# LABORATORY TESTING FOR SECONDARY EFFECTS OF BAYER PROCESS ADDITIVES

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## Abstract

Any chemical additive or other material that enters the Bayer circuit has the potential to impact productivity. These additives are routinely screened to detect any adverse effects on precipitation. This screening process often does not take into account accumulation of the additive within the Bayer process.

This paper outlines improved laboratory procedures for testing the impact of additives on precipitation. The method involves both dosed response and partition testing. The partition testing results are used to determine the potential accumulation of the additive in Precipitation. Combined with the dosed response data, this provides a more quantitative estimate of the potential adverse impact of the additive.

Examples of the application of this method are presented.

## 1. Introduction

Any material added to the Bayer circuit has the potential to impact productivity. As a result, all chemical additives including surfactants, defoamers, descaling agents, flocculants, crystal growth modifiers and water treatment chemicals are routinely screened to detect any adverse effects on precipitation. Graham & Davies (1990) have described some of QAL's previous experiences in this area.

At QAL, this screening process has historically been carried out using simple batch bottle tests simulating agglomeration tank conditions. A single fixed concentration was used, regardless of the proposed plant dose or the point of addition of the additive. The potential for accumulation via liquor recycle was dealt with, to a degree, by setting the standard dose at a relatively high level. The potential for generation of harmful by-products during digestion was also covered, by including a bomb digestion step in the test procedure. However, the screening process did not take into account the addition point, dosage rate or partitioning of the additive during solid-liquid separation steps.

Thus, for example, a boiler additive, which can only report to the precipitation circuit via the washer train, would be subjected to the same screening test as a defoamer to be added directly to Precipitation. There is a risk of either (a) unnecessary rejection of additives which do not accumulate in precipitation, or (b) erroneous acceptance of additives by not accounting for their accumulation in precipitation.

To better quantify the precipitation risks, an improved method was developed that takes into account the proposed plant dose and flow on effects from the point of addition. This method uses a dosed response test to generate a precipitation response curve. This is then combined with partition testing and a simplified plant mass balance to estimate the maximum potential accumulation of the additive within Precipitation.

## 2. Discussion

### 2.1 Previous method

Historically, all additives at QAL were tested using simple batch bottle tests simulating agglomeration tank conditions, using plant liquor and seed, as outlined in Figure 1.

### 2.2 New Method

### 2.2.1 Dosed Response Testing

In the new procedure, the laboratory method is similar to the previous method, but includes a range of concentrations based on the proposed plant dose. Doses of 1, 50, 100 and 200 times the proposed plant dose are generally tested with 4 replicates for the blank and 9 for each additive dose. This gives a total of 40 bottles, which is a compromise between the number of replicates statistically required to detect differences of $3\sigma$ with 90% confidence and ensuring that the full dosed response trial can be run in one water bath (limit of 42 bottles).

This generally results in a linear relationship between yield and dose, as shown in Figure 2 (additional dose rates were tested for this additive). The relationship can then be used to determine a dose for subsequent partition testing, if required. In this case, there is a 2.5g/L yield loss per 100mg/L. Knowing the repeatability of the method to be $\pm 0.2$ g/L ($1\sigma$), further bottle tests could be used to infer concentrations within 25mg/L ($3\sigma$). For further partition testing, a starting concentration of 500mg/L could be used to predict coefficients to within 5%.

### 2.2.2 Partition Testing Procedure

Methods for determining the partitioning of different additives have been discussed in the literature (Bell, 1976; Graham & Davies, 1990; Patra, Panigrahi & Satapathy, 1993). The method adopted for the current work uses yield loss in precipitation tests to infer the partitioning of harmful components. The procedure is described below, using the example of the mud settler after digestion.

