Gardanne Refinery – Lessons Learned on Temporary Shutdown of Bayer-type Process

Laurent Guillaumont[1], Valérie Esquerre-Cacha[2] and Serge Campanaro[3]
1. Technology Director
2. Technical Department Manager
3. UODP and Calcination Production Manager
Alteo Alumina, Gardanne, France
Corresponding author: laurent.guillaumont@alteo-alumina.com
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Abstract

The Gardanne plant, cradle of the Bayer process, transformed itself in 2022 by suspending digestion of bauxite after nearly 130 years of operation, in response to local environmental constraints. As the focus continues to shift towards specialty alumina, controlling precursor quality remains a major challenge, leading the plant to maintain a variation of the Bayer process as hydrate dissolution/re-precipitation process to control quality, known as the UODP (Unit Operation of Dissolution and Precipitation) process. On the other hand, the variety and specificity of our markets, which can lead to significant upsets in volume throughout the year, demand great flexibility in terms of production rates and quality control.

In the second half of 2023, a sharp drop in demand forced a drastic reduction in production, and whereas the high price of energy, Alteo Gardanne decided to stop production of the UODP process for several weeks on two occasions to limit stocks while minimizing energy consumption. This paper reviews the preparation and anticipation of risks, the operating conditions of these shutdowns and their consequences on the quality and the operations, which were generally very well controlled. These two shutdowns demonstrate that, under certain conditions, a Bayer-type process can be shut down without any major risk to hydrate quality.

Keywords: Hydrate digestion, Hydrate quality, Shutdown, Energy saving.

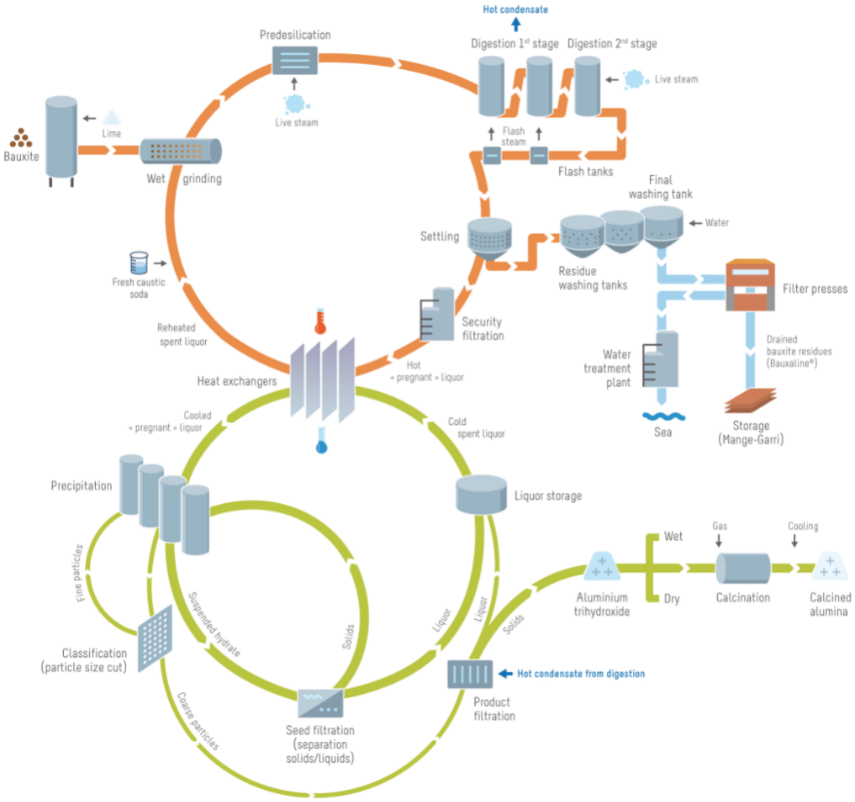
1. Alteo Transformation

1.1 Nature of the Change

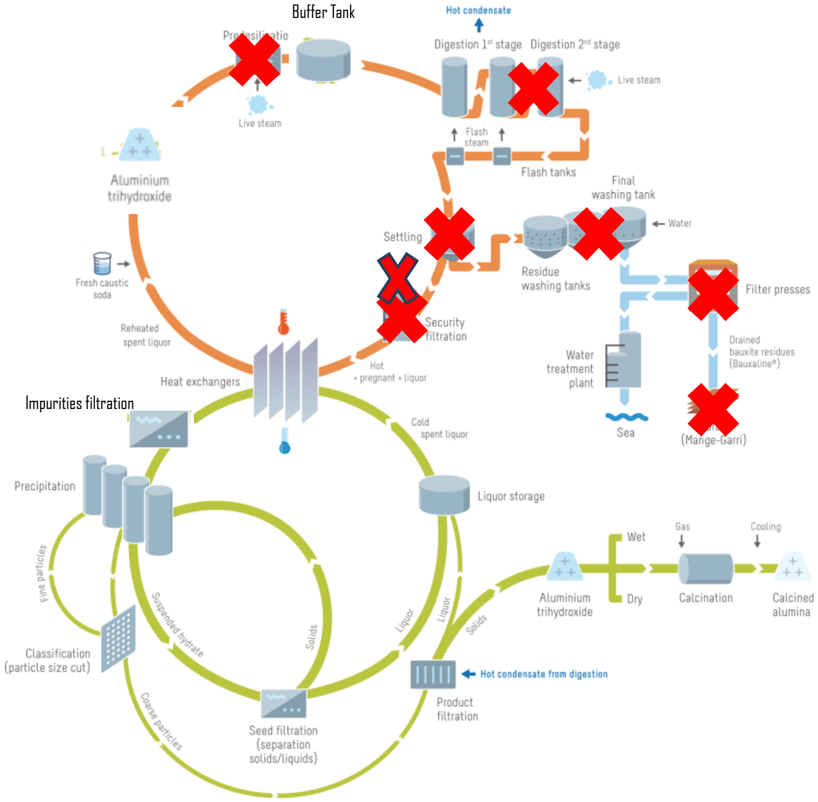
As a reminder, the core steps of a Bayer process are:

