Assessment of Chemical Additives Impact on Alumina Refinery Processes

Raquel Singulani[1], Ahmad Badarani[2], Sanghamitra Panda[3], Aysha Althaibani[4] and Maitha Alqaydi[5]
1. Senior Process Engineer
2. General Superintendent Optimization and Development
3, 4, 5. Senior Chemist
Al Taweelah alumina refinery – Emirates Global Aluminium, Abu Dhabi, UAE
Corresponding author: rsingulani@ega.ae
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Abstract

Introduction of new chemical additives into the Bayer circuit or the replacement of an existing one is required from time to time to support security of supply, cost reduction, better performance, or to align with new technologies. If the steps taken to select a new product are not carefully considered, introduction of these additives could change the liquor characteristics and result in adverse effects on particle sizing, oxalate control, settling, and/or filtration. To mitigate this, Al Taweelah alumina refinery has developed a comprehensive poisoning test methodology to screen and qualify chemical additives prior to field trials and permanent use. This methodology looks at the refinery as a whole, and not the area of use in isolation. Additives are evaluated in the lab for their impacts on agglomeration, growth, and settler/washer circuit, aiming to identify potential changes in nucleation, agglomeration, oxalate imbalance or settling and filtration. This paper provides a comprehensive evaluation of the results obtained from laboratory tests, offering insights into the importance of a careful evaluation before experimenting new chemicals in the plant. The findings have significant implications for alumina refinery operations.

Keywords: Bayer chemical additives, Poisoning test, Nucleation, Agglomeration, Oxalate control.

1. Introduction

Al Taweelah alumina refinery was commissioned in March 2019 and has now significantly exceeded nameplate capacity with continual improvements in different areas. To support the fast growth, some chemical additives were introduced to the process, and others were required to be replaced with the change in the liquor properties.

In 2022, after starting a field trial of a filtration aid, there was an observed nucleation spike in the precipitation circuit a few days later, that exhibited a different behavior from normal, including a change in the oxalate balance. It is always difficult to establish causality in cases like this, since many other factors can affect nucleation and oxalate stability [1], but a more comprehensive problem solving was performed, and the filtration aid additive was disqualified for use.

Another important event occurred in the Clarification circuit, where the introduction of a bauxite handling aid was followed by a disturbance in the slurry settling, leading to a significant production loss. Laboratory tests were conducted, concluding that the high temperature in digestion did not degrade or inactivate the chemical, allowing it to hinder settling behavior and result in the detrimental effect in the clarifiers.

Even in a well-established refinery, the replacement of an additive or the introduction of a new one can be required from time to time to support supply security, reduce cost, improve

performance, or align with new technologies. For this reason, there is a constant drive for lab testing and field trials. The qualification of these products for use is complex since the chemistry is not fully known and the implications of these products in the Bayer process are not always explored by the suppliers. In addition to that, the variety of products for the same application has increased over the years, and new developments are constantly in progress.

In general, any substance added to the Bayer process has potential to be harmful, and sometimes, due to the continuous change of the process, negative effects could be linked to a normal process variability [2]. A poisoned liquor can compromise yield, affect nucleation in precipitation, stabilize or destabilize the oxalate balance, or lead to flow reductions due to settling or filtration issues. Some studies have already explored the effect of dewatering aids in nucleation and sizing control [3], and defoamer and hydrate flocculant in yield [4]. Crystal growth modifiers (CGMs) are made to act on the agglomeration and can also impact oxalate stability [5].

Other important aspects to be considered are the interaction effect of these products, and their accumulation over time [6]. It is unknown whether the chemicals adsorb significantly in the particles or stay in the liquor. Both scenarios pose potential risks. Seed and wash water are recycled back into the precipitation stage, and it is unclear whether all additives are completely degraded during digestion. Refineries have specific particularities, such as low or high digestion temperatures, different precipitation conditions, oxalate free or co-precipitation, among other aspects, and it is always advised to assess its impact on particle sizing, yield, oxalate control, settling, and/or filtration.

The objective of this study is to present the methodology adopted by EGA to screen and qualify chemical additives prior to field trials and permanent use, followed by the results obtained from the experiments.

