PRODUCTION OF SANDY ALUMINA BY A HIGH SOLID CONTENT PRECIPITATION

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ABSTRACT

The Pechiney process in precipitation has been used in the plant of "Aluminium de Grèce" since 1988.

A description of this process with very high solid content, up to 1,000 grams hydrate per liter of slurry, is applied, particularly with addition of a chemical in precipitators.

Further, the improvement of precipitation yield with an innovating interstage cooling in precipitation, is described.

It is shown that combination of this process with the interstage cooling in precipitation allows us to obtain, on a very regular basis, a consistent sandy alumina with the main following characteristics:

- Soda content lower than 3,300 ppm.
- Particle smaller than 45µ less than 8% of weight.

That is achieved with a precipitation yield up to 91 grams per liter of pregnant liquor, with a short residence time.

The technical results of some smelters show the excellent compatibility of this alumina with the most recent smelting technology.

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1.0 INTRODUCTION

"Aluminium de Grèce", subsidiary by 60% of Pechiney group, is a bauxite - alumina - aluminium complex operating since 1964.

The current capacity of the factory is 650 kt a year of sandy alumina and 155 kt a year of primary aluminium destined mainly to the greek market.

45% of alumina is used in on site smelter, while the remaining 55% is either used by other Pechiney group smelters or sold on international market.

Initially, the refinery produced a floury alumina with a classical european process. Evolution of smelters' requirements of all over the world, connected mainly with environmental problems (fluorine emissions), has led Pechiney to implement a process allowing Sandy Alumina production, without any major transformation of plant's installations. The process was developed at the research centre of Gardanne, then tested at the La Barasse refinery and improved by ADG* (1) since 1988.

As a comparison, the main characteristics of precipitation processes such as classical american process, improved american process and actual Pechiney process are shown in table 1 below.

Table 1

Typical parameters of some precipitation processes

		classical american process	improved american process	actual Pechiney process
Pregnant liquor:	Na_2O caustic g • l^{-1} RP**	100 1.10	130 1.15 - 1.20	150 - 170 1.10 - 1.20
Initial temperature, °C		75	75	55 - 65
Liquid/solid separation		Thickener	Thickener	Filtration
Seed charge (g • l^{-1} pregnant liquor - growth stage)		100	200	> 800
Liquor yield g Al_2O_3 • l^{-1}		40 - 50	55 - 70	85 - 95
% < 45µ in calcined alumina		5 - 7	5 - 8	6 - 10

After explanation of process and description of precipitation area, the results of operations for one year referring mainly to precipitation's yield, alumina's quality and its behavior in pots are explained.

* ADG = "Aluminium de Grèce"
** RP = (A/C) • (1.71)

2.0. "ALUMINIUM DE GRECE" PRECIPITATION

2.1. Basic principle of PECHINEY precipitation process

2.1.1. History

In the seventies, the need for reducing emissions of fluoride from smelters has resulted in the generalisation of dry scrubbing process.

This process being incompatible with floury alumina, obliged Pechiney to transform its precipitation plants in such a way to produce SANDY alumina.

Therefore, Pechiney's objective was to obtain alumina with satisfactory particle size distribution with a minimum modification of precipitation area (low investment) and a minimum change in process parameters aiming to hold a high yield (low temperature of precipitation, high solids). The yield is defined as the quantity of alumina expressed in Al_2O_3 precipitated per unit of volume of pregnant liquor.

2.1.2. General principle of the process

In a first time, a method for measuring crystals of small dimension in seed hydrate was developed: counting of particles less than 2µ diameter.

In a second time, the statistical study of chronogramms giving particles' density at 1.5µ ($N_{1.5\mu}$) and minus 45µ of seed has allowed establishment of a correlation between both these data. It is of the type:

$$\% < 45\mu = f\,[N_{1.5\mu}\,(t - \tau_1)] \qquad (1)$$

where t is the date of observation and τ_1 the lag between an extremum of $N_{1.5\mu}$ and an extremum on minus 45µ.