- To dissolve alumina hydrate from bauxite, using concentrated caustic soda at high temperature in sodium aluminate liquor;
- Discard the insoluble material, known as bauxite residue or red mud via a counter-current washing circuit;
- To precipitate alumina trihydrate in a controlled manner from sodium aluminate liquor, decreasing both temperature and caustic concentration, and to separate this solid from the liquor.

The new process flow sheet, using commercial hydrate as a raw material instead of bauxite, has been simplified as this feed stock does not generate any solid residue to be washed and discarded: settling and washing residue areas have thus been definitely shut. Other parts of the process (digestion and precipitation) have been conserved, ensuring the production of the same product for the calcination step. The name “Unit Operation for Dissolution and Precipitation” (UODP) has therefore been put forward for the simplified process and will be used throughout the text. A schematic overview of the simplification is shown in Figure 1.



Bayer process with bauxite



New UODP process without bauxite

Figure 1. Schematics of Bayer process vs UODP process.

1.2 Hydrate Quality Focus

As already mentioned, the core objective of this transformation was to control hydrated alumina quality by avoiding upstream process change to the current technology process tools. Alumina hydrate quality can be fully described by its physical properties and chemical analysis.

In terms of physical properties, alumina quality is described by particle size distribution (PSD) and hydrate morphology. Both are dependent on precipitation conditions which are controlled through the technology design.

Regarding chemical impurities, as a natural mineral resource, bauxite contains traces of several metals. The strength of the Bayer process being that alumina (hydroxide) is soluble in caustic solutions, whereas very few of the other metals are soluble in caustic solutions. Therefore, these trace metals are more readily found in bauxite residue and not in the final product, alumina tri hydrate. The main impurities in hydrated alumina are sodium, iron, calcium and silica which must be controlled. This means that the principles of quality control, and consequently the risks of loss of quality control, remain the same between a Bayer and a new UODP process, and are essentially based on precipitation conditions for a given sodium aluminate liquor.

2. Background and Preparation

The UODP process has been designed for a given nominal production, with the possibility of reducing it by up to 25 % without generating too many constraints on quality and limiting energy consumption. Throughout 2023, sales and sale prospects fell drastically and rapidly, resulting in a production rate less than 50 % of nominal level. As a result, quality control has become more challenging and specific energy consumption has risen sharply against a backdrop of soaring energy prices. This is why another operating mode for UODP process was envisaged to reduce average production to around 50 % of the nominal level, in order to reduce production costs without having a long-lasting impact on quality.

Considering this new process configuration and the relatively low organic carbon and silica levels in the liquors, "batch operation", i.e. with process shutdowns lasting several weeks, were designed and implemented in the summer of 2023. To prepare for these shutdowns, the different process configurations of the units were defined and studied, in particular, how to maintain a minimum temperature in the precipitation unit. A mitigation plan was drawn up to deal with the associated operational risks and loss of quality control.

3. Shutdown Operating Configurations

3.1 Configurations for the Unit Operations

3.1.1 Digestion

The only solution envisaged was a complete shutdown, with no alternative, i.e. no introduction of fresh hydrate nor heating by steam.

3.1.2 Precipitation

The objective was to maintain normal operation of the precipitators, i.e. to avoid any settling and to ensure a minimum temperature. In addition, the last precipitator must not overflow into the overflow safety tank, as was usually the case, to avoid significant heat loss through evaporation. Three operating modes were then considered, with seed filtration deactivated in all cases

1. A complete shutdown without recycling

2. Recycling of slurry from the last precipitator to the first via purge circuits or seed filtration piping.

3.1.3 Steam Production

To cover the need to for heating at any time, a boiler was kept in operation, with all unused steam lines purged and isolated. A few tons of steam were therefore continuously consumed.

3.1.4 Other

Wastewater treatment unit remained in service.