One area where partitioning of an additive could occur is between Settler Underflow, which is pumped to the washer circuit for caustic recovery before disposal of the mud and Settler Overflow, which is pumped to Precipitation via the Press Floor. To determine the partition coefficients, a sample of Settler Feed is collected and allowed to settle in the laboratory. Precipitation bottle tests are carried out on the decanted overflow. The additive is dosed as required, as outlined in Figure 3. The procedure results in three liquors for precipitation testing:

1. No additive
2. Additive added directly to precip test bottle
3. Additive added prior to settling simulation

The first sample corresponds with 0% of the detrimental components of the additive reporting to settler overflow. Conversely, sample 2 corresponds with 100% of the detrimental components reporting to settler overflow. Sample 3, from the actual simulation, will lie somewhere in-between. The percentage of the harmful components of the additive which report to settler overflow is estimated using the equation:

$$\text{Partition Coefficient} = \frac{\text{Yield 1} - \text{Yield 3}}{\text{Yield 1} - \text{Yield 2}}$$

Similar procedures have been developed for other areas of the process as summarised below.

Tertiary Feed to Tertiary Thickener Overflow (TTOF)/ Tertiary Thickener Underflow (TTUF)

In the final stage of classification, spent liquor (TTOF) is pumped to Digestion, while TTUF is pumped to the seed washing circuit. To determine the additive partitioning between the overflow and the underflow, a sample of tertiary feed is collected, slurried with additive as required and filtered. Precipitation bottle tests are done on the filtrates.

*Digestion*

Some additive components may generate harmful by-products during Digestion, while others may be rendered harmless. To determine this, a laboratory bomb digest is done using pregnant liquor from the plant dosed with additive as required, followed by precipitation bottle tests on the resultant liquors.
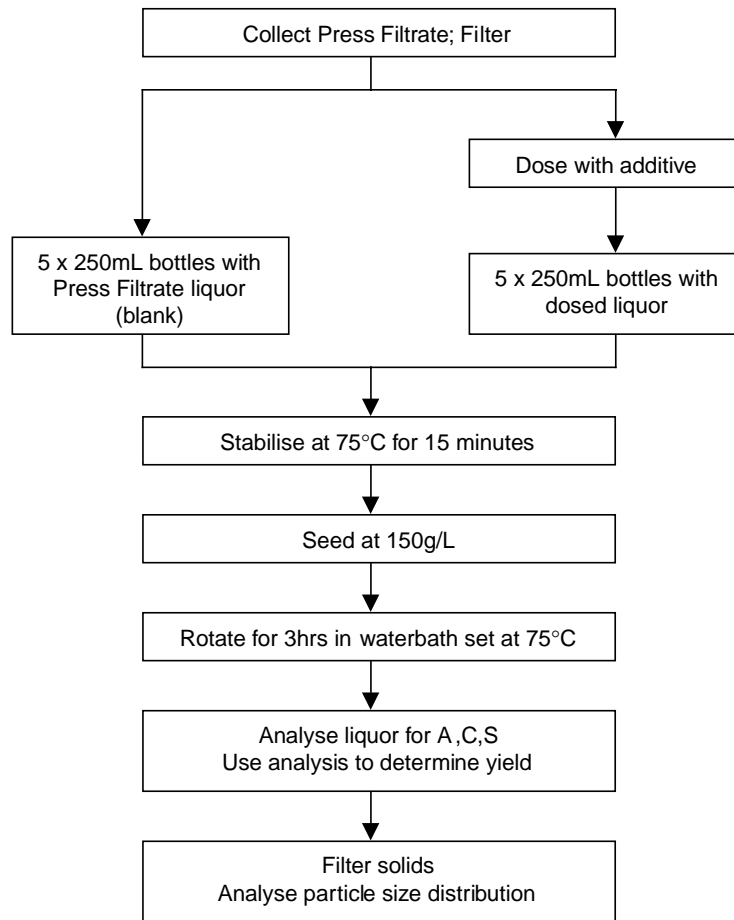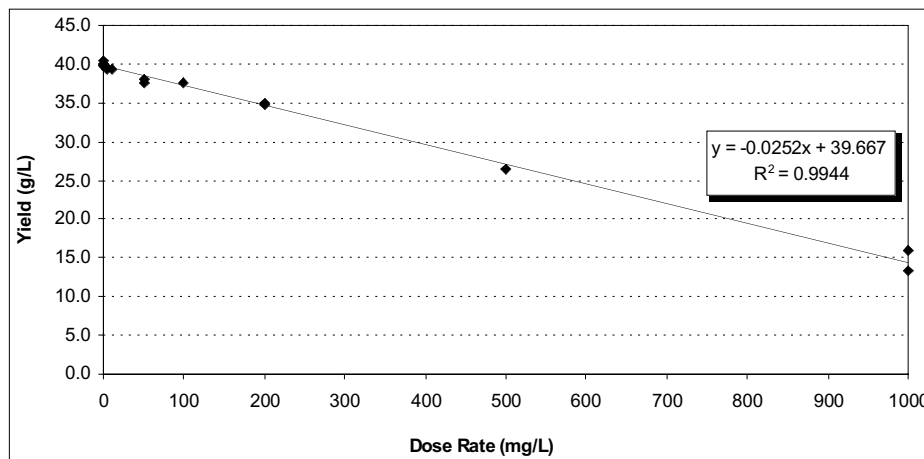


