

MAINTAINING AN OXALATE FREE PRECIPITATION CIRCUIT AT AUGHINISH ALUMINA

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Abstract

Maintaining an oxalate free precipitation circuit is key to product quality at Aughinish Alumina. This is achievable by removing oxalate from a side stream of spent liquor by deep evaporation. A small sidestream of spent liquor is evaporated to approximately double the caustic strength so that the oxalate and other salts become supersaturated. A crystallization process follows whereby with no seeding, oxalate and other salts co precipitate to an end concentration. This concentration is still supersaturated and therefore further atmospheric crystallization follows.

The atmospheric crystallization is a seeded process where time, temperature, and surface area are important to allow further oxalate precipitation. There is evidence that seed poisoning occurs in this part of the process. Testwork has shown that theoretical equilibrium is well below that achieved in the plant. How to affect the equilibrium and maximize oxalate production is presented.

1. Introduction

Aughinish Alumina Limited (AAL) is a high temperature plant. The main bauxite source is from Boké, Guinea in West Africa.

During the process of extracting alumina from the bauxite ore, impurities are also extracted. For the Bayer process at AAL, the most important of these is organic material. Boké bauxite contains typically 0.10–0.11% total organic carbon and approximately 10% of this is converted into sodium oxalate during the high temperature digestion process.

AAL maintains an oxalate ‘free’ precipitation circuit by means of controlling the level of sodium oxalate in the liquor. By ‘free’ we mean precipitating seed through the circuit with a level of <0.1% oxalate on the fine seed, which is unwashed.

2. Balance

The oxalate balance shows that we must remove typically 5-6 tonnes per day to maintain an oxalate free

precipitation circuit. 99% of the time we achieve that. Oxalate precipitating on the hydrate seed unbalances the entire process at Aughinish Alumina- excess fines, reduction in quality and a classification circuit out of control.

3. Oxalate Control

The level of sodium oxalate in the liquor is controlled by a salting out process using a side stream of the main plant spent liquor flow.

Oxalate removal in this manner works on the principal of reducing solubility as caustic concentration increases. A typical oxalate solubility curve is shown in Figure 1.

The process consists of concentrating spent liquor in a multi-effect evaporator to ~450 gpl, followed by a series of crystallisation steps — flash crystallisers and agitated tanks. The crystallised solids are deliquored on a number of horizontal belt filters.

A schematic of the evaporation/flash crystallisation process is shown in Figure 2.