3.2 How to Heat Precipitation: with or without Dilution?

Three options have been identified and used:

1. Injecting 4-bar live steam to the seed tank: the flow rate is limited and will dilute the circuit with steam, but this is very simple to implement and easy to start and stop. This solution was chosen when it did not increase the volume of the recirculating circuit (steam injection to compensate for natural evaporation).
2. Heating the slurry through a monotubular heat exchanger, usually operated for chemical cleaning of precipitators. This has the advantage of heating without dilution and in a controllable way, but with a high risk of blockage when heating slurry. This solution was chosen when the temperature could not be maintained despite the addition of live steam in seed tank.
3. Batch heating of the sodium aluminate liquor through the monotubular heat exchanger, then transfer of the contents to the precipitation line when sufficiently hot requires restarting of seed filtration. This solution was chosen only for the complete restart of the UODP process loop.

4. Operational and Quality Risks Mitigation

4.1 Keep the Precipitators Running Smoothly Until the UODP Process Loop is Restarted

The main operational risk consists in keeping the precipitators running smoothly without having to restart the seed filtration. This means minimizing any ingress of water or liquor into the precipitator, without disregarding the operating routines that ensure its correct functioning over time. In particular, the procedure for precipitator purge has been reviewed to adapt frequency, duration of liquor injection and destination of drained slurry (which could not be entirely sent back to the precipitation line). The objectives are as follows:

- to adapt frequency, duration of liquor injection and destination of drained slurry (could not be entirely sent back to the precipitation line);
- to keep high solid content in precipitators to limit settling.

Another key point is the maintenance of filters to be ready to restart as soon as necessary, in particular, the state of the filter media (cloths). Hence, a chemical cleaning at the time of shutdown followed by a prolonged hot water rinse has been implemented to limit any risk of loss of flexibility and filterability leading to loss of efficiency during restart.

4.2 Preliminary Laboratory Tests for Quality Control

Shutdown operation of the UODP results in precipitation cooling (with the expected precipitation of impurities from the liquor, notably oxalate and silica) and increased residence time, which impacts hydrate quality during shutdown but also at the restart, when a hot liquor is brought into contact with a cold slurry.

To mitigate these quality risks, laboratory tests were carried out to quantify the effects of cooling as a function of the temperature and to evaluate restart conditions for two different hot liquor temperatures. The experimental design can be summarized as follows:

1. Slurry sampling directly from a precipitator (not in the first precipitator, since precaution will be taken to desaturate the liquor before shutdown)
2. Distribution in different laboratory reactors for different durations
3. Three (3) temperature settings: ambient temperature (32 °C), 40 °C and 50 °C

4.2.1 Laboratory Tests to Simulate Shutdown

Alumina / Soda weight Ratio (RP)

The evolution of the RP over time shows a decrease for 7 days, after which it hardly moves at all, meaning that there is no more hydrate precipitation. At the same time caustic concentration increases and then stabilizes, as shown in Figure 2.

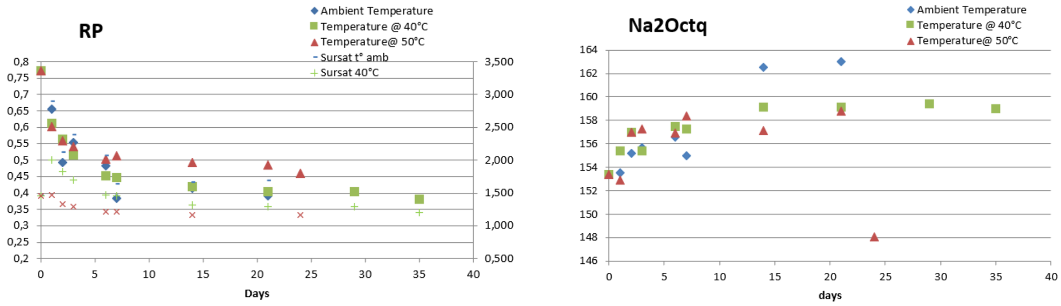


Figure 2. Laboratory tests: evolution of RP and caustic concentration.

Oxalate precipitation and nucleation consequences

Figure 3 shows that oxalate precipitation is observed as early as 3 days at ambient temperature, after 5 days at 40 °C and around 10 days at 50 °C, and in this last case while being very limited up to 20 days.

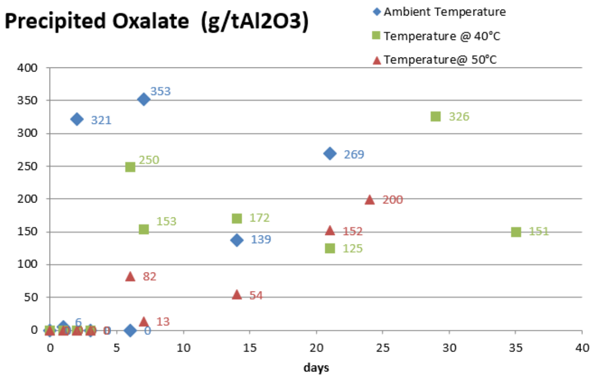


Figure 3. Laboratory tests: precipitated oxalate.

There was little impact on nucleation: between 40 and 50 °C, particularly at days 14 and 21, there is no marked trend, as the results can be considered as falling within the measurement variability.

At ambient temperature, where oxalate precipitation is observed much earlier and is more intense, the increase in ultrafine level is significant.