Figure 1 — Previous Testing Procedure



Figure 2 — Dosed Response Results

*Settler Overflow to Liquor to Precipitation
(L-P)/Press Cake*

To reduce the solids in pregnant liquor overflow from the Settlers, the liquor is filtered through Kelly Presses using tricalcium aluminate as filter aid. The filtrate is then transferred to Precipitation. This process is simulated in the laboratory, by adding filter aid to pregnant liquor and then filtering.

*Washer Train to Dilution/Last Washer Underflow
(LWUF)*

In the countercurrent washer circuit, overflow from washer (n-1) mixes with underflow from washer (n + 1) in the feed pipe of washer (n). To determine the partitioning between underflow and overflow in a particular washer, the washer conditions are simulated in the laboratory, using a similar procedure to that described above for the settler. Although the wash circuit at QAL has 5 washing stages, the simulation of only a single stage washer is used for simplicity.

*Seed Wash to A-Filtrate/Washed Seed/B-Filtrate*

The oxalate control plant can be split into two sections — seed washing and oxalate destruction. In the seed washing section, a two stage washing system is used. In the first stage, the seed is deliquored with a displacement wash of cold water to decrease the caustic concentration of the slurry (A-Wash). The second stage consists of a hot water wash, where the sodium oxalate is dissolved and removed in the filtrate (B-Wash). The washed seed is returned to the circuit and the filtrate is pumped to the oxalate destruction section. To determine partitioning in the seed wash section, this two stage washing system is simulated in the lab, with the final bottle tests using the seed prepared in the lab and plant pregnant liquor.

*Oxalate Destruction to Lime Settler Overflow
(LSOF)/Lime Settler Underflow (LSUF)*

In the second stage of oxalate destruction plant, lime is added to the filtrate from B-Wash (B-Filtrate) to react with sodium oxalate to precipitate insoluble calcium oxalate. The slurry is allowed to settle in a thickener and the calcium oxalate solids removed to waste, while the liquor is returned to the circuit. This process is simulated in the lab to determine the amount of harmful components reporting to LSOF.

*Primary Underflow (PTUF) to Kiln Feed/Filtrate*

Hydrate from the primary thickener underflow is washed and filtered before calcination. The soda recovered from the washing step is returned to Precipitation. To determine the partitioning between kiln feed and filtrate, a sample of primary underflow is dosed with additive as required, washed and filtered, with the final bottle tests using the seed prepared in the lab and plant pregnant liquor.

A procedure for simulating the Classification circuit was not developed. However, the assumption that that the additive partitions in the same ratio as the gibbsite surface area was adopted.

**2.2.3** *Plant Mass Balance*

Once the appropriate partition testing has been completed, the results are entered into an Excel spreadsheet to calculate the accumulation in the First Precipitator Tank. The model is based on the simplified flow sheet of the process shown in Figure 4. From these results, a decision can be made regarding further testwork or plant trials of the proposed additive.

