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HYDRODYNAMICS EFFECT ON PRECIPITATION YIELD

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1 - Introduction

A large amount of work has been carried out over recent years at the FRIGUIA plant (GUINEA) to increase production capacity.

Improvements currently being studied or which have already been implemented can be classified into two categories.

- those making it possible to increase circulating flow rates: debottlenecking of evaporation, optimization of pumping, improvement of operating rates, etc...
- those making it possible to improve the yield of liquors: increase in supersaturation at the head of precipitation, suppression of loss due to redissolution of hydrate during evaporation, optimization of soda concentration, drop in precipitation temperature, better use of the volume of the installed precipitators etc... .

In this paper we will present the studies and tests performed to improve the yield of liquors by optimization of the hydrodynamics of the precipitators. This study was originally started because of three factors :

1) the design of precipitators, built in 1960, presents a fair risk of slurry by-passing; in fact these precipitators do not have bottom discharge, unlike those built by PECHINEY in the ten last years.
2) mean residence time in the part of the precipitation process where a high solid content is present (growth section) has been considerably decreased since1986 due to:
   - implementation of an agglomeration phase which has used a part of the installed volume.
   - increase in the aluminate flow (~ 20 %) .

   And, the difference in performance due to poor hydrodynamics increases as residence time decreases [1].
3) modelling based on the results of laboratory tests [2] have always led to yield values higher than those observed industrially when precipitation is assimilated to a series of perfectly stirred reactors

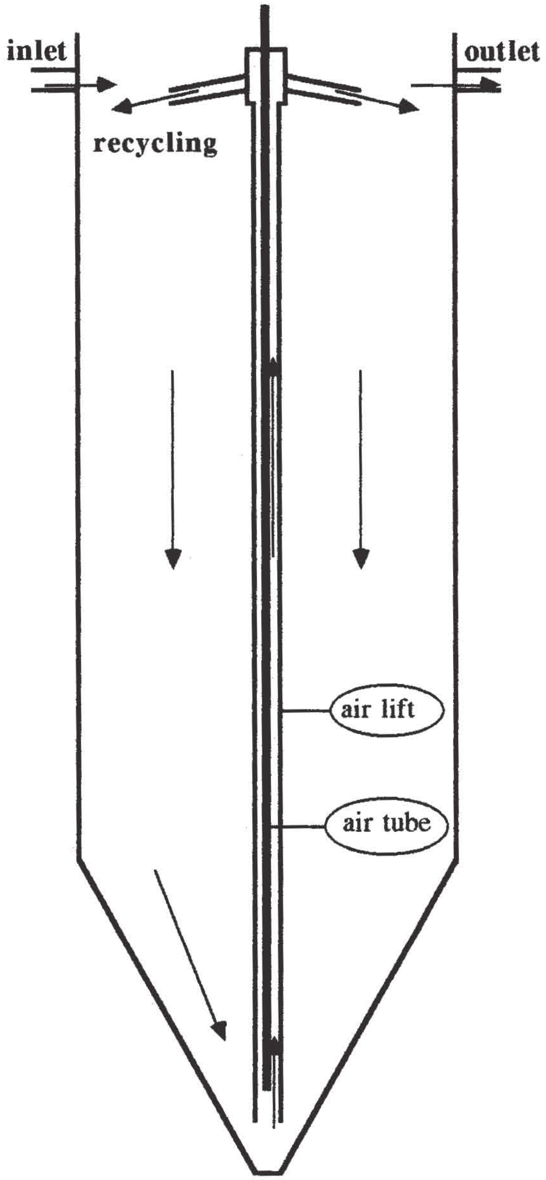

Figure 1 : design of original precipitator

Our study includes three stages :

1) Determination of the actual residence time distribution (RTD) in industrial precipitators
2) Estimation of the gain that can be achieved by modification of the design of the precipitators (bottom discharge with stirring maintained and stirring-free operation as per PECHINEY patent [3]).
3) Implementation of the economically viable technological improvements on a precipitator in order to test their reliability and performance.

The first two stages have already been carried out and the third one is underway.

