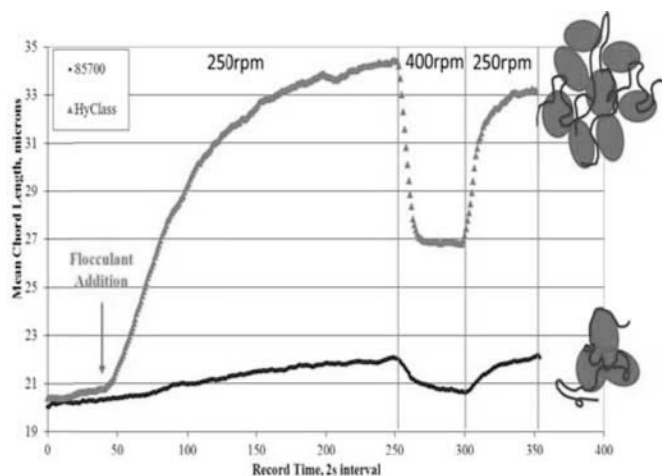


Figure 6. FBRM mean chord length of alumina trihydrate flocculated with 85700 and HyClass vs. time and mixing conditions (50g/l solid loading)

Field Evaluation

In order to determine the economical and operational advantages of the HyClass technology, a field test was conducted over a five-week time frame in two of the three operating trays in the classification area of Noranda Alumina. The objective of the trial was to evaluate the new HyClass product against 85700 with respect to overflow clarity, settling dose response and tray thickener underflow rheology (hydrate flowability).

In detail, the field test was conducted in tray B and C at an initial HyClass dose of 2.0 ppm; a 20% reduction compared to the normal 2.5 ppm dose of the 85700. To obtain a dose profile and evaluate the performance of the HyClass at different doses, the flocculant dose was further reduced to 1.6 ppm and then 1.0 ppm. At 1.6 ppm, the average overflow solid was 0.41 g/l, and 0.6 g/l solids at 1.0 ppm. During the first phase of the field test, the overflow solids were reduced from an average of 0.6 g/l with 85700 to 0.34 g/l with HyClass flocculant, a 43% reduction in overflow solids.

Figures 7 and 8 show the dose profile of HyClass flocculant in tray B and D respectively. It was found that in tray B, at 2.4ppm, overflow solids were reduced by 59% using HyClass at an equivalent dose to 85700. And the tray underflow solids were increased by 44% at the same dosage and average feed solids. On the other hand, as shown in Figure 9, in tray D, at 2.6ppm, overflow solids were reduced by 50% using HyClass flocculant. Furthermore, the underflow solids were increased by 44% at equivalent dosage and feed solids. Both charts show an excellent HyClass dose-response with regards to improved overflow solids capture and higher underflow solids. It should be noted that the injection liquor line that is normally added to the underflow line of the trays to improve hydrate flows was closed and remained closed during the test period. No underflow pumping issues were reported even with the dramatically higher underflow solids during the trial period. The substantial increase in the underflow solids with no impact on the vessels rake torque and underflow pumpability confirms better compaction of the aluminum trihydrate and improved settled hydrate rheology observed in the laboratory.

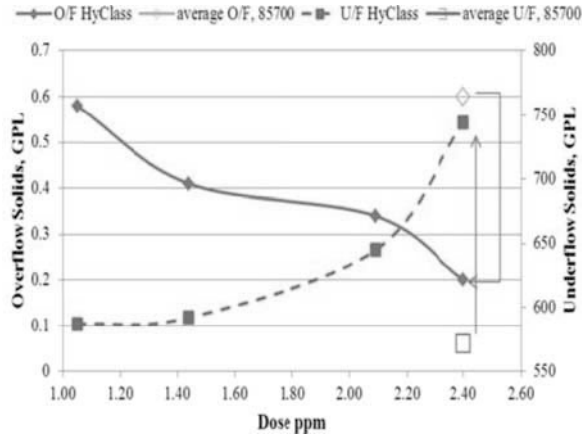


Figure 7. Overflow (O/F) and underflow (U/F) solids response to HyClass flocculant dose on Tertiary Tray B