Although specific to the current QAL process, the procedure can be readily adapted to simulate other flowsheets if required.

**2.3** *Examples*

**2.3.1** *Additive "x"*

After completing the settler simulation as shown in Figure 3 for Additive "x" at 1000mg/L, the yields obtained were:

Bottle 1 (100% to underflow) = 23.4 g/L
Bottle 2 (100% to overflow) = 9.4 g/L
Bottle 3 (settler simulation) = 17.8 g/L

The calculation of the partition coefficient indicated that 40% of the harmful components reported to the Settler Overflow.

The remaining partition coefficients were also determined:
Tertiary Feed to TTOF/TTUF
— 58% of the harmful component report to TTOF
Digestion to Settler Feed
— 4% reports to Settler Feed (ie. 96% destroyed in Digestion)

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                    ┌─────────────────────┐
                    │ Collect Settler Feed │
                    └─────────────────────┘
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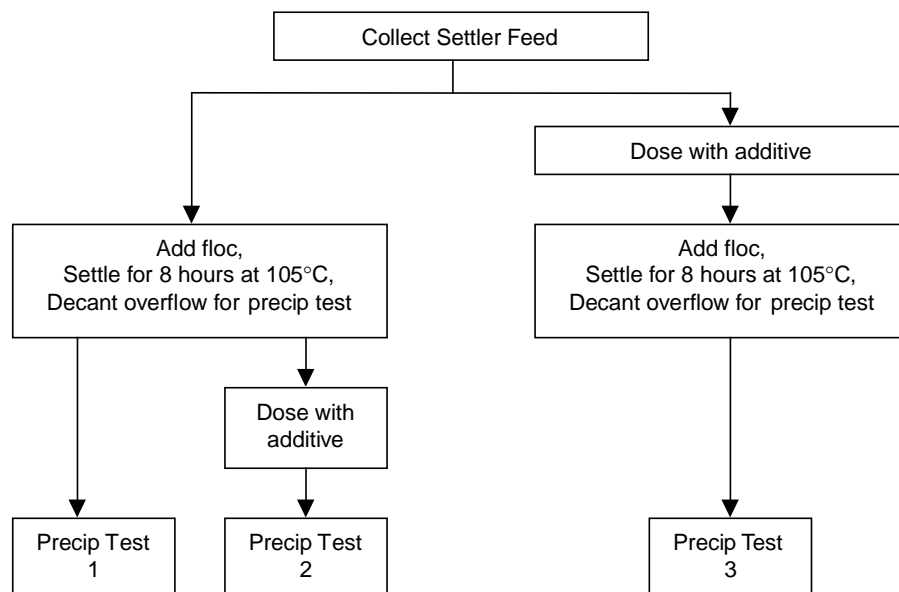


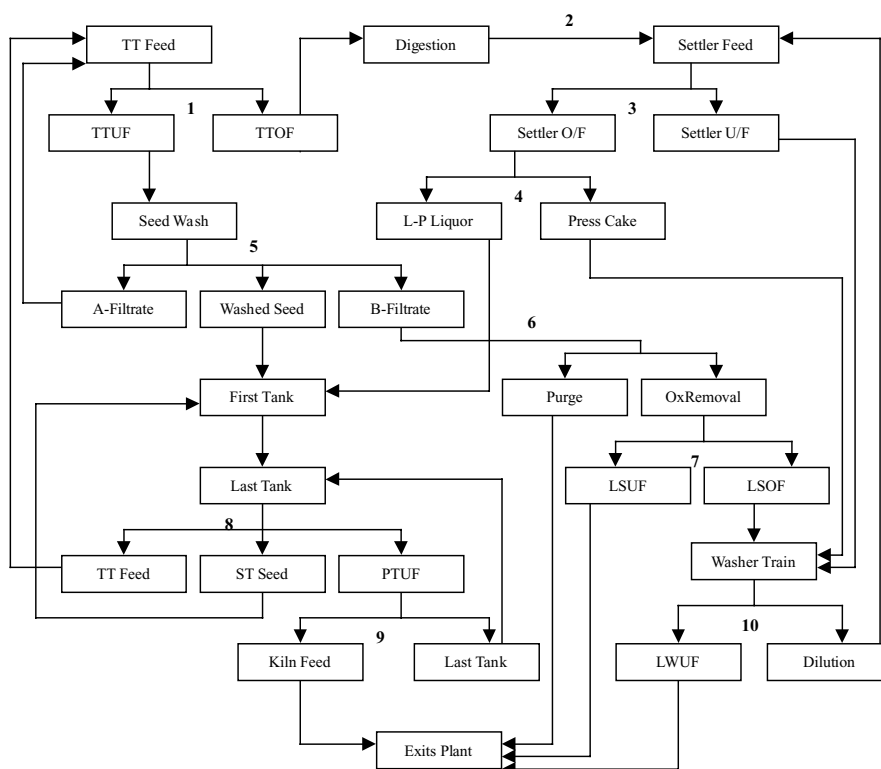Figure 3 — Simulation of Settler Conditions