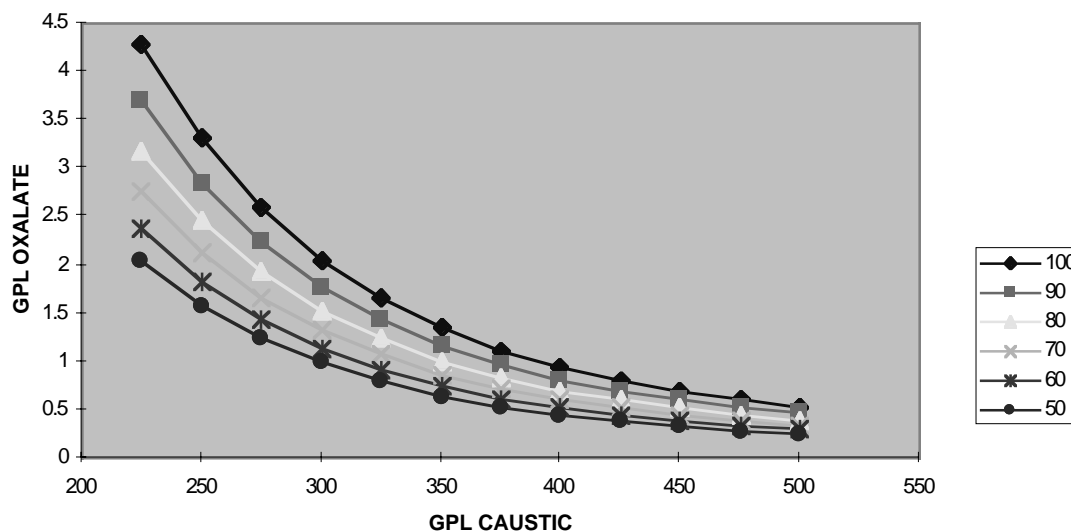


Figure 1 — Oxalate solubility at varying temperatures

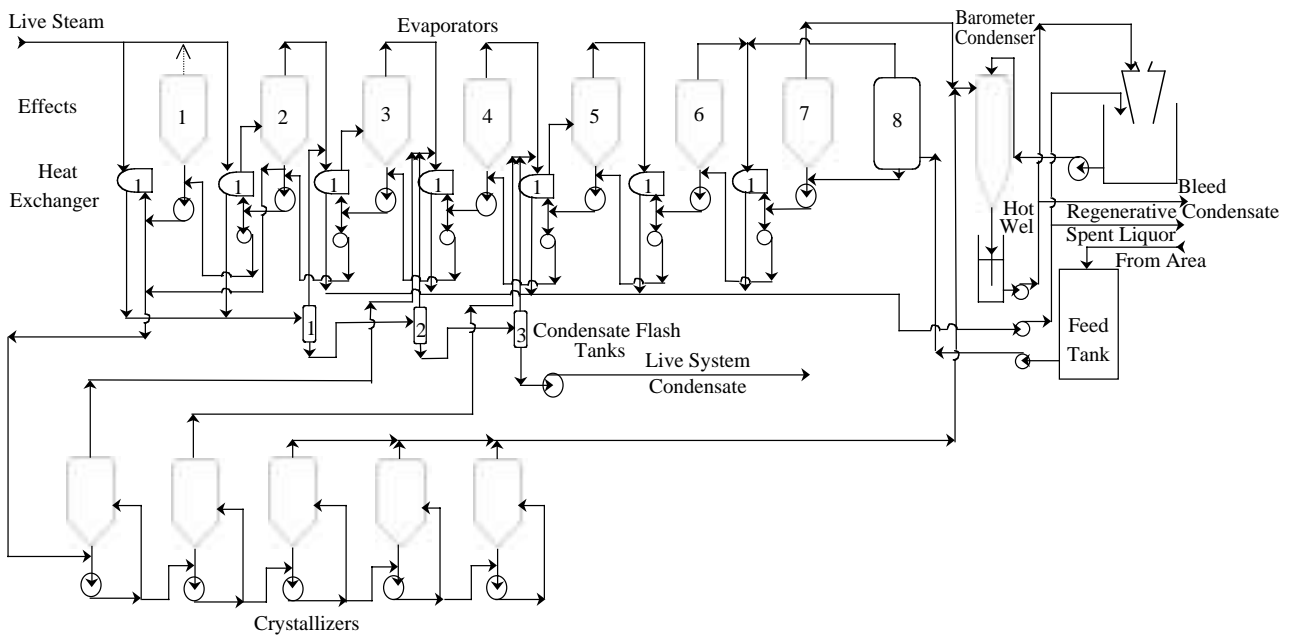


Figure 2

A schematic of the agitated tank/filtration process is shown in Figure 3.