$N_{1.5\mu}$ represents the number of fine particles per gram of seed which are present in a window of 0.1µ wide, centred on 1.5µ. $N_{1.5\mu}$ is in fact the result of two elementary phenomena: true nucleation generating particles smaller than 1µ and agglomeration of ultrafine particles (1).

Finally, a relationship has been evident between supersaturation, seed surface area and density of ultrafine particles $N_{1.5\mu}$.

Supersaturation β is defined as the following ratio:

$$\beta = \frac{RP}{RP_{eq.}} \qquad (2)$$

with $RP = \dfrac{Al_2O_3}{Na_2O_{ctc}}$ of liquor entering seed tank

and RP_{eq} = equilibrium RP for the related soda concentration and temperatures.

Surface area S, expressed in $m^2 \bullet l^{-1}$ of slurry, represents the surface area developed by seed, where each particle of hydrated alumina is assimilated to a sphere.

This relation can be expressed as:

$$N_{1.5\mu} = f\,[\beta\,(t - \tau_2),\ S\,(t - \tau_2)] \qquad (3)$$

where t is the date of observation and τ_2 the lag between given physico-chemical conditions and appearance of a population at a diameter of 1.5µ.

The combination of (1) and (3) gives a direct relationship, in steady state, between supersaturation, seed surface and minus 45µ of seed:

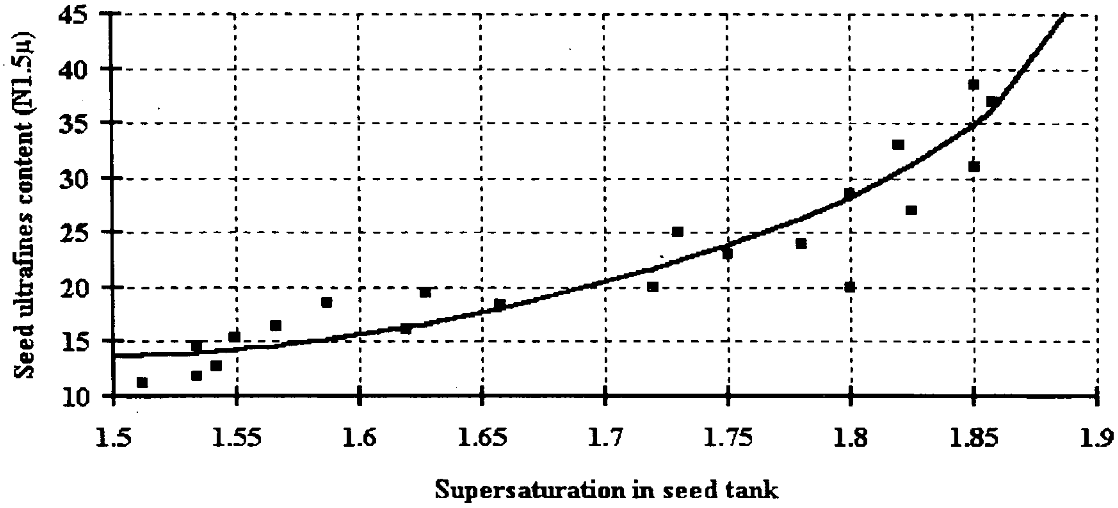
$$\boxed{\% < 45\mu = f\,(\beta, S)} \qquad (4)$$

2.1.3. Process control.

Every day, the density of ultrafine particles at 1.5μ ($N_{1.5\mu}$) is measured by counting particles.

This value is compared with the value coming from the equation (1). In case of deviation referring to the latter, the supersaturation is controlled in the seed tank in a way to satisfy equation (3) and guaranteeing a mean value compatible with particle size distribution objectives of calcined alumina (figure 1). Any increase in nucleation involves an immediate action for lowering the supersaturation and vice-versa: the main parameter for supersaturation control is temperature. Actually, the RP of pregnant liquor is maintained regularly at a high level, compatible with economically acceptable digestion yield.