Impurities

The initial silica level in the liquor was 0.40 g/L (~ 0.285 % ctq) and around 35 to 50 ppm on hydrate seed. A theoretical calculation from these data (silica level of the sodium aluminate liquor and the initial silica hydrate seed content) gave an increase between 5 and 10 ppm by week (without hydrate precipitation). Laboratory results depicted in Figure 4 reveal no significant variation in silica in hydrate while a very slight drop in liquor concentration was observed.

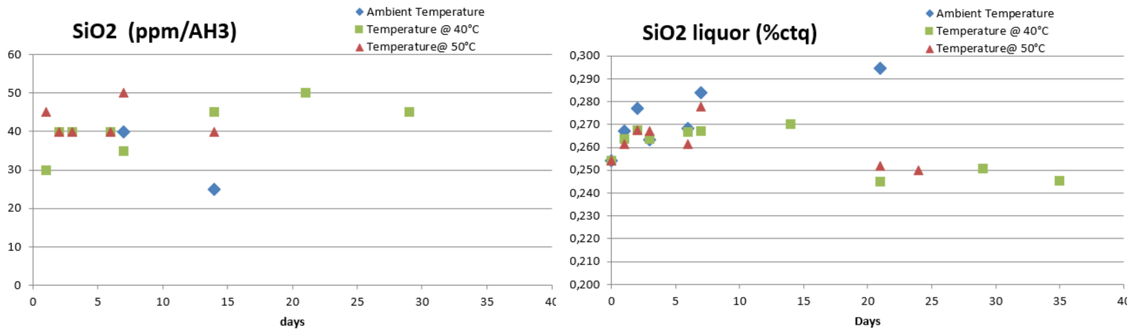


Figure 4. Laboratory tests: silica impurity.

4.2.2 Laboratory Tests to Simulate Restart Conditions

The aim of these tests was to reproduce restart conditions where a cooled precipitation-slurry is brought into contact with hot sodium aluminate liquor, previously heated at the digestion. Two hot liquor temperatures were tested, while three cooled-down temperature were trialed.

RP evolution

- With 80 °C liquor, no significant difference was observed compared with the initial value.
- With 95 °C liquor, a more marked increase is observed, particularly with the 50 °C initial slurry (where the contact duration appears higher).

Consequences on hydrate granulometry

In the 50 °C case, substantial fining is observed when in contact with a 95 °C liquor (increase in < 15 µm), in contrast to contact with an 80 °C liquor, see Figure 5.

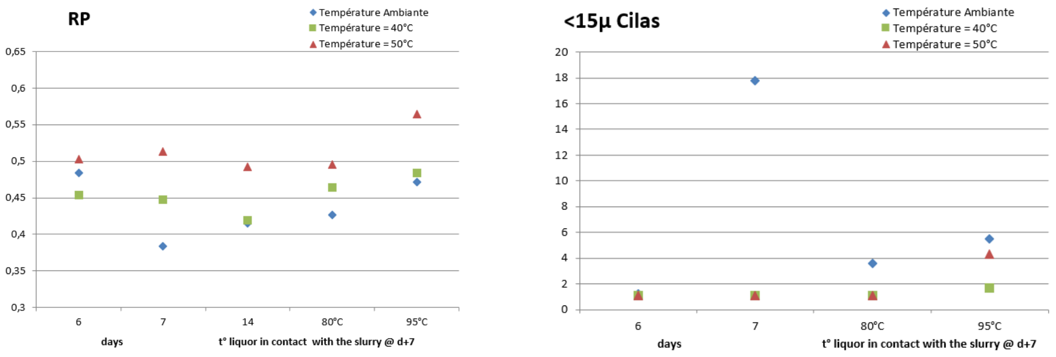


Figure 5. Laboratory tests: "RP" and "< 15 µm" evolution upon restart.

4.3 Recommendations

Based on these laboratory tests, for the shutdown, the main initial conditions targeted are low soda concentration, high precipitation solids and a minimum temperature of 50 °C. For the restart, an initial start-up temperature of 80 °C for pregnant liquor is chosen, followed by a slight increase in temperature over 24 hours until the final target temperature is reached.

Quality monitoring is of course a crucial point during the whole process: reinforced follow-up must be carried out throughout shutdown and restart (non-exhaustive list): nucleation and hydrate granulometry, liquid and solid phase oxalate (LPO and SPO respectively), caustic soda concentration in the liquor, various impurities in the liquor and hydrate, especially silica and iron.

5. First Shutdown

The first shutdown lasted three weeks; it took place from July 17th to August 7th, 2023. The choice of this summer period for Gardanne's first experience with a prolonged shutdown was taken to limit the risk of a sudden and uncontrollable cooling. The average outside temperature was around 25 °C. Initial liquor conditions are listed in Table 1.

Table 1. Aluminate liquor characteristics.

Head precipitator temperature	80 °C
Solid content in precipitation	550 g Al_2O_3/L
1st head precipitator RP	0.72
Caustic soda concentration	140 g Na_2O/L
Silica concentration	0.38 g SiO_2/L
LPO oxalate concentration	0.22 C_{ox} (%Na_2O_{total})

5.1 Main Results

5.1.1 Temperature

The lowest temperature of the last precipitator was 48 °C, corresponding to the starting point. Otherwise, it never dropped below 52 °C, as shown in Figure 6.