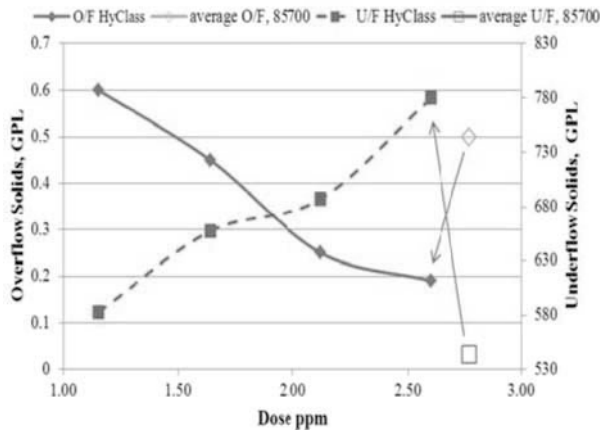


Figure 8. Overflow (O/F) and underflow (U/F) solids response to HyClass flocculant dose on Tertiary Tray D

	85700		HyClass	
	Tray B	Tray D	Tray B	Tray D
Dose ppm	2.50	2.60	2.4	2.6
U/F readings	268.27	245.04	288.7	277.3
Feed gpl	37.90	38.30	39.82	40.3
O/F gpl	0.60	0.50	0.2	0.19
U/F gpl	571.83	543.15	744	780
AMPS	33.06	29.22	34.1	32

Table 1. Comparison data (averages) collected before the trial with 85700 and during the trial with HyClass product

The overall results of the field study demonstrate that the HyClass technology is superior to the 85700 chemistry with respect to fine solid capture, dose-responsiveness and underflow rheology modification. Compared to 85700, HyClass flocculant was able to produce equivalent overflow solids with a >35% reduction in dosage.

Alternatively, replacing 85700 with HyClass flocculant at the same dosage will result in lower tray overflow solids. Switching from the 85700 flocculant to HyClass technology (at the same dose) in the tertiary thickeners reduced the tertiary thickener overflow solids by 0.4 gpl on an Al₂O₃ basis. The total estimated savings from switching to the HyClass flocculant is \$1.3M per year with 99% of that savings attributable to the reduction of alumina trihydrate in the tertiary thickener overflow. Due to the large potential savings associated with reducing the alumina trihydrate in the tertiary thickener overflow, additional savings are expected at higher flocculant dosages.

The improved rheology of the settled alumina trihydrate in the tertiary thickeners after switching to the HyClass flocculant is apparent; the tertiary thickener rakes can handle much higher hydrate loading during upset conditions.

Conclusions

1. A novel hydrate flocculant, HyClass, has been successfully developed in Nalco. Initial lab test results clearly demonstrated that compared to 85700, the addition of HyClass flocculant can significantly improve the overflow clarity, increase hydrate settling rate and improve the flow properties of settled trihydrate. FBRM studies confirmed that the trihydrate particles treated with HyClass product form larger and stronger floccules compared to 85700.
2. During the field trial, the HyClass technology performed superior to 85700 with respect to fine solid capture and settling dose response. Switching from the conventional flocculant to the new HyClass technology resulted in much lower tray overflow solids and provided significant cost savings to Noranda.
3. Moreover, a significant decrease of overflow solids and substantial increase in the underflow solids was achieved with no impact in the vessels rake, and underflow pumpability, which indicates better compaction and rheology of the aluminum trihydrate in the cone of the vessel with the treatment of HyClass product.

References

1. Malito, J.T., "Use of Designed Experiments for Optimizing an Alumina Trihydrate Flocculant in the Tray Classifiers", *Light Metals*, 1995, pp.107-112.
2. A. Aboagye et al, "Advances in Control of Trihydrate Classification using High Performance Flocculation", *AQW*, 2012, pp. 71-74.
3. Moody, G. M.; Rushforth, C. A., "Recovery of Alumina Trihydrate in the Bayer Process", U.S. Patent 5,041,269, 1991.
4. M. Hereda et al, "Aluminum Trihydroxide Deliquoring with Anionic Polymers", U.S. Patent 4,478,795
5. Henrickson, L., "The Need for Energy Efficiency in Bayer Refining", *Light Metals*, 2010, pp. 173-178.
6. Phillips, E. C., "Continued Efforts on the Development of Salicylic Acid Containing Red Mud Flocculants", *Light Metals*, 2004, pp. 21-26