2. Experiments

The laboratory sequence presented below refers to the methodology adopted to evaluate the impact of the chemicals in precipitation and clarification, and it is divided into poisoning tests and settling/filtration tests.

2.1 Lab Methodology for Poisoning Test

The poisoning test is designed such that it simulates the precipitation conditions in the lab, including agglomeration and growth sections. This is carried out in a temperature-controlled rotating water bath using plant liquors, namely pregnant liquor (PGL), which is the alumina rich stream from the clarifiers, and filtered dilution liquor (FDL) which is sourced from the 1st washer overflow, as well as plant seed (washed and dried fine seed) and plant slurry (coarse seed slurry). The liquor is first dosed with the chemical additive and mixed properly, then the fine seed is added. The slurry is left in the water bath for 5 hours at 80 °C to simulate agglomeration conditions. After the agglomeration simulation is completed, coarse seed slurry is introduced to the mixture. The samples are kept overnight (approximately 16–18 hours) at growth conditions, with the temperature dropping until it reaches 60 °C. A total of 25 bottles is prepared: 10 bottles for the agglomeration test, 15 bottles for the growth test.

The experiment investigates the effects of different additive concentrations on the precipitation circuit. It includes a control group with no additive (blank), a medium dose group (20 ppm), and a high dose group (100 ppm) in v/v basis. The impact of the additive is studied on the yield, the hydrate particle size distribution (PSD) and nucleation, impurities in the liquor, trace impurities in the precipitated hydrate, and oxalate concentration. Analyses are done in duplication for liquor concentration, impurities, PSD, and single test for oxalate and nucleation. The choice of plant

slurry (coarse seed slurry) and plant liquors (PGL and FDL) is done to combine the impact of the other chemicals already presented in the liquor or in the seed returning to the circuit. Some of the lab equipment is shown in Figure 1.

Figure 1. Left: Water bath, Right: Coulter equipment for particle sizing distribution analysis.

2.2 Lab Methodology for Settling/Filtration Test

The settling test simulates the refinery clarification process in the lab. The idea is to verify if the straight dosage of a chemical additive (other than the normal clarifier flocculants) could interfere in the performance of the clarifiers. First, Digestion blow-off samples are collected as close as possible to the test timing and kept in a water bath at 95 °C. 1-L cylinders equal to the number of control sample(s) and product(s) to be tested are prepared, and flocculants are diluted to 0.1 % to match the field concentration. Experiments are done in duplicate, and chemicals are tested for 20 ppm and 100 ppm. Control or blank cylinders corresponds to the current flocculant set up in the plant without any chemical. The following cylinders should have the same flocculant set up, varying the chemical dosage to be tested.

Settling rates are determined using the timing for the solid bed to reach the 600 mL level mark in each experiment after the chemical and flocculant(s) addition. Overflow clarity solids concentration is determined with a sample collected after 10 minutes of settling readings from the top of the cylinder. A second sample, collected at the same time, is used to determine filtration rate using a vacuum funnel test. Compaction measurement is done after 30 minutes of the start, recording the volume of the solids bed for each of the cylinders. Figure 2 illustrates a typical settling test apparatus. Tests are performed under atmospheric conditions.

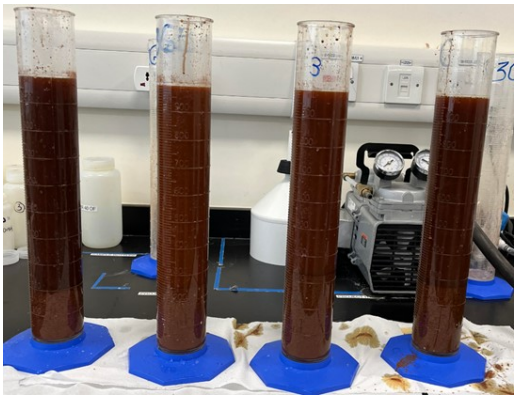

Figure 2. Settling test set up.

3. Proposed Methodology

The methodology described in Figure 3 is used at Al Taweelah alumina to technically approve an alternative product for an application already in place. In the case of a new application, the process must follow the same approach, but ideally at least two similar products should be selected for performance, poison, and settling test.