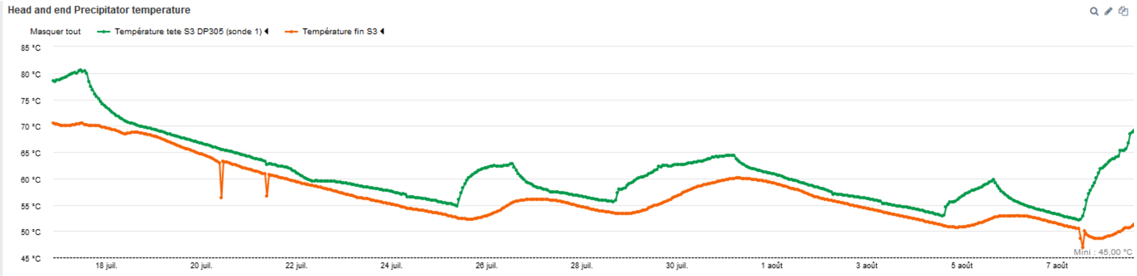


Figure 6. First shutdown results: 1st and last precipitators temperature (scale of Y-axis [45-85 °C]).

5.1.2 RP and Soda

Data outlined in Figure 7 show that the Al_2O_3 / Na_2O weight ratio decreased from 0.72 to 0.47 during the first 10 days and then remained stable with slight rises when the slurry was heated by the mono-tubular heat exchanger (indirect heating).

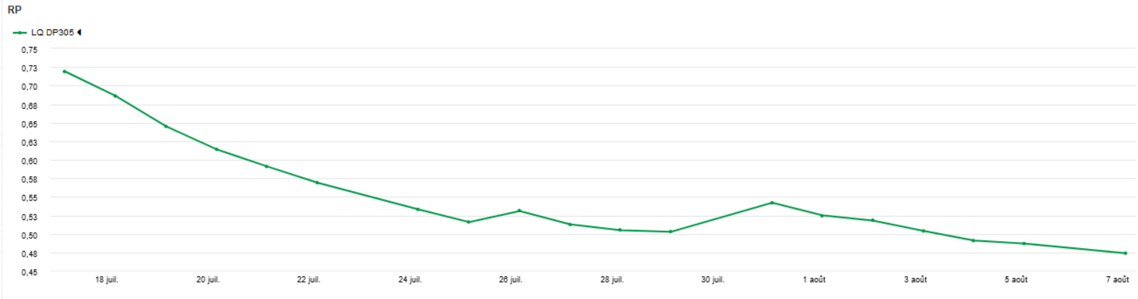


Figure 7. First shutdown results (RP= ratio alumina/soda; scale of Y-axis [0.45-0.75]).

As expected, the soda concentration liquor increased as the RP decreased, as shown in Figure 8.

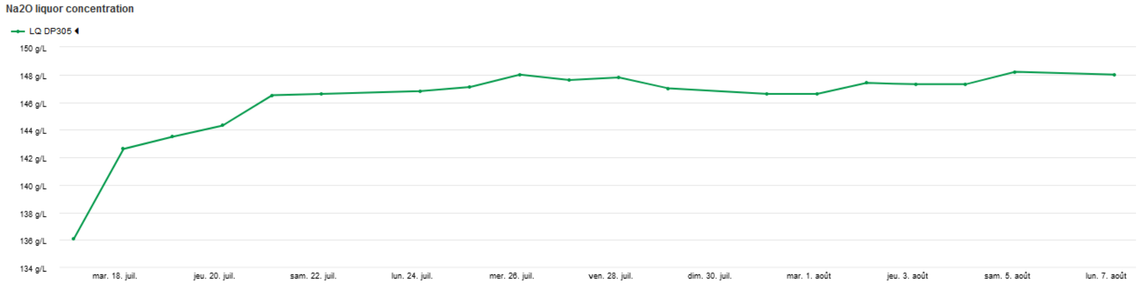


Figure 8. First shutdown results, soda concentration (scale of Y-axis [134-150 g/L Na2O]).

5.1.3 Oxalate and Nucleation

The Cox / Na2O ratio (LPO) remained stable overall between 0.22 % and 0.21 % (see Figure 9) confirming the absence of oxalate precipitation. As a result, a fining crisis was avoided. However, the number of very fine particles doubled between the beginning and end of the shutdown, as shown in Figure 10, probably due to some form of attrition in the indirect slurry heater and piping.

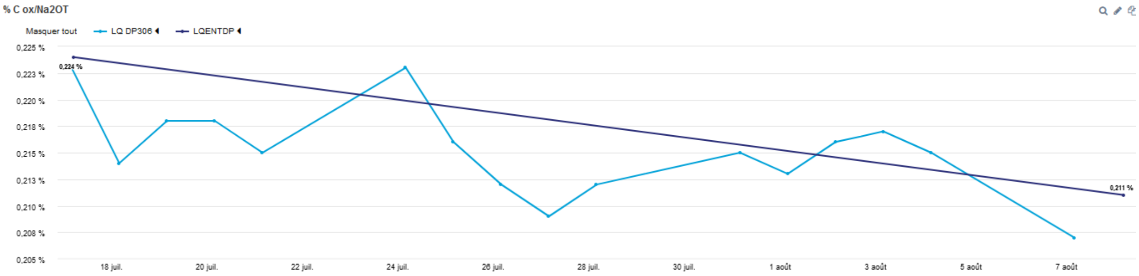


Figure 9. First shutdown results: oxalate concentration in liquor (scale of Y-axis [0.205–0.225 %]).