2- Measurement of the RTD of the precipitators

2-1 Method

This consists of instantaneously marking a fraction of the product entering the studied tank and observing at the outlet the time distribution of the tracer concentration.
The RTD E (t) of the marked product between inlet and outlet is calculated [4] by using the expression

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} \qquad (1)$$

in which C (t) represents the instantaneous concentration of the tracer at instant t. E (t) represents the probability density that a particle of matter entering the reactor at instant t = 0 will leave it between time t and t + dt.

It is also useful to introduce function F (t) representing the fraction of matter that left the reactor at instant t.

$$F(t) = \frac{\int_0^t C(t)\,dt}{\int_0^\infty C(t)\,dt} \qquad (2)$$

2-2 Potentialities of the measurement

2-2-1 Dead volume

Mean residence time $\bar{t}$ is characterized by the x-axis of the gravity center of the concentration-time curves

$$\bar{t} = \frac{\int_0^\infty t\,C(t)\,dt}{\int_0^\infty C(t)\,dt} \qquad (3)$$

When this mean residence time is lower than the holding time t = V/Q (where V is the geometrical volume of the reactor and Q feed flow rate) an unused volume can be calculated

$$Vm = V - Q\bar{t} \qquad (4)$$

2-2-2 Short-circuit

When the residence time distribution demonstrates the presence of a narrow peak for low values of t, a short-circuit rate can be defined from the ratio of the area of this peak to the total area of the curve.

2-2-3 Convolution

The convolution equation makes it possible to determine, by calculation, the outlet function O (t) of a tank for which the inlet function I (t) and the pulse response E (t) is known.

$$O(t) = \int_0^t I(u)\;E(t-u)\,du \qquad (5)$$

This relation was used to check the hydrodynamic behavior of precipitators in series.

For this, we compared the experimental signal O ex (t) obtained at the outlet of the precipitators in row 2, 3 and 4, to the theoretical value O th (t) which can be calculated by relation (5).

2-3 Choice of tracer

Numerous problems raised by the choice of tracer in the BAYER process, have been analyzed by GROCOTT and Mc GUINESS [5]. The authors recommend using halogenic derivatives of carboxylic acids.

For reasons of simplicity in the implementation and detection processes we thought it preferable to use a radioactive tracer that is very soluble in an alcaline medium and which has already been used by PECHINEY [11].

The actual distance between the plant and the radionuclide production center meant using a radioactive tracer with a .decay period compatible with the duration of the operation and transportation times.

We chose iodine 131 in the form of sodium iodide. This isotope emits gamma radiation with an energy of 364 keV and has a radioactive decay period of 8.05 days.

Activity injected was approximatively 500 mCi for each test.

2-4 Implementation

The tracer was injected by pouring it into the feed chute of the first precipitator of the growth section.

The radioactive batch (20 ml) was first homogenized in 10 liters of aluminate liquor placed in a recipient suspended above the inlet chute.

Detectors were placed under the outlet chute of each of the precipitators used in the measurements.

The signals were transmitted by cable to a data acquisition center.

