AA21 - Optimization of Sodium Oxalate Removal within the Bayer Process

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Abstract

Oxalate removal is a critical process within the Bayer Liquor Circuit which minimizes the propensity of co-precipitation of sodium oxalate with aluminum hydrate in the Precipitation area by lowering the sodium oxalate concentration within the liquor circuit. Minimization of this co-precipitation is a quality critical element in ensuring proper alumina particle sizing. As the quality of bauxite feedstocks declines with respects to available alumina there is the need to process increased tonnage to sustain refinery nameplate operation. This has increased the oxalate input into the refineries and necessitated investigations into low-cost oxalate removal capacity expansion approaches. An investigation was done to identify and model the nature and magnitude of the relationships that exist between oxalate yield and process parameters of seed charge, temperature, holding time and solubility in elevated TA solutions, all deemed as critical parameters in precipitation theory. Process optimization models were then applied to an oxalate removal unit operation within an operating alumina refinery immediately following a period of curtailment. These adjustments resulted in an up to 30 % increase in attained yields with no significant change in initial oxalate concentration. To sustain throughput capacities at observed elevated yields, high permeability filter media were tested and compared to previous media, across the operating cycle of the filters. This paper outlines the methodology used during the investigation, the outcomes, observations as well as future steps to be taken.

Keywords: Sodium oxalate, Filtration, Oxalate precipitation, Process optimization.

1. Introduction

Oxalate removal is a critical process within the Bayer liquor Circuit, as it minimizes the propensity of co-precipitation of sodium oxalate with aluminum hydrate in the Precipitation area by lowering the sodium oxalate concentration within the liquor circuit [1]. With the quality of ores in existing bauxite reserves expected to decline, the Clarendon Alumina Works (CAW) refinery is faced with the challenge of sustaining production targets with reduced available alumina in bauxite. Stoichiometrically, it is understood that as the available alumina in bauxite declines, the required bauxite (bauxite factor) to achieve production target will increase. As this bauxite contains impurities, their loading also increases [2]. In the case of sodium oxalate, it was found, within the context of CAW that 2 % change in available alumina resulted in a net increase of > 0.5 tonne/day of sodium oxalate delivered to the process based on plant data for the past 5 years.

Plant data also indicated that there is more than 37 % change in the sodium oxalate content of "wash water" between wet and dry seasons. Further, a general increase has been observed in oxalate within lake water over the past 9 years despite general declines in the oxalate in bauxite as shown in Figures 1 and 2 below. The variation in concentrations between wet and dry seasons suggests that if there are increased intense dry periods, potentially influenced by climate change this trend will continue. This represents an increase of sodium oxalate to process of 4 tonnes per day on average during dry period due to impacts of increased evaporation in the residue storage areas.

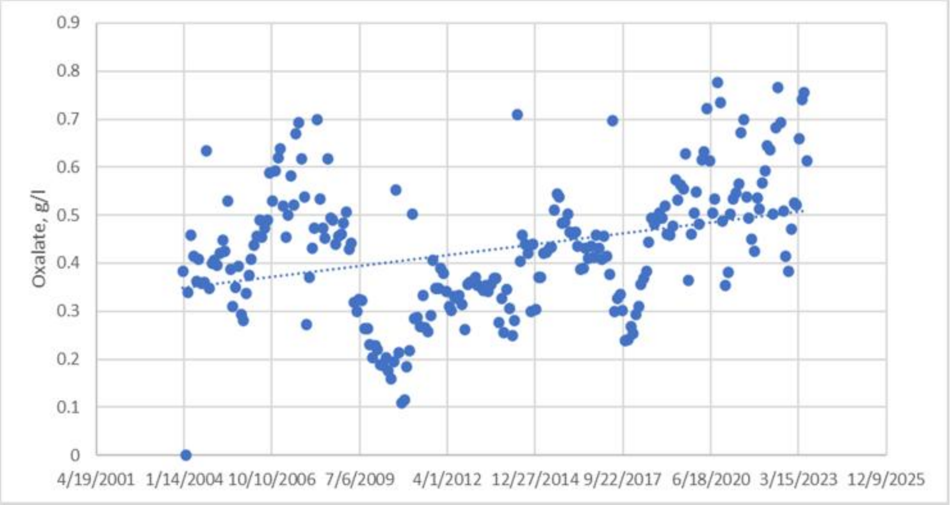

Figure 1. Oxalate in wash water to decanters.