FIGURE 1 : RELATION BETWEEN SUPERSATURATION AND $N_{1.5\mu}$



A supplementary way to control product particle size distribution is given by pump off classification.

2.1.4. Additive of precipitation

Addition of chemical (crystal growth modifier) promoting fine particles agglomeration (2) allows partially to reduce temperature variations in seed tank, resulting in keeping yield at a high level and reducing fluctuations of bound soda in hydrate.

2.2. Description of precipitation plant

2.2.1. Precipitation

Pregnant liquor at target temperature is mixed with hydrate for promoting ulterior precipitation of alumina from solution. This operation is carried out in the seed tank where solid concentration is very high: more than $800\ g \bullet l^{-1}$.

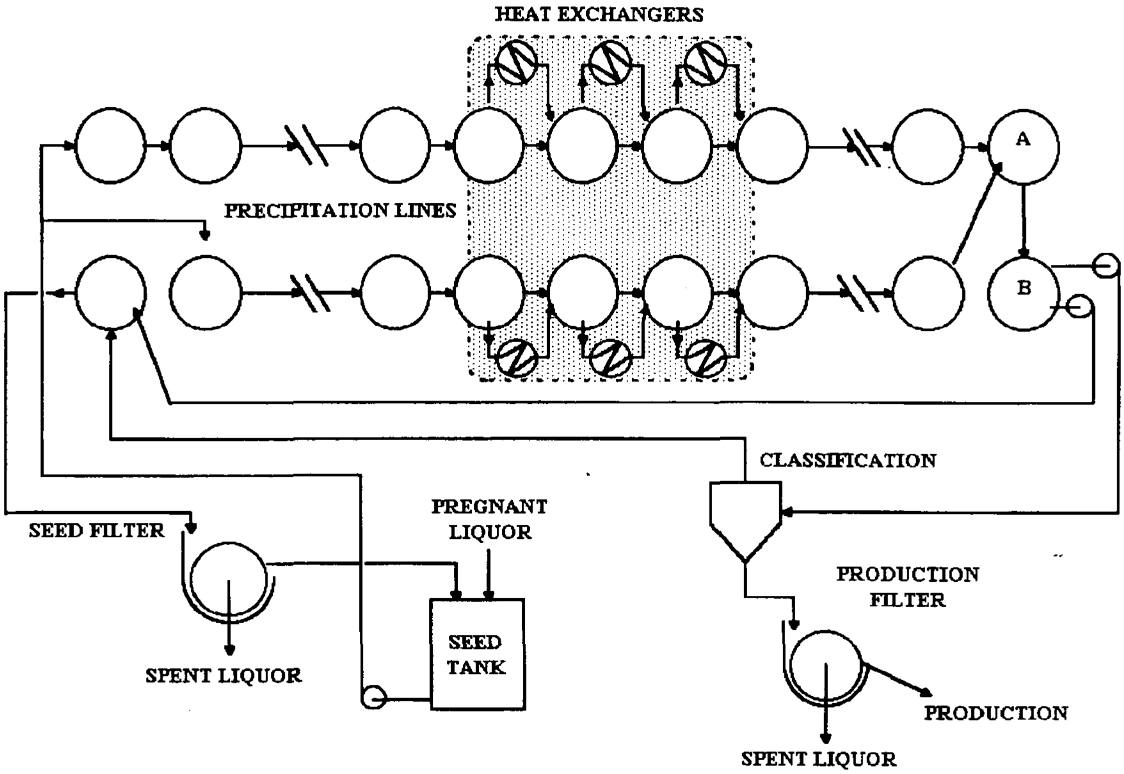
Crystal growth modifier is injected at this level in perfectly defined proportions according to the particle size distribution objectives and bound soda aimed in precipitation.