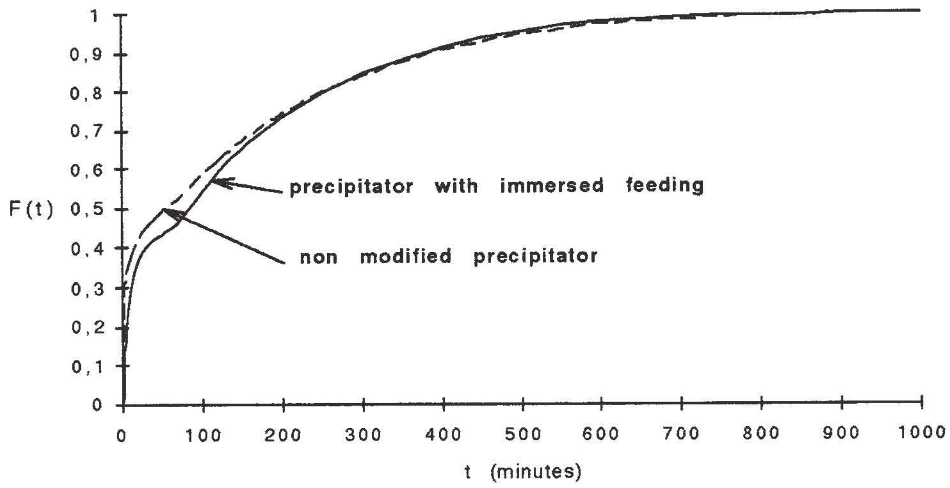

Figure 2 : Fraction of tracer escaped versus time

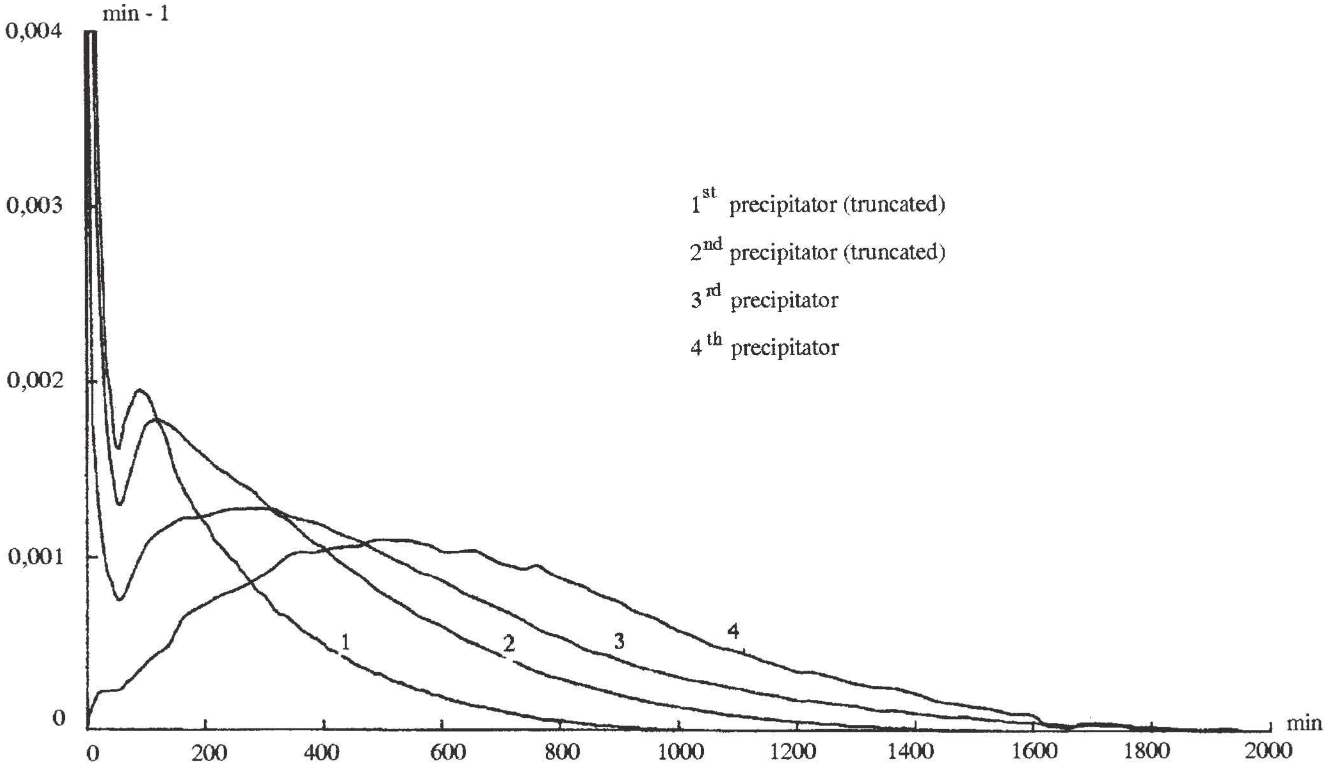

Figure 3 : Normalized responses to pulse input for the first four precipitators (unmodified line).

2-5 Results

Two series of measurements were carried out, the first on a series of unmodified precipitators and the second on a series of precipitators equipped with immersed feeding at - 2 m.

The functions F (t) obtained at the outlet of the first precipitators are shown on figure 2 and demonstrate very strong short circuits.

2-5-1 Unmodified line

The pulse responses were measured for 1,2,3 and 4 precipitators in series; they are represented on figure 3 and are truncated for short residence times.