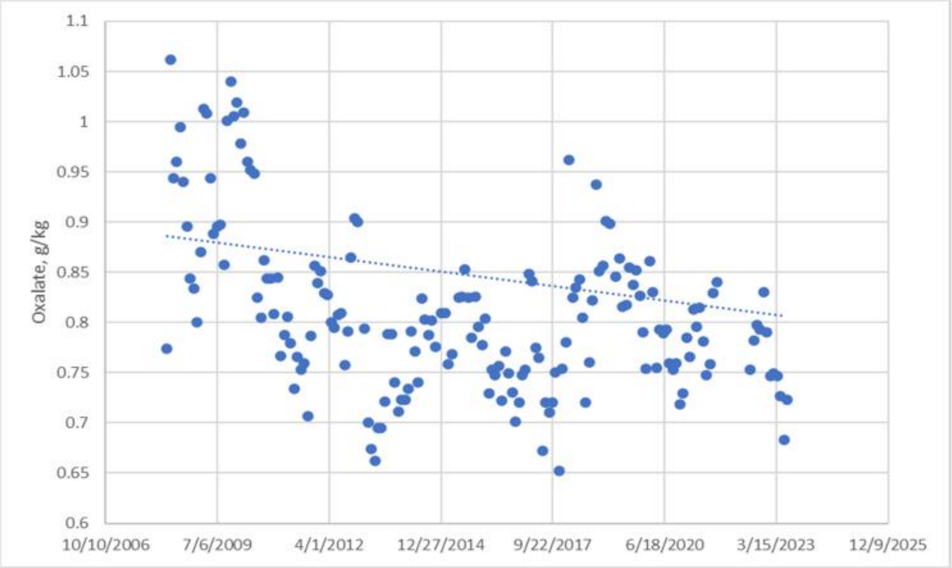

Figure 2. Oxalate in bauxite.

An increase in sodium oxalate removal capacity to manage inputs is dependent on two key factors: maximization of sodium oxalate precipitation yields and the maximization of supersaturated liquor flows. As both factors exist in an inversely proportional relationship, achieving optimal balance between both is essential. In line with general precipitation theory [1], a series of experiments was conducted to determine the relationship between oxalate yield and controllable process parameters: seed ratio, temperature, holding time and solubility in high total alkalinity (TA) solutions. Further, it was expected that an increase in sodium ion concentration would decrease the solubility of sodium oxalate. Stability studies done with synthetic liquor have indicated circa 0.8 g/L reduction in stability for every 40 g/L increase in TA [4]. Within the refinery context such could be achieved via addition of sodium hydroxide, sodium sulphate or via Bayer liquor evaporation. Solubility investigations were done to determine maximum total alkalinity for supersaturation and precipitation of sodium oxalate within plant liquor samples.

Kelly presses utilized at CAW are pressure vessels containing 10–12 spigots connected to metal frames. These metal frames are covered in semi-permeable filter cloth. In operation, the press body is filled with Bayer liquor (including precipitated oxalate crystals), with the process liquor passing through the pores of the filter cloth leaving sodium oxalate crystals on the outside of the filter cloth. Filtered liquor passes through channels in the frames to the spigots, and is returned to main Bayer liquor circuit. At two hour intervals, the press bodies are opened and accumulated solid phase oxalate is manually removed using medium pressure water jet. Maintaining capacity of the press is critical to removing sufficient quantity of sodium oxalate from Bayer liquor to prevent accumulation. Summary of the oxalate removal process is described in Figure 3 below.