Slurry is then transferred by pumping in two precipitation lines (figure 2). Each line contains 3,000 m^3 tanks which are stirred mechanically. The slurry flows by gravity from tank to tank and the two lines join in precipitator A which overflows into precipitator B at variable level. From the latter, one part of slurry is transfered into the tank that feeds by gravity the seed's separation area, and the remaining part feeds the classification line.

Seed is separated directly by 70 to 80% of the flow coming from precipitation by filtration on disc filters. Filters cake is re-entered by gravity in the seed tank, although the spent liquor comes back again to evaporation and digestion.

Classification is implemented on the 20 to 30% of the remaining flow by means of two "turbiflux"(gravimetric separators). The underflow is sent, after filtration and washing, towards the calcination area while the overflow is also used as seed in precipitation by recycling it in the precipitator feeding the disc filters.

FIGURE 2 : SCHEME OF ADG PRECIPITATION (PECHINEY PROCESS)



2.2.2. Interstage cooling in continuous precipitation

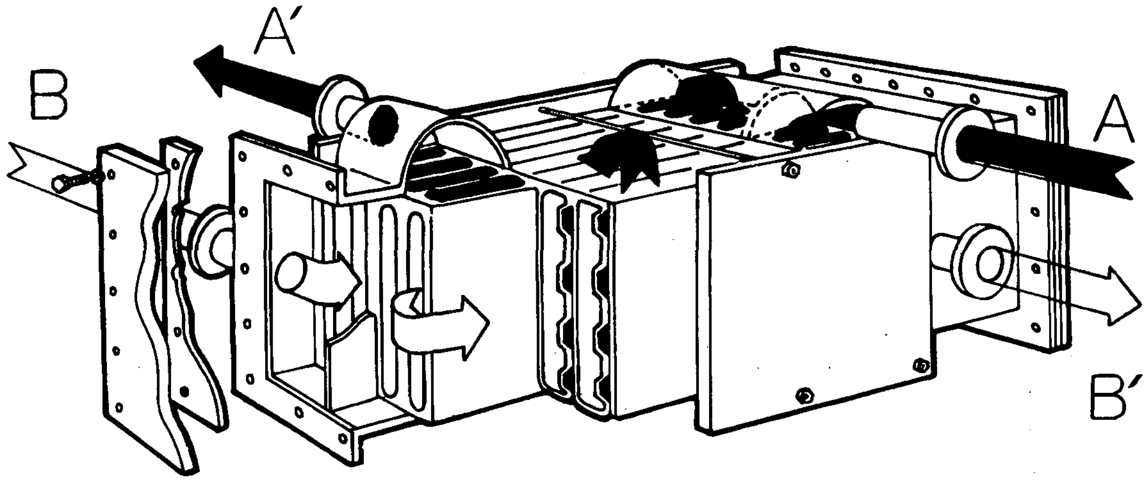
For a further improvement of yield a cooling system in continuous precipitation (figure 2) has been installed (3). It is composed of three "platulaire" exchangers per precipitation line. Their scheme is given in figure 3.

These exchangers installed on the top of the precipitators are fed with slurry by immersed pumps. Every apparatus receives a flow between 250 and 400 $m^3 \bullet h^{-1}$ of slurry (stream B). Cooling is achieved by a closed water circuit (stream A).

Every exchanger has an exchange surface area of around 250 m^2 and an average exchange coefficient of nearly 1,000 $kcal \bullet h^{-1} \bullet m^{-2} \bullet °C^{-1}$.

It should be noticed that the operation with high solid content (from 800 to more than 1,000 $g \bullet l^{-1}$) does not cause any particular operation problem in precipitators, filters or heat exchangers.