Detailed analysis of the short-circuit is shown in table I

	Fraction of total flow %	x-axis of center of gravity (mn)
short-circuit	55	4.3
output ex short-circuit	45	262.4
total RTD	100	153.0

TABLE I : Analysis of the short-circuit of an unmodified precipitator.

The unused volume determined according to (4) is 7%; this volume probably corresponds to the aeration of the slurry stirred by an air-lift.

The second peak found at 97 minutes (figure 3) corresponds to the time when the fraction of the tracer not concerned by the short circuit [1] comes to air-lift outlet. This peak makes it possible to estimate air-lift flow at 1700 m^3/h and shows the discharge below the by-pass area is near a plug flow, at a speed of around 15 m/h in the cylindrical part of the precipitator.

2-5-2 Modified lines

The same measurements as those carried out on the unmodified line were done; the pulse response of the first precipitator is shown on figure 4.
A detailed analysis of the short-circuit is given in table II.

	Fraction of total flow%	x-axis of center of gravity (mn)
short-circuit	42	13.2
output ex short-circuit	58	243.7
total RTD	100	147.5

TABLE II : Analysis of the short-circuit of a precipitator with immersed feeding

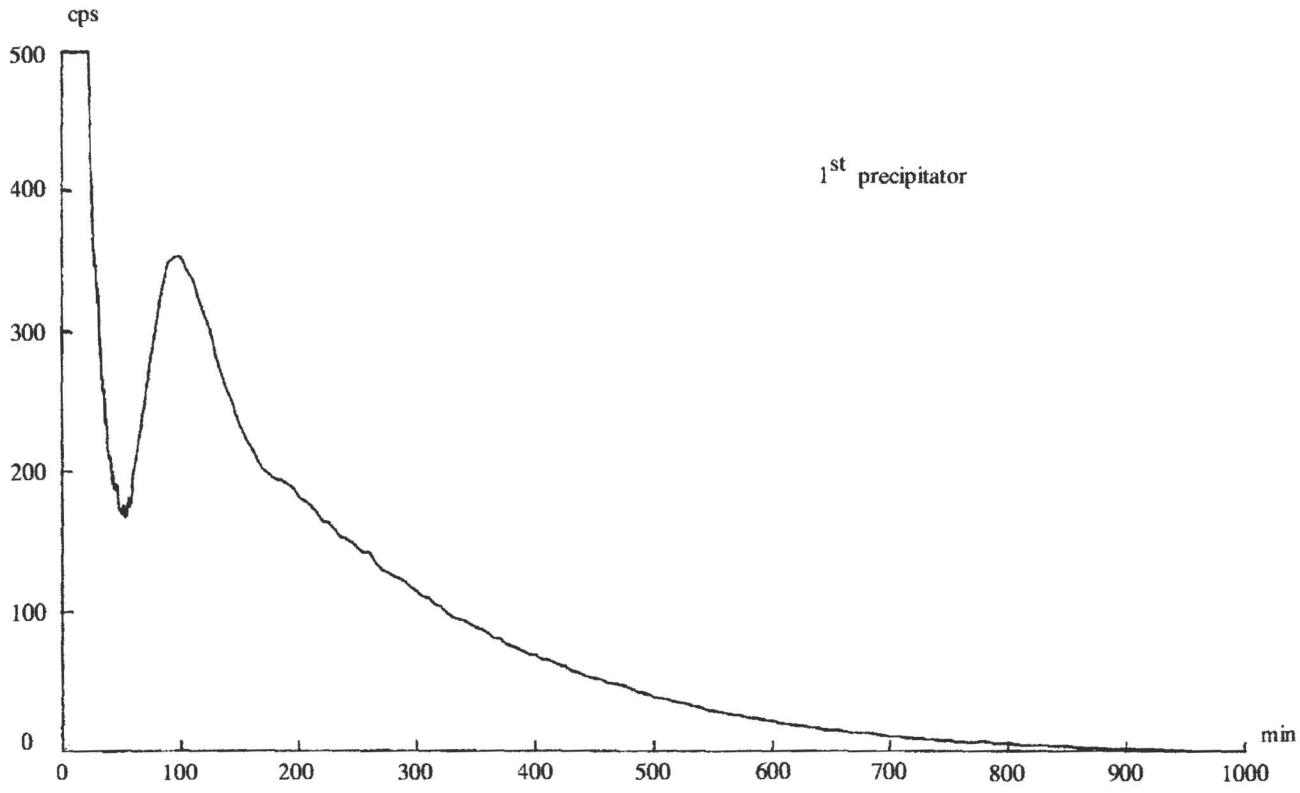

figure 4 : response to pulse input for the first precipitator with immersed feeding

It can be seen that immersed feeding reduces the by-pass rate and increases the mean residence time of the fraction that is not recycled by the air-lift; the device is still extremely insufficient.