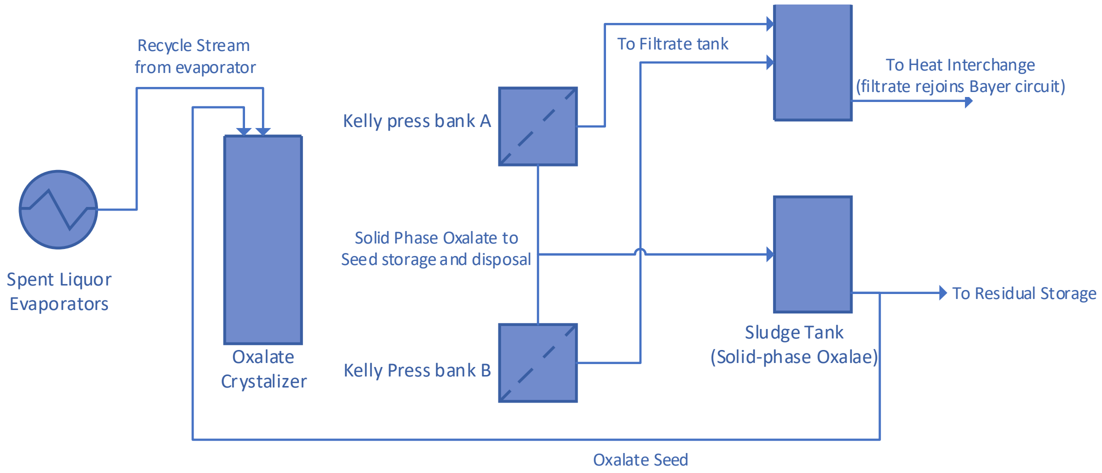

Figure 3. Oxalate Removal at CAW.

An observed linear relationship between air and water permeability of monofilament, polypropylene filter fabrics suggests that, if a pore size is kept constant, there is potential for increased liquid throughput if permeability is increased [5]. Bayer liquors are more viscous than the test fluid, water. Hence, it is appreciated that associated filtration rates would be lower. However, in the context of liquor as the test solution, it is still expected that there could be observable differences in throughput between fabrics of differing permeability. Further, equipment downtime due to fabric damage and inevitable, gradual blinding of pores with alumina tri-hydrate particles impacts average daily throughput. A secondary investigation was conducted to determine if alternative filter fabric design could improve Kelly press throughput. During an extended period of refinery curtailment, opportunity was taken to utilize plant liquor to model the sodium oxalate removal process, in part to optimize the oxalate precipitation process in the expected low dissolved oxalate regime of restart, as well as during steady-state operations.

2. Methodology

2.1 Yield Optimization

Plant liquor samples of known total alkalinity (TA) concentration were evaporated to yield ~350 g/L. The oxalate and TA content of the evaporated liquor was then confirmed via gas chromatography and Metrohm analysis respectively. Yield samples were then prepared via combination sheet (generated using Design Expert Software). Samples were dosed with 1.05–3 % oxalate seed slurry of known percentage solids, then grouped by holding temperature (60–65.6 °C) and placed in water baths for 210 to 335 min holding time. Samples were then filtered, and both filtrate and residue analyzed for sodium oxalate contents via gas chromatography. The experiments were split across three days resulting in variances in the relative starting concentration daily (Bulk sample kept at > 93 °C to minimize risk of premature precipitation).

2.2 Solubility

Initial solubility tests were done using "process" oxalate seed (at 187 g/L 30 %w/w sodium oxalate obtained from the process). A dosage value of 10 g/L oxalate (charged in excess to ensure solution becomes saturated) was added to each prepared sample. TA concentration adjustments were done through a combination of evaporation and solid caustic soda addition. Following determination of the solution saturation range (360–380 g/L), additional investigation was done for refinement. Plant liquor samples of known TA were evaporated to yield ~280 g/L TA. 50 % of the concentrated sample was then evaporated according to randomly generated total caustic concentrations between 358 and 445 g/L, and at each step a 250 mL sample was collected and dosed with 13.5 mL of 10 g/L equivalent oxalate solids. The remainder of the bulk liquor was dosed with caustic soda pellets in a stepwise manner according to the concentration list with 250 mL samples being taken and dosed with 10 g/L oxalate solids. The filtrate and residue were then analyzed for sodium oxalate content and the filtrate was further analyzed for total alkalinity concentration.

2.3 Throughput Optimization

Sample filter fabric were obtained and installed on filter frames within select Kelly press(es) of the oxalate removal building. Analysis of baseline press data for 90 days prior to trial start was done, including press flows, average run times, filter media failure rate. Daily analysis of press flows was done along with adjustment to press cycle-time based on observed flow regime.

3. Results and Analysis

3.1 The Relationship between Yield and Critical Parameters

Table 1 below indicates the combination of parameters used in conducting the yield optimization study as well as the obtained response.

Table 1. Combination sheet and response.