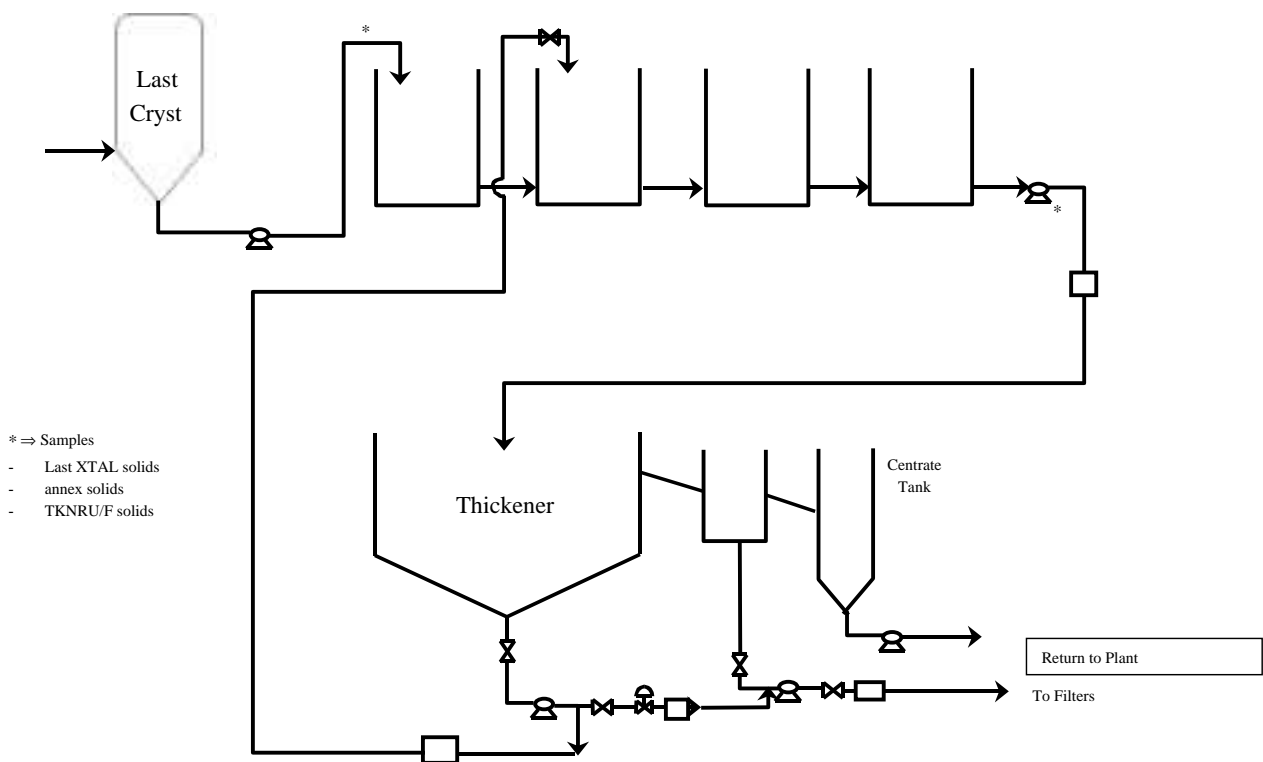


Figure 3 — Agitated tanks/recycle

4. How it actually works

Oxalate removal by the salting out process is theoretically straightforward — evaporate the liquor, precipitate the solids and filter the slurry.

However, in practise a number of complications arise. The oxalate/caustic profile through the unit is shown in Figure 4.

- too little evaporation. If the caustic target is not met then little or no auto precipitation takes place and therefore little or no oxalate removal.
- Too much evaporation. If the caustic target is exceeded then precipitation in needle form is produced. This is impossible to filter and renders the whole crystallisation process as a gel like slurry requiring complete flushing out.