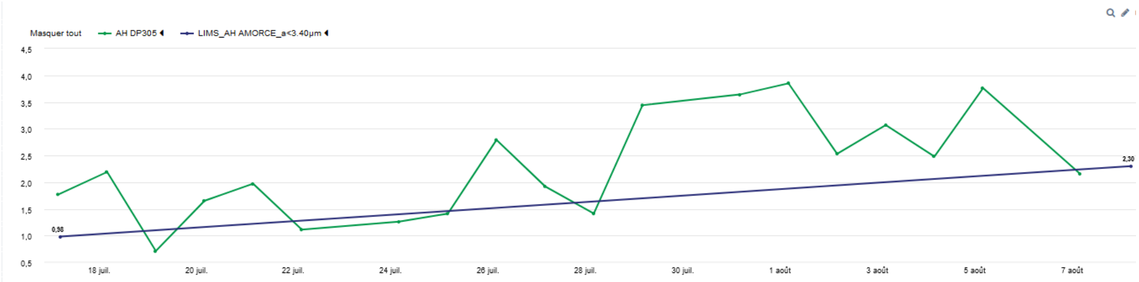


Figure 10. First shutdown results: number of fine particles (scale of Y-axis [0.5–4.5×10^5]).

It should be noted that the only precipitator where massive oxalate precipitation was observed leading to strong nucleation, was the end-of-series safety tank, hence the importance at restart time of not returning it to the main circuit to avoid contamination is underlined. Indeed, some overflow of the last precipitator to the overflow security tank did happen during the first shutdown.

5.1.4 Impurities

While the iron level remained stable, the industrial results for silica, shown in Figure 11 and 12, were consistent with those found during the laboratory tests:

- The silica liquor concentration varied from 0.38 to 0.34 g/L, a decrease of 10%.
- Precipitated silica rose very slightly by 10 to 15 ppm, close to the measurement uncertainty.

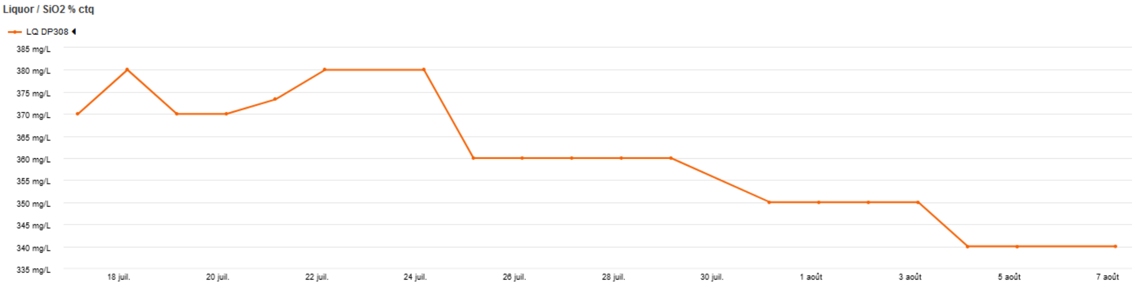


Figure 11. First shutdown results: silica in liquor (scale of Y-axis [335–385 mg/L]).

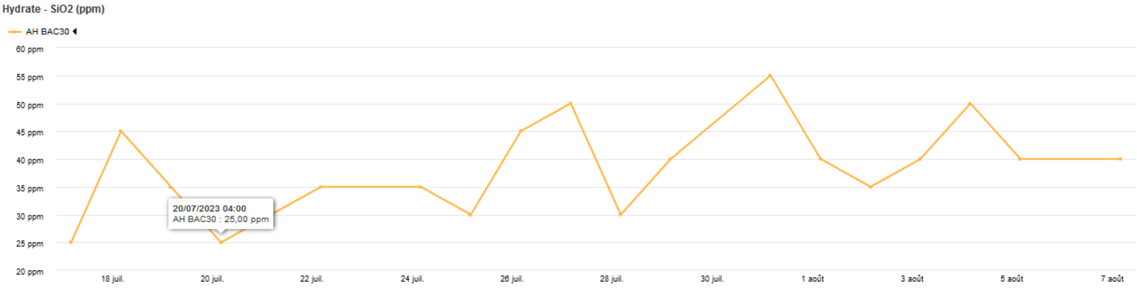


Figure 12. First shutdown results: silica in hydrate (scale of Y-axis [20–60 ppm]).

5.2 Energy Balance

The graph below shows steam consumption before, during and after shutdown:

Figure 13. Steam consumption before, during and after the first shutdown.