Determination of the aeration rates and the air-lift flow rate give results that are identical to those of the unmodified line.

Comparison of the signal obtained at the outlet of the second precipitator with the result of the autoconvolution of the signal of the first precipitator, is shown in figure 5.
It can be seen that:

$$E2(t) = \int_0^t E1(u)\ E1(t-u)\, du \qquad (6)$$

which confirms the validity of the pulse response of the first precipitator

3 - Consequences of hydrodynamic improvement

3-1 Method

The determination of E (t) in all cases, makes it possible to calculate the progress of a first order reaction [1,4] by the relation

$$X = \int_0^\infty X_{BR}(t)\ E(t)\, dt \qquad (7)$$

where X is the reaction yield at the outlet of the reactor of RTD E (t).

X_{BR} is the reaction yield in a batch reactor at the end of time t.
In the case of a non linear reaction rate, the relation (7) remains valid if the micromix phenomena are insignificant [1,4].

The precipitation of aluminate liquors is a second-order reaction [6,7,8,2]. Given that industrial stirring devices are not designed to achieve a micromix, we assume that the relation (7) is applicable.

By using this relation, the actual reactor can be assimilated to a line of plug flow reactors installed in parallel with a residence time t and a feed rate proportional to E (t) dt [4].

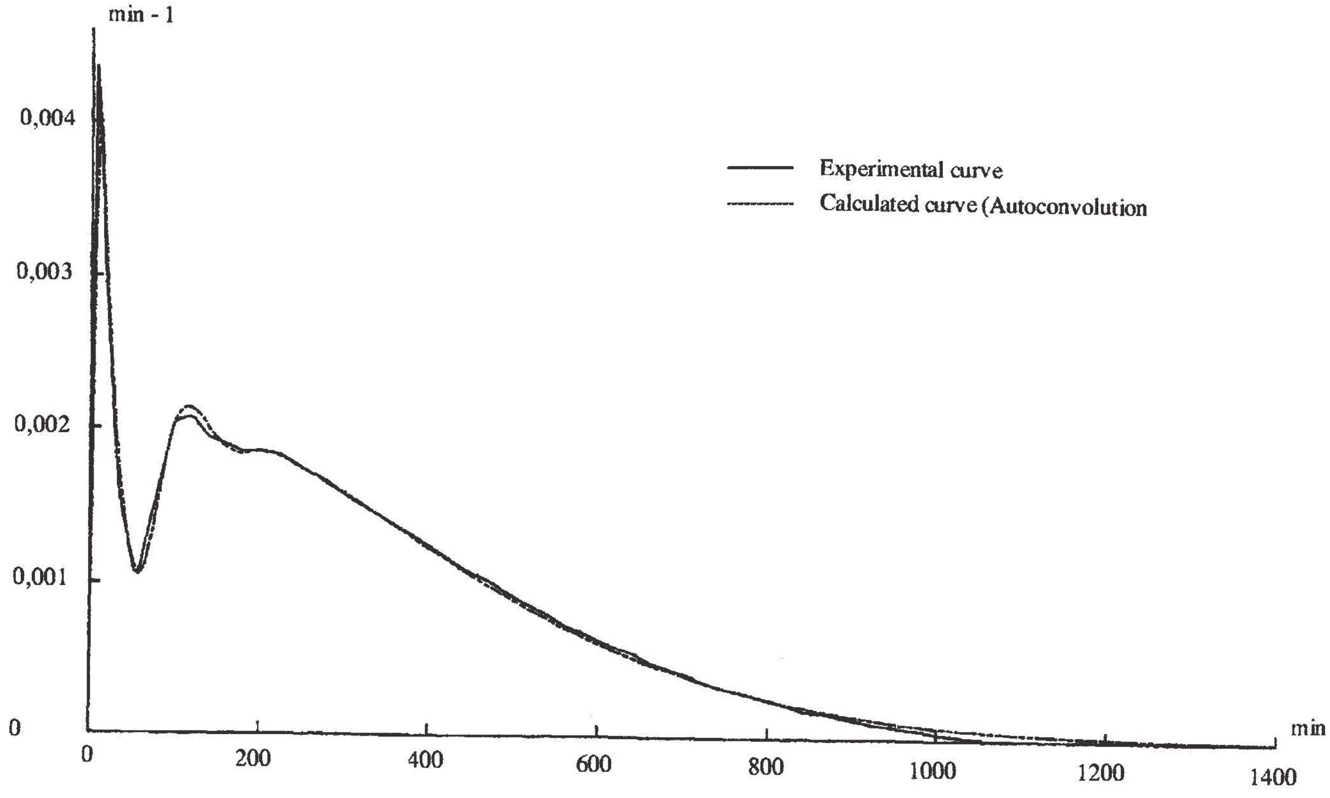

figure 5 : comparaison between experimental pulse response at the outlet of the second precipitator and autoconvolution of the pulse response of the first precipitator (modified line)

3-2 Calculation of the performance of the actual reactor

By using the usual PECHINEY notations, the kinetics of a batch reactor can be expressed as [2]

$$\frac{dRP}{dt} = K\ (RP - RPeq)^2 \qquad (8)$$

where RP is the mass ratio Al_2O_3/Na_2O ctq

RP eq is the value of RP at equilibrium

K is the kinetic constant which is a function of temperature, composition of the liquor and the seed surface area.