Figure 4 — Partitioning Flow Sheet

Settler Overflow to L-P/Press Cake
— 29% to L-P (ie. 71.3% adsorbs on press cake)
Washer Train to Dilution/LWUF
— 81% to Underflow when simulating Lead Washer
— 93% to Underflow when simulating Last Washer
Seed Wash to A-Filtrate/Washed Seed/B-Filtrate
— 93% to A-Filtrate
— 4% to Washed Seed
Oxalate Destruction to LSOF/LSUF
— 8% to LSOF
PTUF to Kiln Feed/Filtrate
— 10% to Filtrate
From the model, these results indicated that:
— the addition of 10mg/L of this additive to the Tertiaries would result in 7.3 mg/L in First Tank
— the addition of 10mg/L to Settler Feed would result in 3.4mg/L in First Tank
— the addition of 10mg/L to the Washers would result in 0.2mg/L in First Tank

Thus it can be seen that the addition point plays a strong role in determining the magnitude of the precipitation impact, and that this particular additive does not tend to accumulate to high multiples of the feed rate.

### 2.3.2 *Evaluating an Alternative Water Source*

The procedure can be readily adapted to individual cases if required. For example, the methodology has been recently used for evaluating an alternative water source for QAL. Additional evaporation steps had to be included to concentrate components in the water, to reduce the volume of water required for dosed response testing.

The initial dosed response test indicated that at the proposed dose there was the potential for detrimental components to accumulate in Precipitation and give significant yield losses. Assuming worst case partition coefficients in all areas, it was shown that a yield loss of up to 1.5 g/L was conceivable. Analysis of the partition model showed that the most critical partition coefficients were the mud washers and the generation of by-products in digestion.

Therefore, partition coefficients for the digestion and washer areas were determined to assess the potential accumulation in precipitation. The results showed that 100% partitioning of harmful components to washer underflow occurred, as well as about 90% destruction in digestion. The calculated accumulation in precipitation was therefore zero and no yield loss is expected.

Based on these results, it was recommended that the proposed water source be considered for use in the plant.

### 3. Conclusions

A laboratory method has been developed for determining the partitioning characteristics of additives, which can be used in conjunction with dosed response testing to calculate an accumulation factor in Precipitation.

The advantage of this method compared to the previous method is that it takes into account addition points, removal routes and accumulation mechanisms in assessing the risk associated with a given additive.

Although the method described is specific to the QAL process, the procedure can be readily adapted to other flowsheets.

**REFERENCES**

**Bell, G.** (1976). The Partition of Starch between Bayer Plant Liquor and Red Mud. Light Metals, 99–113.

**Graham, G.A., Davies, T.J.** (1990), Chemical Additives for the Bayer Process — Buyer Beware. Second International Alumina Quality Workshop, 142–152.

**Patra, A., Panigrahi, A.K., Satapathy, B.K.** (1993). Evaluation of Impurities Level and their effect across the Precipitators in the Bayer Process. Light Metals, 135–139.