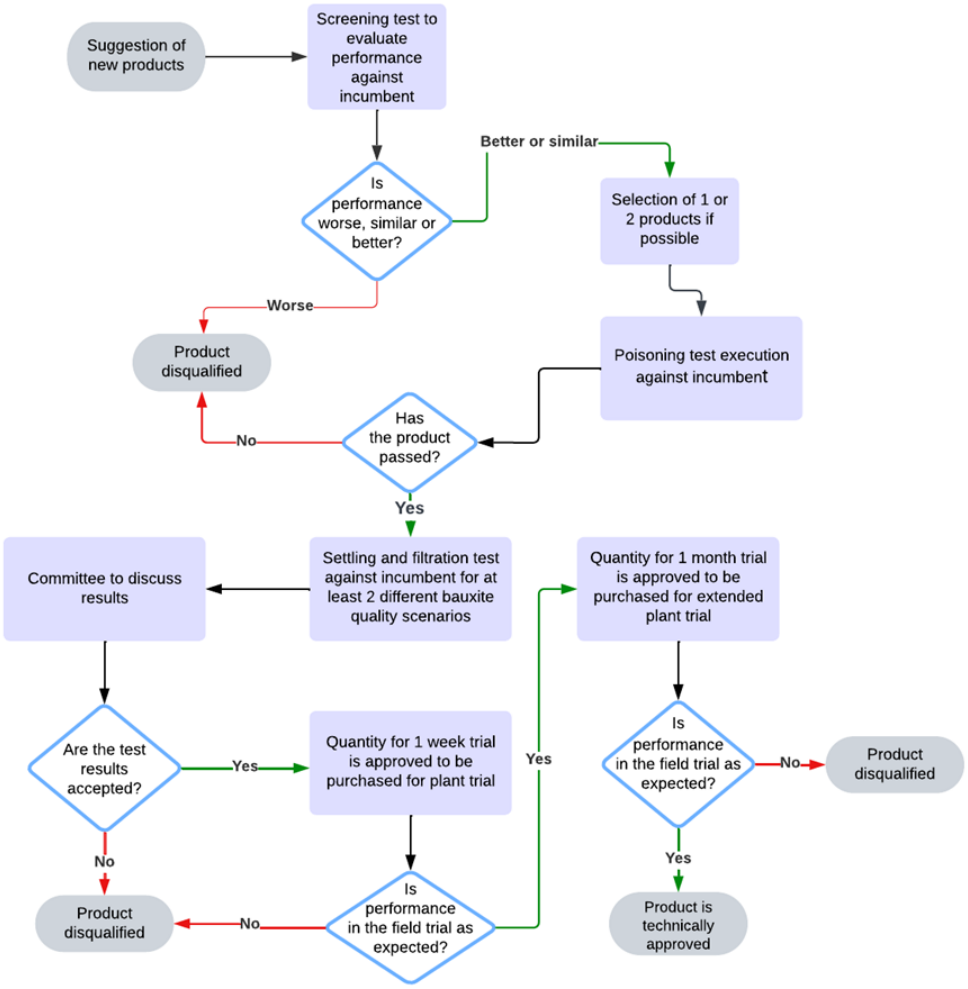

Figure 3. Methodology to technically approve a chemical additive.

A similar performance between products is accepted to be within ± 10 % when comparing products in the same application, such as moisture and leachable soda for dewatering aid products, as an example.
A product will pass in the poisoning test if it follows the same behaviour as the incumbent with regards to the parameters investigated, within ± 10 % in difference between them. A second run in the lab can be suggested in case of an outlier.
Final test results are accepted after passing the poisoning test, and if no impact in the settling rate is observed, also respecting the margin of ± 10 %.

4. Results

To determine the potential detrimental effect of a product in a downstream area, the following items are investigated: yield impact, oxalate stability, nucleation/particle size distribution, clarifier settling performance, and liquor filtration performance. The results are presented as a

difference between the sample at 20 ppm or 100 ppm and the blank (control sample). The precision or uncertainty of the lab analyses are highlighted when applicable. The chemicals tested in this study are the most common used in an alumina refinery: antifoam, dewatering aid, crystal growth modifier, clarifier flocculant, lead washer flocculant, and filtration aid. For Al Taweelah alumina, the dosage rate of these products in their applications ranges from 2 to 20 ppm.