The RP_o at the outlet of a plug flow reactor with a residence time t or at the outlet of a batch reactor with the same residence time, is given by the relation (9)

$$RP_o = RP_{eq} + \frac{RP_i - RP_{eq}}{1 + K\ (RP_i - RP_{eq})\ t} \qquad (9)$$

Using relation (7) the RP_o at the outlet of any reactor with an RTD E (t) can be deduced.

$$RP_o = RP_{eq} + \int_o^\infty \frac{(RP_i - RP_{eq})\ E\ (t)}{1 + Kt\ (RP_i - RP_{eq})} dt \qquad (10)$$

The results obtained with experimental RTD are given in table III for a series of 7 precipitators.

The values taken for the different constants intervening in equation (10) are mean values measured at the plant :

$K = 0.45$
$RP_i = 0.88$ (growth section inlet)
$RP_{eq} = 0.55$

The real mean residence time is taken as being equal to 2.3 hours per stage.

Stage no	RP at the outlet of unmodified precipitator	RP at the outlet of modified precipitator
1	0.820	0.818
2	0.776	0.774
3	0.743	0.741
4	0,718	0.715
5	0.698	0.696
6	0.682	0.680
7	0,669	0.667

TABLE III : RP obtained for 7 stages with a mean residence time of 2.3 hours and actual RTD.

It is confirmed that the installation of immersed feeding, in spite of the reduction of the short circuit rate from 55 to 42%, does not allow significant gains.

3-3 Comparison of results with ideal reactors

To assess the gains that could be achieved by modification of the RTD, we calculated the RP output by a line of perfectly stirred tanks and a line of plug flow reactors with the same holding time as the existing reactors.

The relations used are as follows: [2]

$$\text{plug flow reactor } RP_{om} = RP_{eq} + \frac{RP_i - RP_{eq}}{1 + K\ t\ (RP_i - RP_{eq})} \qquad (11)$$

$$\text{mixed reactor } RP_{om} = RP_{eq} + \frac{\sqrt{1 + 4K\ (RP_i - RP_{eq})} - 1}{2K\ t} \qquad (12)$$

The results are given in table IV

stage no	mixed Reactor	plug flow Reactor
1	0.810	0.796
2	0.63	0.746
3	0.730	0.713
4	0.705	0.689
5	0.686	0.672
6	0.671	0.658
7	0.658	0.647

TABLE IV : RP obtained for 7 stages with a mean residence time of 2.3 h and RTD of ideal reactors.