Four periods were observed:

1. Operation before July 3rd, corresponding to consumption for a UODP process at its technical minimum (about 60 % of the nominal).
2. Operation from July 3rd to July 17th, UODP process nominal production: about 20 % of extra steam consumption vs previous period.
3. Shutdown, from July 18th to August 7th. with a basic consumption of around 4 t_{steam}/h and an increase to about half of period 1 rate when the precipitator slurry is reheated.
4. Restart and gradual return to minimum technical operation of UODP process.

To estimate the energy saved during this shutdown, we compare the period 1 to a mix of periods 2 and 3 for a given duration and production, and we observe a 15 % reduction of steam consumption.

5.3 Lessons Learned:

This first shutdown showed that when outside temperatures are sufficiently high, few major operational and quality risks are to be feared as long as:

1. the level of impurities (oxalate and silica) is sufficiently low at the start of the shutdown;
2. precipitator temperature is kept above 50 °C;
3. precipitation solid content is sufficiently high at the start of the shutdown to allow maintenance of circuits, drain valves, etc. by injecting liquor;
4. no tanks containing cooled slurry are recycled to the precipitator line.

6. Second Shutdown

A new shutdown was conducted in autumn, when outside temperatures were lower.

6.1 Complementary Laboratory Tests

Following the positive results of the first shutdown when precipitation temperature was maintained above 50 °C, laboratory tests were carried out to better assess risks involved for precipitation at temperatures lower than 50 °C.

Unlike the first tests, where the hydrate slurry has been maintained at a constant (and colder) temperature to evaluate impacts on quality, a temperature profile was applied here. It has been calculated from data obtained during the first shutdown, and is depicted in the following figure.

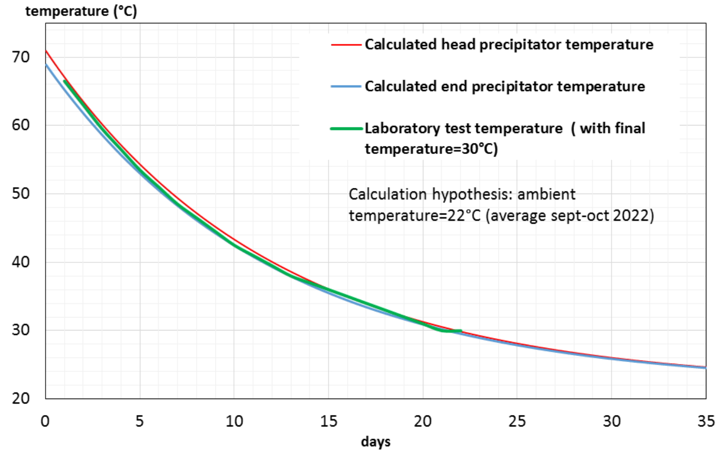


Figure 14. Laboratory tests: temperature profile decrease.

Laboratory results showed that:

- the risk of oxalate precipitation (see Figure 15) becomes very high between day 7 and day 10, when temperature drops below 50 °C.
- no impact on silica or iron is observed, as in previous tests

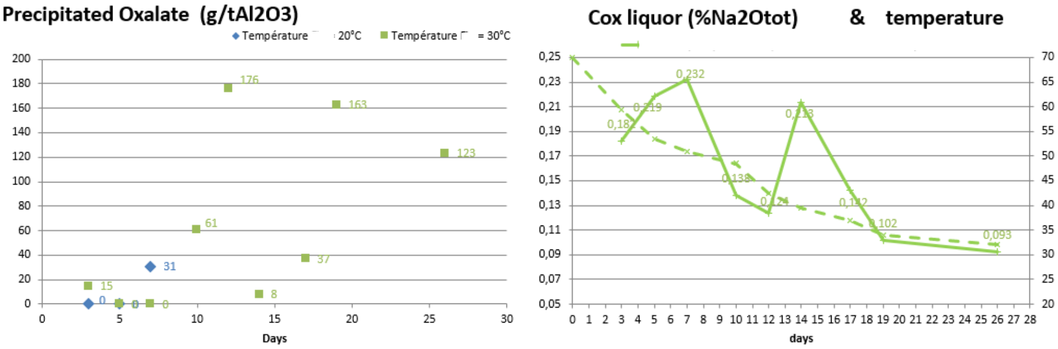


Figure 15. Laboratory tests: oxalate precipitation at low temperatures.

6.2 Conditions

This shutdown lasted approximately 8 weeks, from September 18th to November 20th, with starting conditions broadly identical to those of the first shutdown. The average outside temperature varied between 20 and 13 °C. The main control objective was to maintain the temperature above 50 °C, which was successfully achieved (see Figure 16), in order to avoid oxalate precipitation and consequent loss of particle size control in accordance with laboratory tests.