FIGURE 3 : "PLATULAIRE" HEAT EXCHANGER



Stream A : **Cooling water circuit.**
Stream B : **Slurry circuit.**

3.0. RESULTS

3.1. Yield with cooling in continuous precipitation

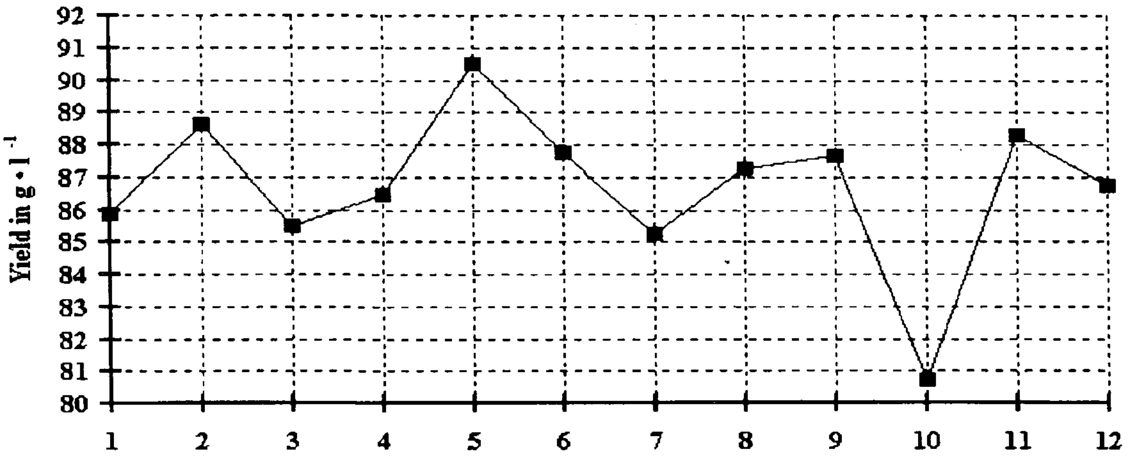
Apart from obtaining alumina according to international specifications, we care to have a maximal yield with a minimum residence time in precipitation for the optimisation of operation and capital costs.

The basic process of Pechiney precipitation (operation with very high solid in precipitation) has already proved a high yield: nearly 80 g • l^{-1} of Al_2O_3.

Installation of cooling system in continuous precipitation allows an improvement of it and achievement of about 90 g • l^{-1}, with an average residence time for precipitation of only 30 to 36 hours.

In figure 4 evolution of yield is shown, drawn from monthly operation results in one year.