Figure 4 presents the yield impact across different chemical additives from both white and red side (using the letters from A to J). Yield was calculated after the growth period simulated in the lab, and caustic and alumina analyses determine by liquor titration. In general, most samples have shown a positive impact for yield, and the variability seems to increase at higher dosage. The uncertainty for yield determination is ± 0.6 g/L. It is important to mention that red side flocculants are not expected to reach precipitation at higher doses, but since the accumulation of these products is unknown and flocculants carry over may occur, it is expected that some fraction will reach precipitation.

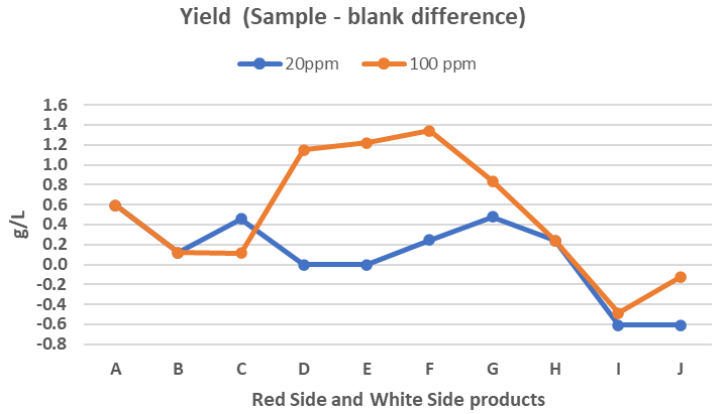

Figure 4. Yield variation against blank for different additives (uncertainty is ± 0.6 g/L).

The impact in oxalate stability is presented in Figures 5 and 6. Oxalate concentration in both phases, liquor phase oxalate (LPO) and solid phase oxalate (SPO) are analysed via ion chromatography instrument (IC) in the end of the growth period. As per Figure 5 and 6 some products have enhanced oxalate stability, increasing LPO (liquor phase oxalate), and others have stimulated the presence of SPO in the growth circuit, which can potentially lead to negative impacts in nucleation, and consequently sizing control [1].

This behaviour affecting SPO and LPO can be detrimental to plant stability if the dosage of these products is required to be adjusted. This secondary effect on oxalate stability was also observed in the plant, and product C for instance, is aimed to keep the dosage as stable as possible.

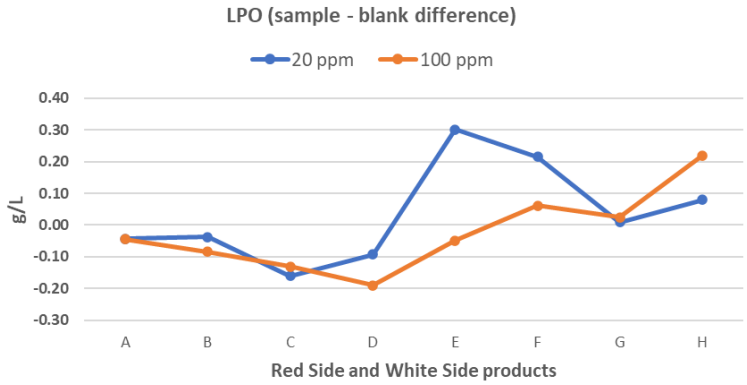

Figure 5. LPO variation against blank for different additives (uncertainty ± 0.08 g/L).

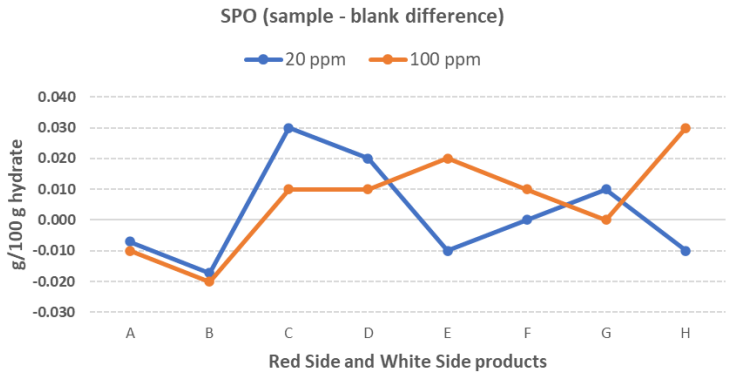

Figure 6. SPO variation against blank for different additives (uncertainty is ± 0.008 g/100g hydrate).