The yield gain that can be achieved is calculated by the relation (13)

$$\Delta P = N \Delta RP_o \qquad (13)$$

ou N is the soda concentration of the aluminate (150 g/l)
ΔRP_o is the difference between the RP calculated with the actual RTD and RP calculated with the RTD of ideal reactors
ΔP is the yield gain that can be achieved (en g Al_2O_3/l aluminate)

The results are given in table V for a total residence time of 7 x 2.3 = 16.1 h

Mixed reactors in series	$\Delta P = 1.5$ g/l
Plug flow reactor	$\Delta P = 3.1$ g/l

TABLE V : Yield gains that can be achieved by modification of the real residence time distribution.

Comment :

The performance of the actual reactor is clearly represented by that of a perfect mixer with a short-circuit rate of 32%.

The reactor with immersed feeding is clearly represented by a perfect mixer with a short-circuit rate of 27%..

These short-circuit rates are lower than those determined directly by plotting. This result comes from the fact that:

- the by-pass systems do not have zero residence time
- the RTD ex by pass are on the intermediate level between those of a mixed reactor and those of a plug flow reactor.

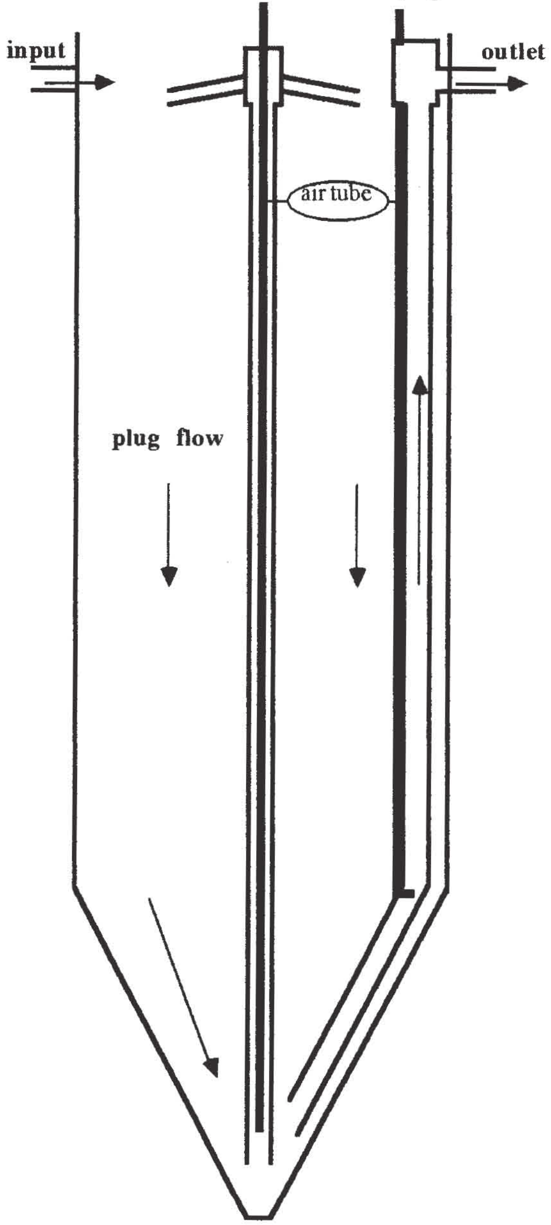

figure 6 : design of test precipitator with bottom discharge

4 - Test precipitator with bottom discharge

The gains that can be achieved ranging from 1.5 and 3.1 g/l calculated using ideal reactors, represent a production potential of 17 and 35 kt/year respectively at a very low marginal cost.

FRIGUIA and PECHINEY therefore decided to continue experimentation by testing the reliability and performance of a precipitator equipped with bottom discharge.

The modified tank shown on figure 6 can operate with an air-lift or without one [3].

4-1 Operation with an air-lift

It is assumed that the residence time distribution is that of a plug flow reactor with recycling (fig 7). The recycling flow rate is the same as the air-lift flow rate.