Run	Oxalate Seed Charge, % v/v	Holding Time, min	Tempera-ture, °C	Initial dissolved oxalate	TA, g/L	Response: Oxalate Yield, g/L
1	1.73	272	60.00	3.54	364.60	1.08
2	3.00	272	60.00	3.54	364.60	1.12
5	2.41	210	60.00	3.54	364.60	1.10
6	1.80	210	60.00	3.54	364.60	1.06
9	1.05	300	61.70	3.40	342.50	0.85
10	2.66	300	61.70	3.40	342.50	0.92
7	2.07	272	62.80	3.42	341.20	1.04
8	2.30	272	62.80	3.42	341.20	1.04
15	2.10	335	63.90	3.42	341.20	1.01
16	1.05	335	63.90	3.42	341.20	0.95
11	2.70	230	65.60	3.67	352.80	1.25
12	1.05	230	65.60	3.67	352.80	1.26
3	1.34	300	65.60	3.67	352.80	1.31
4	3.00	300	65.60	3.67	352.80	1.18

Initial attempt at model development incorporating the entire temperature range yielded limited fit. However, utilizing the temperature range 60 °C to 63.9 °C (representative of refinery process capability without jeopardizing evaporation rate and downstream processes) yielded a regression model of improved fit as shown in the comparative graph in Figure 4.

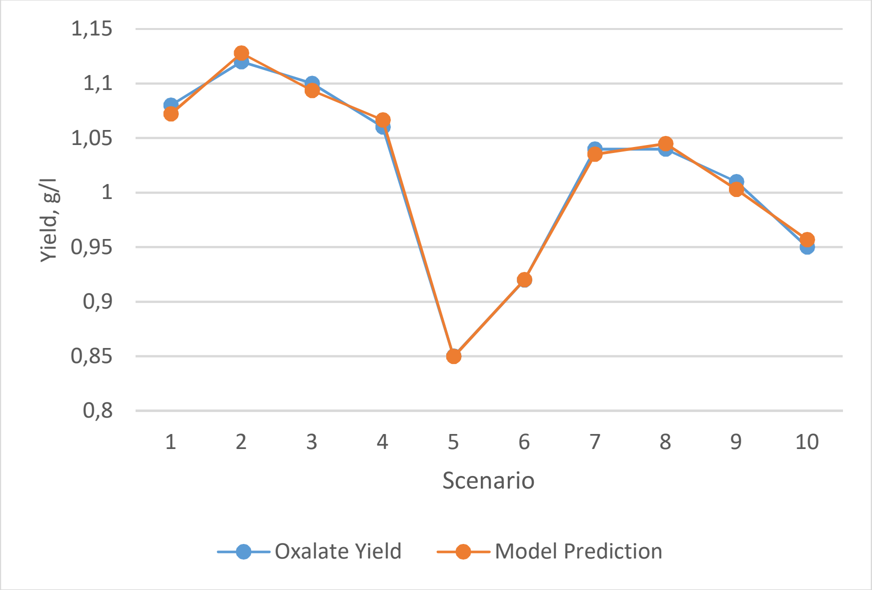

Figure 4. Oxalate Yield: actual vs. model prediction.

Summarized model:

$$Yield = A + (Seed\ Ratio \times B) + (Holding\ Time \times C) + (Crystalizer\ Temperature\ \times D) + (Initial\ oxalate\ concentration \times E) + (Crystalizer\ TA \times F)$$

where:

A	-6.58244
B	0.043799
C	0.000138
D	-0.02886
E	7.941363
F	-0.04534

The multiple R at 0.997 suggests significant correlation between yield and the variables: seed charge, holding time, temperature, initial dissolved oxalate concentration and TA. With a significance F of 0.000122, this model has a low probability of being incorrect. However, it was noted that holding time had the least impact on yield (based on the magnitude of its coefficient) by a factor of > 200 compared to the nearest factor (temperature). It was therefore suggested that this model be considered as a tool for predicting and optimizing oxalate yield with the following caveats:

A. Starting liquor used for the analysis was ~30 % more diluted than typical for steady state process operations (due to operational curtailment). While evaporation was used to concentrate the solution prior to the start of the experiment, it is possible that the relative concentrations of some impurities in liquor may have changed. Such changes in their absolute levels could impact on oxalate yield, as stabilizers or oxalate seed poisons [4]. Predicted oxalate yield values may therefore be higher than those traditionally obtained in the process.

B. While the general relationships between yield and the examined factors are not expected to change considerably, refinement using process data will improve model utility.

3.2 Solubility Investigation

Initial solubility tests were done using various TA values achieved by evaporating the liquor to a maximum of 380 g/L then via caustic soda addition to 490 g/L. These results are indicated below in the resulting solubility curve of Figure 5.