Nucleation was evaluated using an Accusizer, which counts the total number of ultra-fine particles, measured as million particles of 0.8, 1.5, and 2.5 µm size per gram of sample (million/µm·g), with analyses done at the end of the growth period.

The impact on nucleation is presented in Figures 7 to 9, where positive values represent an increase in the particle population for that fraction in comparison to the blank sample. Any abrupt variation in nucleation can be detrimental to the normal sizing variation in precipitation. In general, while selecting a new product, a comparison against the incumbent, for which the behaviour is already known in the plant, is crucial before progressing to a field trial.

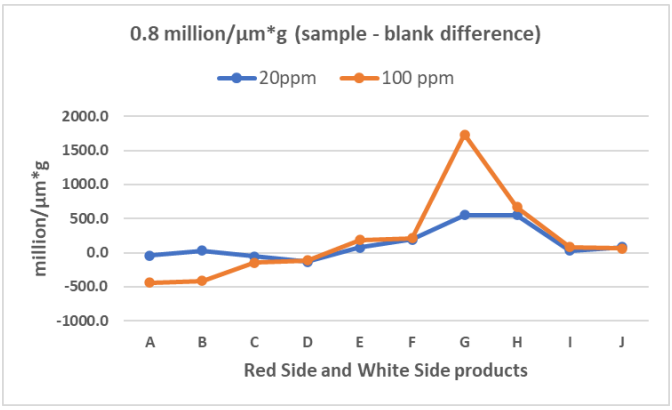

Figure 7. Nucleation variation against blank for different additives (uncertainty is ± 18 million/µm·g).

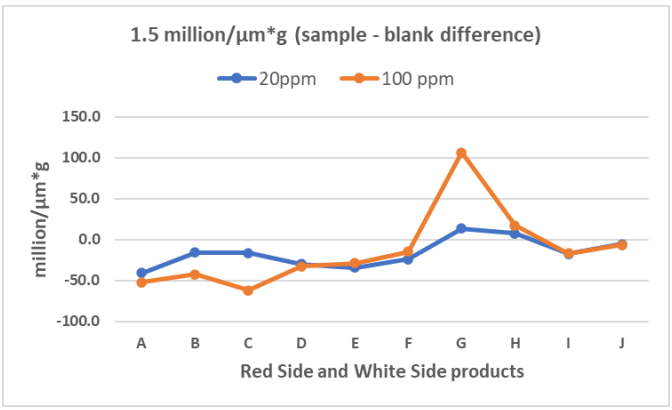

Figure 8. Nucleation variation against blank for different additives. (uncertainty is ± 3 million/µm·g).

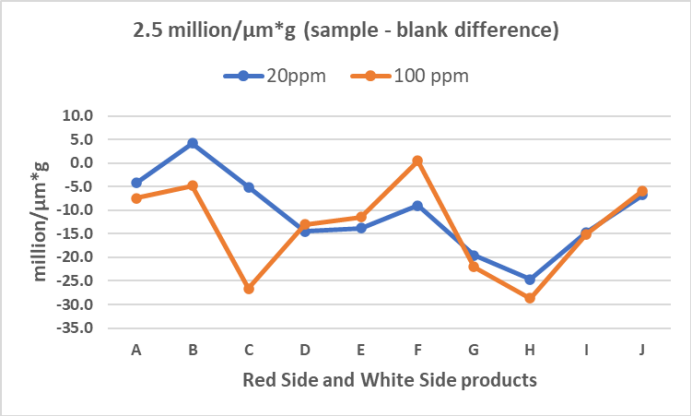

Figure 9. Nucleation variation against blank for different additives (uncertainty is ±1 million/µm·g).