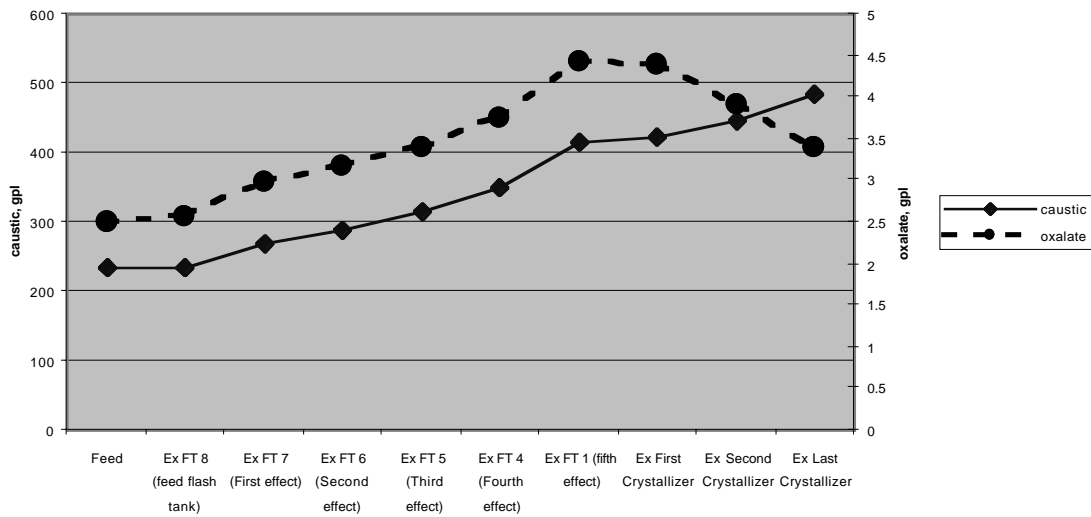


Figure 4 — Caustic and oxalate profile

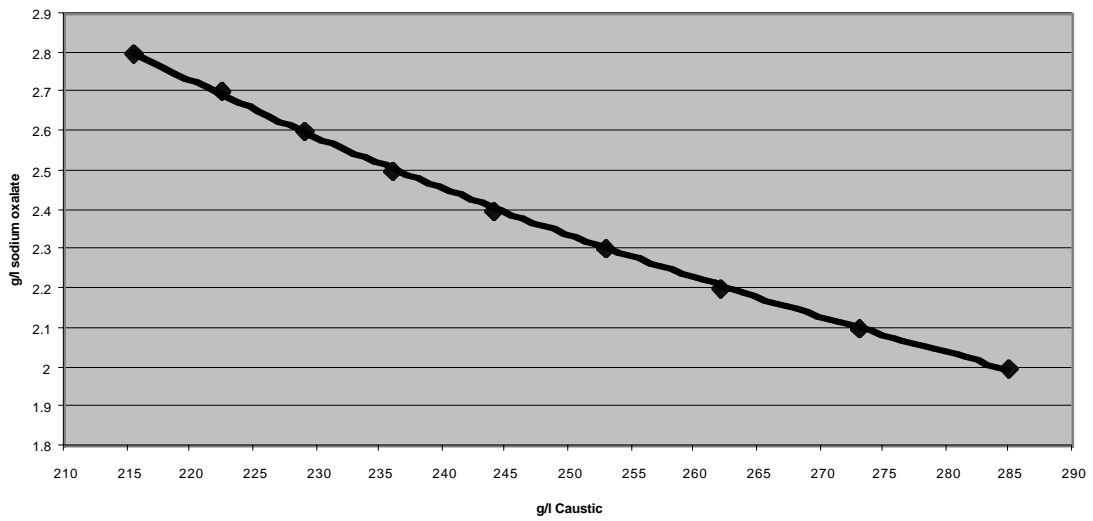


Figure 5 — Oxalate vs Caustic curve spent liquor

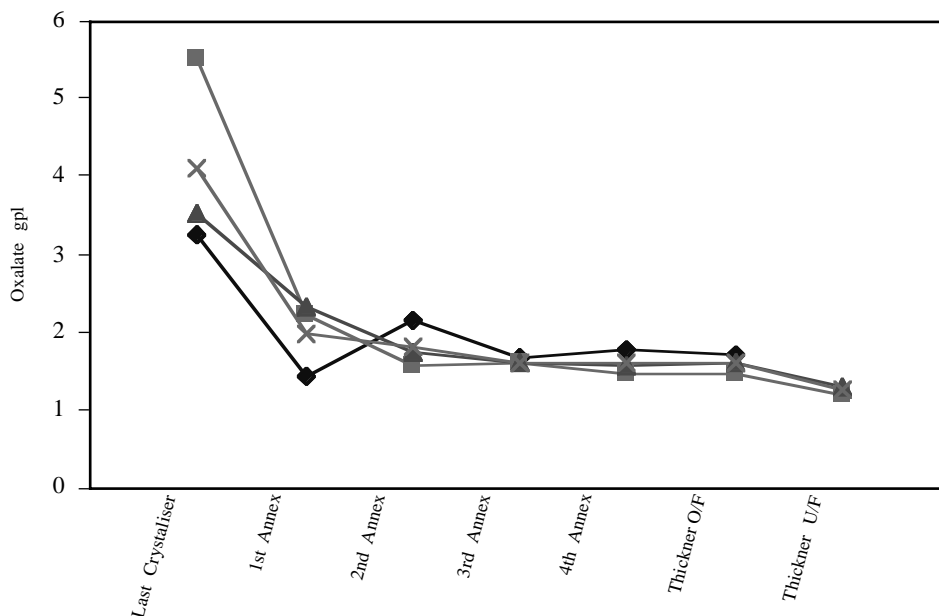


Figure 6

- Feed liquor composition. The feed liquor composition affects oxalate removal efficiency. Co-precipitation is critical in the flash crystalliser section — carbonate, sulphate, and oxalate precipitate to various levels en route to the agitated tanks. By the end of the flash train virtually all the carbonate that is going to precipitate has precipitated. However, only a small amount of oxalate and sulphate has precipitated — the extra agitated residence time is key to optimising the oxalate precipitation.

As the efficiency of this removal process alters or the input to the plant alters then the plant liquor composition varies. This in turn impacts on the ability to precipitate the salts in the first place due to the varying driving force.

Incredible as it might sound, AAL sometimes add sulphate to the process to ensure sulphate is present to aid the oxalate precipitation. Below a critical sulphate level of ~ 1.5 gpl in spent liquor oxalate removal efficiency decreases.

- Oxalate concentration target. Maintaining an oxalate free precipitation circuit is dependent on achieving an oxalate concentration in plant liquor. The oxalate concentration target depends on the spent liquor caustic charged to the digestion and is dictated by a supersaturation level in precipitation i.e. too high a concentration and oxalate precipitates on the hydrate seed and so affects productivity and quality. Too low a concentration and an opportunity for a productivity increase is lost. Figure 5 shows the oxalate target in spent liquor.

5. Poisoning

Precipitating oxalate follows normal precipitation kinetics in that

Precip Rate =

$f k$ (Area, time, temperature, supersaturation)

However, in the AAL salting out process a number of indicators lead to a conclusion of seed poisoning. Increasing residence time or seed charge has little or no effect. Reducing temperature also has little or no effect. Figure 6 is a typical oxalate profile at the agitated tanks process after initial crystallisation. The agitated tanks also receive a recycle stream allowing for increased seed charge whilst the tanks themselves provide ~ 2 hours of residence.

The typical end concentration of oxalate in the liquor exiting the removal process is ~ 1.5 gpl, despite repeated laboratory studies showing 'equilibrium' to the ~ 0.9 gpl. This means we are supersaturated by ~ 0.6 gpl despite the correct conditions to precipitate. Seed poisoning has been concluded to be responsible for this reduction in productivity.

6. Conclusions and Recommendations

AAL need to continuously invest in the oxalate removal process in terms of development and capital.

The latest productivity potential being inhibited currently by seed poisoning is equivalent to ~15% increase in oxalate production. This is the current development focus to find a means of unleashing this.