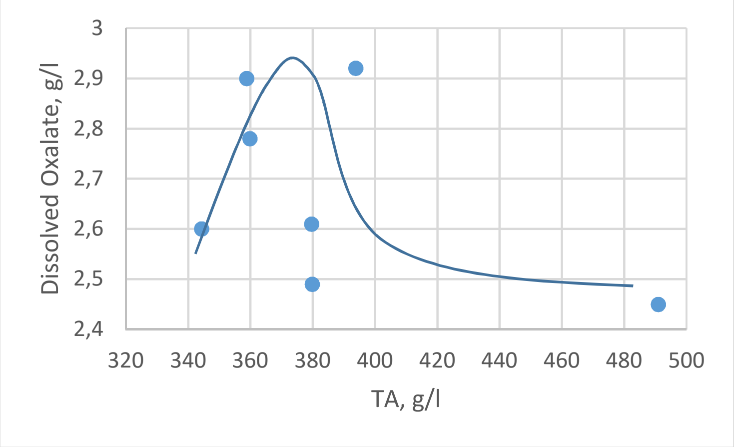

Figure 5:. Curve of Maximum dissolved sodium oxalate in plant liquor at various TA and 62.8 °C.

The results suggested that maximum liquor saturation with respects to sodium oxalate occurred between 360– 80 g/L TA, with the given initial dissolved sodium oxalate concentration being 3.59 g/L. To narrow down this range, the solubility tests were re-done with the following changes:

1. Synthetic sodium oxalate was used to eliminate errors in mass of oxalate dosed as well as limit introduced impurities and dilution.
2. Two set of tests were done:
    a. TA adjustment via evaporation only
    b. TA adjustment via caustic addition only

*Both using the same starting liquor.

Initial tests were done using "process" oxalate seed which contains ~30 % w/w sodium oxalate. Comparative tests done using synthetic sodium oxalate at > 95 % w/w yielded noted differences in attainable minimum dissolved sodium oxalate following excess charge. While dosed in excess relative to typical seed charge (< 1.5 % v/v), process seed was found to reduce oxalate concentration in liquor to a lesser extent that reagent grade oxalate. For process seed, a minimum of 2.45 g/L dissolved oxalate remained after dosage at a TA of 490 g/L, whereas for the reagent grade sodium oxalate the value was 1.87 g/l oxalate in 423.9 g/L TA solution created via evaporation, and 2.12 g/L dissolved oxalate in 384.92 g/L solution created via caustic soda addition. Figures 6 and 7 indicate the varying maximum dissolved sodium oxalate concentration following TA adjustment and excess seed addition.

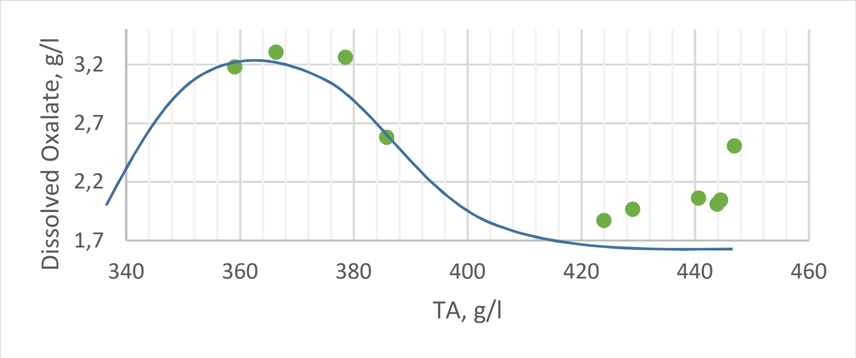

Figure 6. Maximum dissolved sodium oxalate in plant liquor at various TA (via evaporation) and 62.8 °C.

The maximum TA achieved before dissolved oxalate began to reduce was found to be ~370 g/L as shown in Figure 6. Thus, the point of maximum saturation can be said to be ~ 370 g/L. It is therefore expected that attempts to achieve high TA in the process, via evaporation would result in the precipitation of sodium oxalate on heat transfer surfaces, process lines and pumps - a potential "salting out" risk for the shell and tube heat exchangers within the evaporator. However, if purpose-built unit operations are considered, opportunity exist to reduce the dissolved oxalate to > 2 g/L by evaporation driven TA greater than 420 g/L.