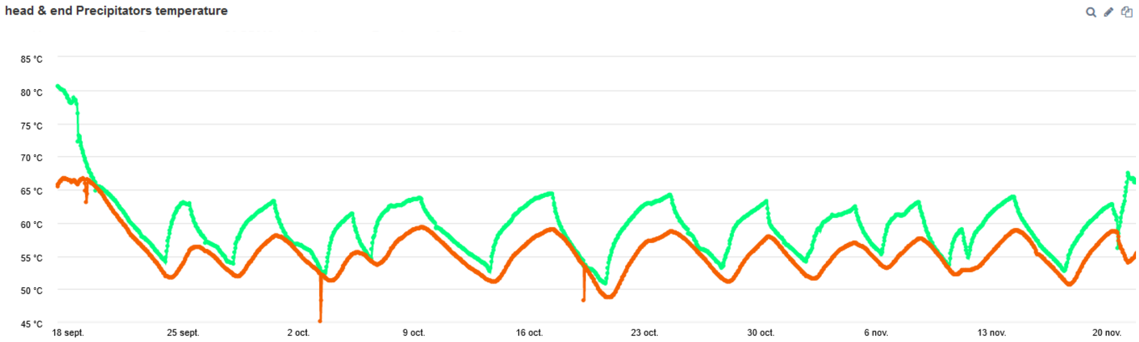


Figure 16. Second shutdown conditions: temperature (scale of Y-axis [45-85 °C]).

As the shutdown becomes longer and the outside temperature drops, the need for heating increases in frequency. As a result, energy savings were much lower for the second shutdown.

6.3 Additional Lessons from the First Shutdown: Iron Pollution from Heating

The need to heat every 3 days through the monotubular heat exchanger resulted in almost 40 ppm of iron contamination on the hydrate inventory. The trend shown in Figure 17 indicates that this phenomenon accelerated at the end of the shutdown period.

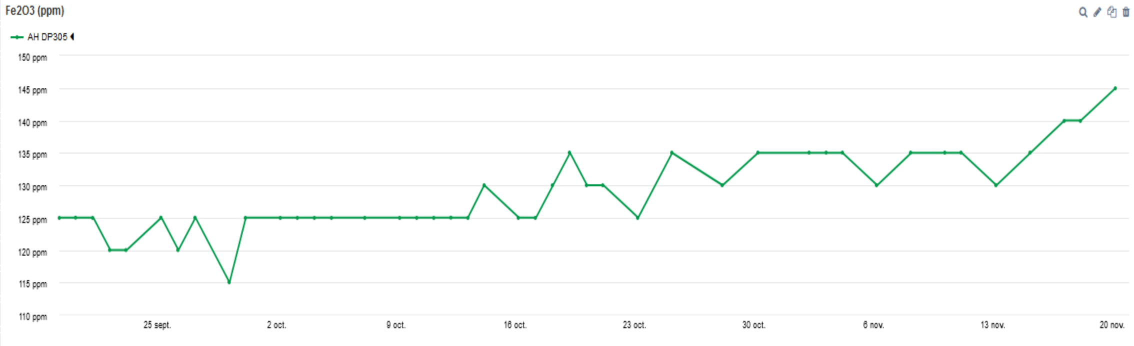


Figure 17. Second shutdown results: iron in hydrate (scale of Y-axis [110-150 ppm]).

The liquor has also shown a marked increase in chromium, as shown by the trend in Figure 18. This suggests that this contamination is linked to wear in the piping, particularly in the valves of the circuit used to heat the slurry.

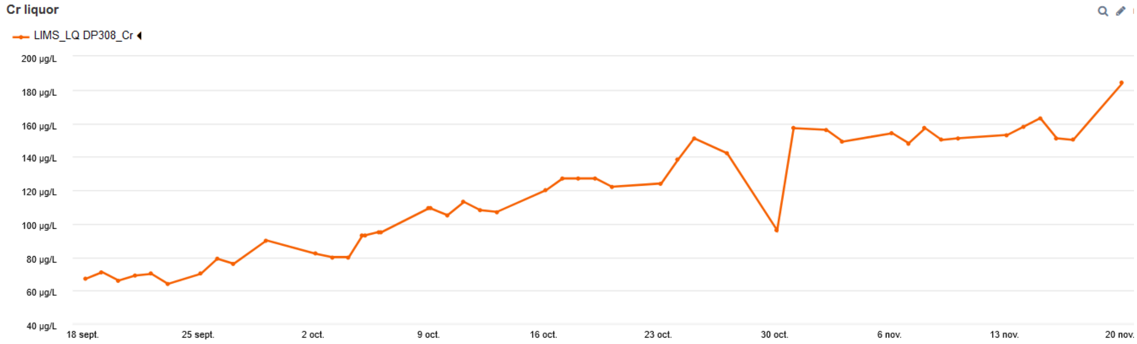


Figure 18. Second shutdown results: chromium in liquor (scale of Y-axis [40-200 µg/L]).

7. Conclusion

Before deciding to launch these prolonged shutdowns of the UODP process, a number of questions had to be addressed. Quality control was of prime concern, particularly particle size control and silica precipitation. Laboratory tests enabled us to eliminate concerns due to silica and to establish the necessary conditions for oxalate control.

By operating at temperatures above 50 °C, with an intermittent heating of the hydrate slurry, ensuring that any cooled hydrate suspension is not mixed, and adapting operational routines to keep the precipitators running smoothly, we have not encountered any problems linked to the risks we had identified. On the other hand, we had not anticipated the rise in iron content due to wear on the equipment when the slurry is reheated.

The initial conditions, particularly in terms of impurities in the pregnant liquor, are a decisive factor in the success of this type of shutdown.