Considering the effect on nucleation, the impact on the agglomeration of the fine particles can also be evaluated, as shown in Figure 10. Particle sizing distribution analyses were done using a Coulter equipment. Some products seem to enhance the agglomeration process (positive values), expressed by the degree of agglomeration calculation (DoA), behaviour that can also create an imbalance in the particle's population [1]. Degree of agglomeration is calculated after agglomeration phase.

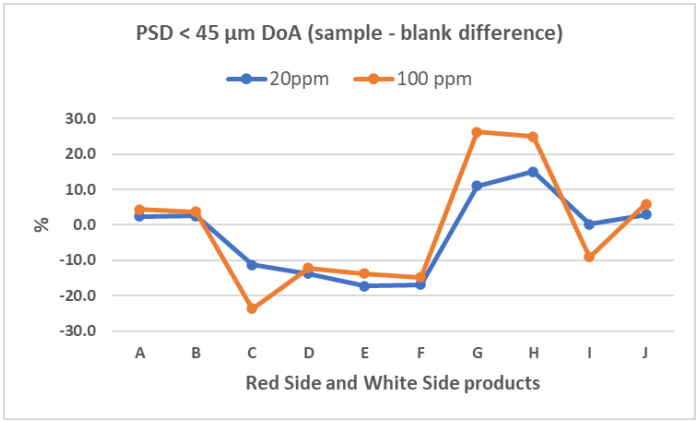

Figure 10. Degree of agglomeration variability.

A settling test evaluation is demonstrated in Figure 11, where two different additives were tested. The settling rate of product R and the combination of products R and S were tested against a blank (blow-off sample with a normal flocculant setup). Product R at a lower dose has similar performance in comparison to the blank, but the combination with a second product has shown a significant impact and would demand precaution during field trial. The uncertainty for this method is ± 5 m/h, but differences within ±10% are considered similar results.

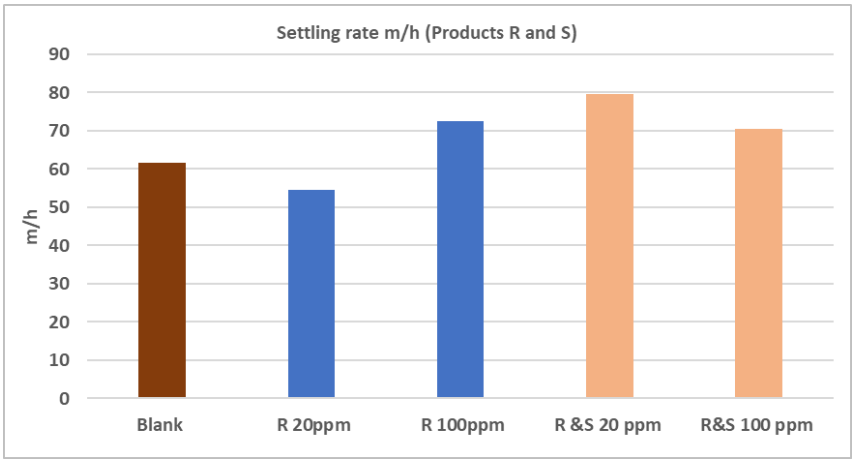

Figure 11. Settling test variability of products R and S against a blank (uncertainty is calculated at ± 5 m/h).

5. Conclusions

Based on the lab work presented in this paper, it was demonstrated that chemical additives can cause collateral effects in downstream areas of the Bayer process, with important variation presented for yield, oxalate stability and nucleation, and they must be used with caution, if not rejected, when negative impacts occur, especially in nucleation. The methodology developed by Al Taweelah alumina effectively qualifies new products before field trials, considering both resource limitations and time constraints. Alumina refineries should be aware of these potential effects and collaborate closely with suppliers to gain a deeper understanding of additives and improve their performance. Understanding the residual concentration of recirculating products in the liquor and their impact on yield, especially regarding partitioning into the hydrate, is an area to be explored. Additionally, investigating the impact of these additives on liquor density (which can affect digestion hydraulics) and their degradation at high temperatures are also valuable pursuits.

6. References

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