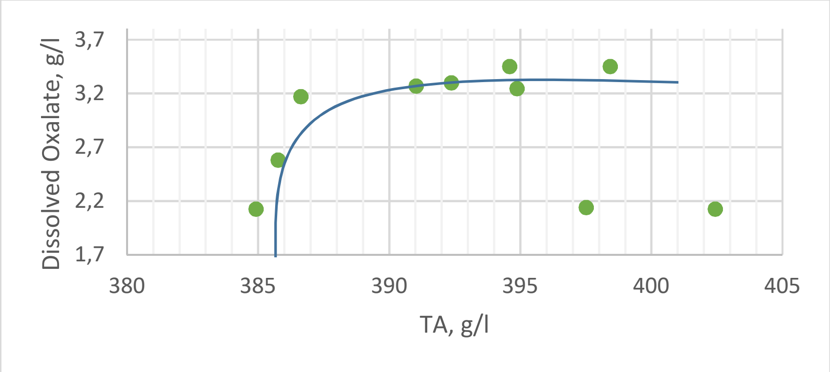

Figure 7. Maximum dissolved sodium oxalate in plant liquor at various TA (via evaporation) and 62.8 °C.

There was some difference in the observed saturation point when TA was adjusted using 99 % caustic soda. As shown in Figure 7, maximum dissolved sodium oxalate in liquor remained relatively unchanged (~3.4 g/L) beyond 390 g/L. There was also a noted shift (increase) of ~25 g/L TA to hit this maximum compared with evaporation. Consistent with theory, this suggest that increasing the caustic content relative to the existing impurities in liquor stabilized the dissolved sodium oxalate such that there was no significant change with further increase in TA [4].

Limited utilization of experimental findings based on the magnitude of the coefficients of the defined parameters was done during plant restoration activities. This, to further reduce the oxalate content of Bayer liquor, both prior to resumption of gibbsite digestion, as well as following normalization of operations. Particular attention was given to increasing seed charge, from a maximum of 1.5 % to 2.5 %, though as noted in the solubility studies it is possible to further improve yield through even higher values. A 5 g/L increase in the press feed TA setpoint presented a two-fold benefit of increasing the liquor concentration with respects to starting oxalate and total soda content (towards, but not exceeding observed maximum oxalate solubility), since regulated upstream via evaporation. Summarized result following implementation are described below in Figure 8 and 9.

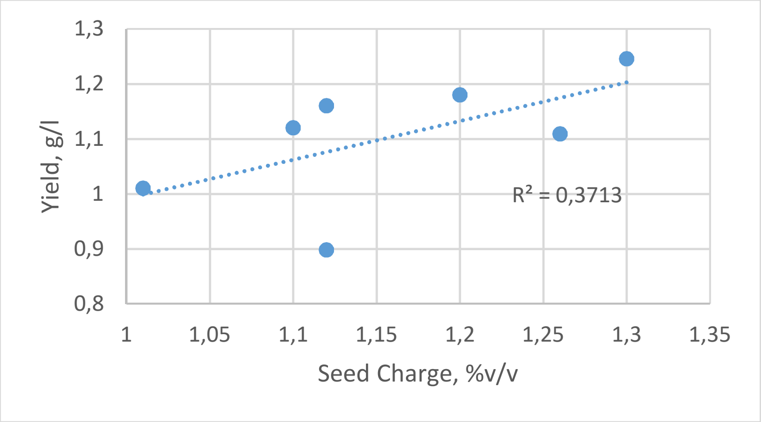

Figure 8. Impact of seed charge on oxalate yield in process trials.

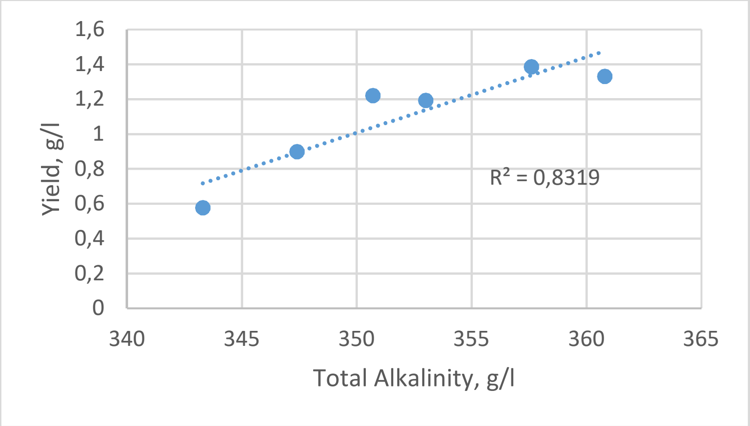

Figure 9. Impact of Total Alkalinity on oxalate yield in process trials.