The RP output from the tank is given by resolution of the equation system

$$\Delta RP_o = \frac{\Delta RP_p}{1 + K\tau_p \, \Delta RP_p} \qquad (14)$$

$$\tau_p = \frac{\tau}{1+a} \qquad (15)$$

$$\Delta RP_p = (a\,\Delta RP_o + \Delta RP_i)/(1+a) \qquad (16)$$

where

Δ RP is the difference between the RP of the slurry and the equilibrium RP.

i,o,p are the indices relative to precipitator feeding,the precipitator outlet and plug flow reactor feeding with recycling.

a is the ratio of the recycled flow to the precipitator feed flow rate

τ , τ_p are respectively the holding times of the precipitator and the plug flow reactor with recycling.

finally we obtain for a $\neq$ o

$$\Delta RP_o = \frac{-1-K\tau\frac{\Delta RP_i}{(1+a)} + \sqrt{\left(1+K\tau\frac{\Delta RP_i}{(1+a)}\right)^2 + 4\,\Delta RP_i\,K\tau\frac{a}{(1+a)}}}{2K\tau\frac{a}{(1+a)}} \qquad (17)$$

This relation clearly gives for a $\longrightarrow$ o relation (11) and for a $\longrightarrow \infty$ relation (12).

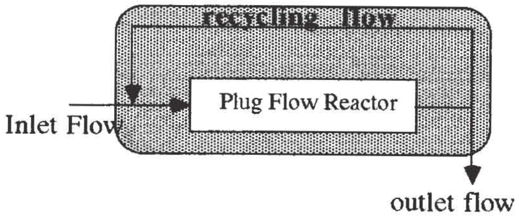

figure 7 : flow diagram used to calculate the yield of bottom discharge precipitator stirred by air-lift.

In the special case of FRIGUIA plant precipitation with an air-lift flow rate of 1700 m^3/h and a total holding time of 2.3 h per stage the results shown in table VI are obtained for

$$\Delta RP_i = 0,33 \text{ , } K = 0,45 \text{ et } RP_{eq} = 0,55$$

	RP 1st precipitator	Δ Yield 7 stages (g/l)
Current precipitator	0.8197	/
Perfectly stirred tank	0.8100	1.51
Air-lift and bottom discharge	**0.8047**	**2.18**
Plug flow reactor	0,7960	3,13

TABLE VI : Situation of a precipitator with an air-lift and bottom discharge with regard to ideal reactors and the current reactor.

4-2 Operation without air-lift

The principle is identical to that presented in the Aluminium Pechiney Patent [3].

To estimate the performance of a non stirred precipitator, the seed surface area inside the tank has to be calculated because

- the particle settling velocity becomes important compared to the liquor velocity; as a result, grain size distribution and solid content inside the precipitator are different from that of feeding.
- the kinetic constant of equation (8) is proportional to the seed surface area (m^2/l liquor) [2].

In the case of the FRIGUIA growth section

- 700 g hydrate/l slurry
- 6% < 45 μ in the pump-off hydrate

calculations were achieved, based on PECHINEY studies about hydrate slurry settling [9,10].

The following is obtained :

$$\underset{m^2/l}{S} \text{ inside tank} = 0,924 \underset{m^2/l}{S} \text{ feeding}$$

This result and equation (11) allowed to calculate performance for an unstirred precipitator (table VII)

	RP 1st precipitator	Δ Yield 7 stages (g/l)
Current precipitator	0.8197	/
Perfectly stirred tank	0.8100	1.51
Unstirred precipitator	**0.8008**	**3.07**
Plug flow reactor	0.7960	3.13

TABLE VII Situation of an unstirred precipitator in relation to ideal reactors and the current reactor.

Conclusion

Radioactive tracing is an effective and accurate method for determining RTD in the BAYER process.

Application of this method to precipitation at FRIGUIA plant made it possible to demonstrate a very important short-circuit related to

- the position of the slurry outlet with regard to the feed inlet
- the relatively high value of the ratio feed flow / stirring flow.

The gain that can be achieved on yield by installing a bottom discharge was estimated by modelling of the hydrodynamics of the precipitators; it is approximately

- 2 g/l if the air-lift is maintained at its current flow rate.
- 3 g/l by stopping the air-lift.

The last configuration, the principle of which has been patented [3], has already been experimented over a long period at the LA BARASSE plant in 86-87 using a slightly different technology.

The test precipitator at FRIGUIA plant should make it possible to confirm

- the process performance predicted by calculation
- the reliability of the technology proposed in the case of variation or stoppage of the circulating flow rate during precipitation.

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