As predicted by lab trials, increases in seed charge and TA positively affected oxalate yields from trial band to band. However, it is noted that in the process, the correlation differed as shown by the r-square value for each factor. 83 % correlation between TA and yield in process confirms that solubility and the relative increase in concentration of all species present in the liquor during evaporation affected attainable oxalate yield to a greater extent than does seed charge.

During refinery restart, experimental observation was confirmed in the process with regards to attainable oxalate yield at lower initial dissolved oxalate concentrations. With Bayer liquor having remained cold and unmixed for an extended period, ample opportunity was available for reduction of impurities concentrations to equilibrium levels at ambient temperature. Yields averaged 0.84 g/L, below the expected > 1 g/L at steady state operations and confirming the role of initial dissolved oxalate concentration, in this case ~3.2 g/L (versus > 3.9 g/L for steady-state operations.)

A look at the dissolved oxalate in filtrate revealed that a minimum dissolved oxalate concentration of 2.32 g/L was sustained across multiple days, 16 % below typically achieved values at stable plant production. This may represent the limits of capability of the process at existent conditions, but also indicates possible revision point for dissolved oxalate in filtrate target-setting. In the context of oxalate yield and removal, this represents a potential 35 % improvement opportunity with no need for capital expenditure.

3.3 Optimizing Throughput

The performance of two sets of filter cloth of similar pore size (30 microns), but of differing thickness, 350 microns (incumbent, 05-1020-SK025) [7] and 540 microns (trial, 05-1001-C030) air permeability, 5 cfm (05-1020-SK025) and 25 cfm (05-1001-C030) [8] were compared over 8.5 months. Durability, as measured as days run without damage, and throughput were evaluated as shown in Figures 10 and 11. In phase 1 of the trial only 1 press was treated with trial fabric, favorable results led to phase 2 and 3 trials on 2 presses.

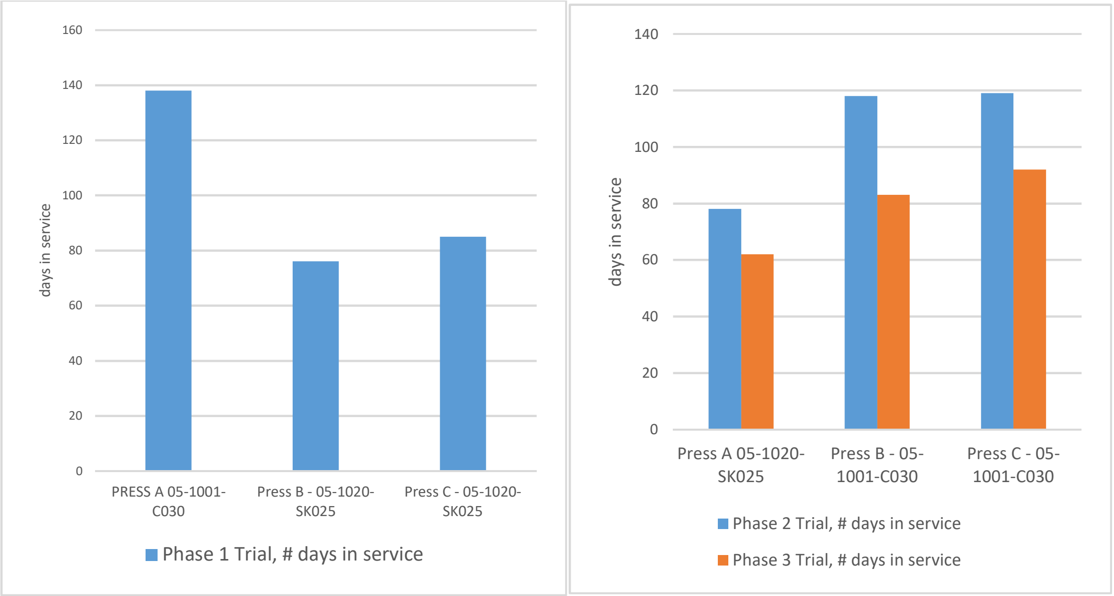

Figure 10. Service life of filter media.

Figure 7 indicates that in phase 1 the test fabric lasted up to 62 % longer than the incumbent fabric. Phase 2 trials showed some decline to 52 % longer run times without damage. Phase 3 trial is ongoing and is expected to yield similar results. In the context of refinery operation, this presents a unique opportunity to extend the time between filter fabric changes beyond the standard 90 days, reducing materials' costs and oxalate removal capacity reduction due to press outage.

However, durability with declining throughput is of little value. Figure 8 indicates that in phases 1 and 2 of the trial average Kelly press throughput remained highest for presses fitted with the higher permeability trial fabric (11 % better in phase 1, 5 % for phase 2). The exception is phase 3, confirmed to contain a mixture of fabrics in press A. This mix combined with shorter days in service to-date may support the elevated flows therein. It should be noted that these average throughputs at extended runtimes were achieved despite the presence of fine, pore-blinding alumina trihydrate values of 1.5–3.50 % and oxalate yield as high as 1.24 g/L average. Thus, the combination of apparent improved durability and higher average throughputs throughout the life of the filter fabric presents the trial material as a suitable candidate for further use, and confirms theory, at-least in this case, that an increase air permeability can be used as a guide to improve throughputs.

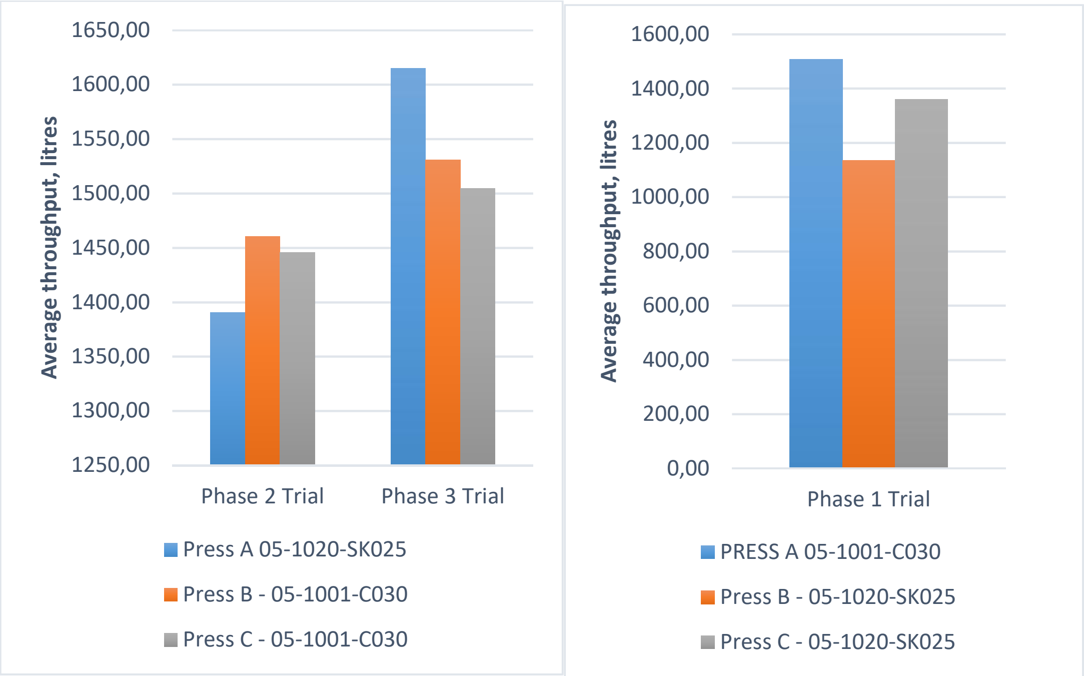

Figure 11. Average Press Flows Across Filter Media Lifecycle.

4. Conclusion

Attainable sodium oxalate removal capacity increase realized through yield and throughput optimization was found to be up to 25 %. This is the equivalent of operating 1.2 additional Kelly presses based on current throughputs, but without the capital required for such an addition. However, continued management and optimization of supporting systems for Bayer liquor conveyance, absolute filter frame availability, and minimization Kelly press cycle time and down times remain critical to sustain maximum process flows. Periodic assessment of oxalate solubility within Bayer liquor is crucial to fine-tuning of developed predictive models and the actual oxalate precipitation and removal process, especially where there continues to be noteworthy changes in bauxite or recovered lake water characteristics. Throughput gains obtained via use of higher permeability and strength fabric should be maximized through standardization of the fabric use across all Kelly presses. Consideration should also be given to revising maintenance cycles to accommodate extended runtimes achieved through use of the more durable trial fabric (05-1001-C030). Additional opportunity remains to explore and document the impacts and interactions of other organic species present with the refinery's Bayer liquor, both in terms of oxalate removal optimization but also general liquor stability.

5. Acknowledgement

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6. References

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