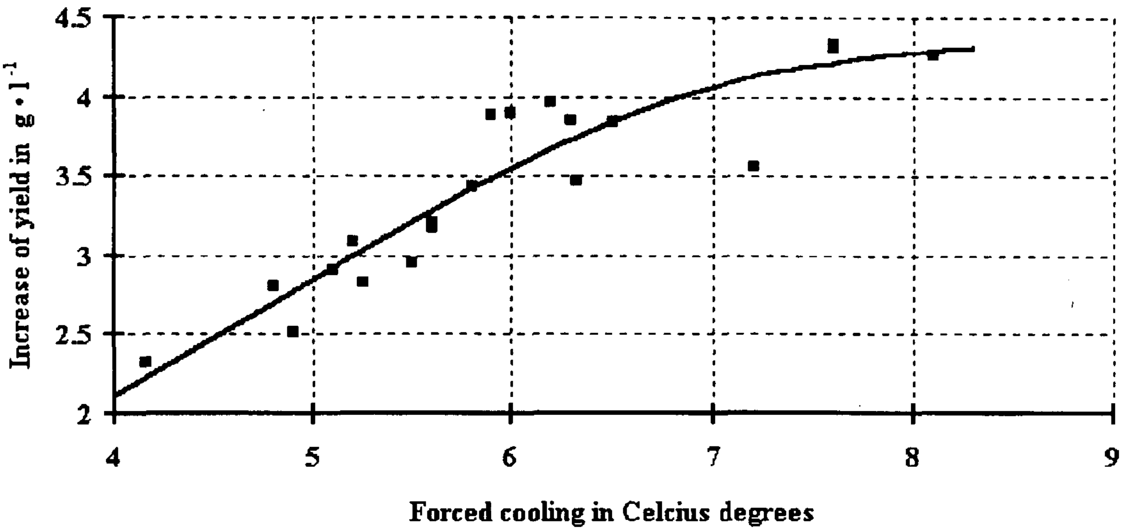
FIGURE 4 : YIELD EVOLUTION



It is interesting to note that yield is maintained continuously in a range between 85 and 91 g • l^{-1}, with one exception for the 10th month where the BAYER cycle was disturbed by a dysfunction external to the process.

In figure 5, is shown the yield increase according to cooling level aimed at the end of precipitation line.

FIGURE 5 : INCREASE OF YIELD



During the period mentioned previously, average forced cooling was 6°C, corresponding to an average yield increase of nearly 4 g • l^{-1}.

Previous study of arrangement of these devices has avoided any disturbance on process control and therefore on product quality.

Finally, it should be noticed that return on investment was less than two years (4).

3.2. Quality of alumina

The above described process allows to get alumina of steady and good quality as far as chemical and physical characteristics are concerned.

In figures 6, 7, 8 and 9 for the considered period the following points are mentioned:

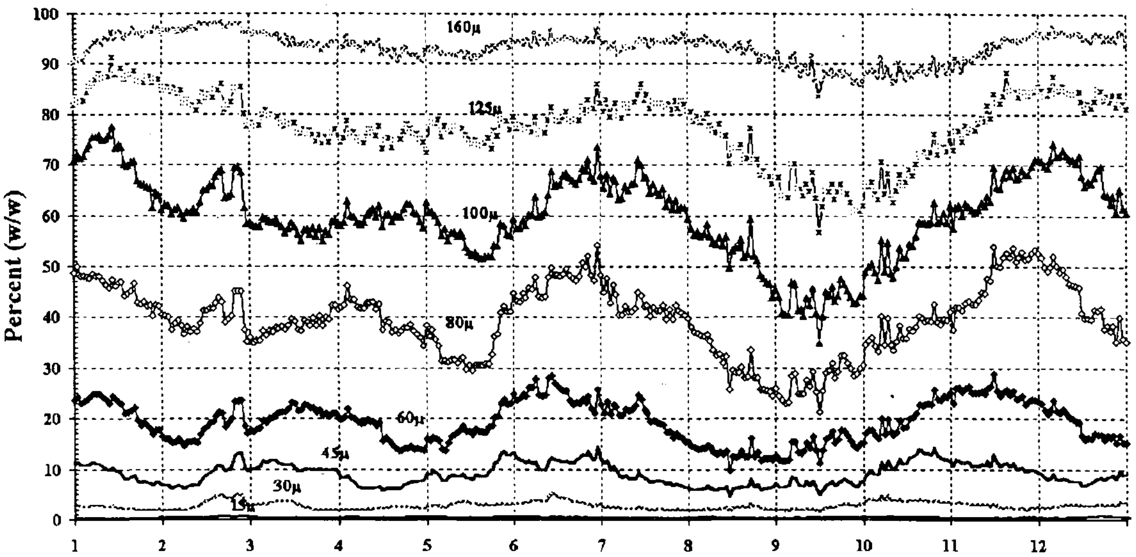
- Particle size distribution of the seed.
- Percentage of minus 45 microns ROTAP on calcined alumina.
- Attrition index (ALCOA test).
- Soda content on calcined alumina.

3.2.1. Particle size distribution of seed.

As shown in figure 6, achieved from daily measurements, it is confirmed that Pechiney process, with high yield in precipitation, allows a steady seed to be obtained. As a result, minus 45µ evolves in the reduced range of 6 to 14% for a long time. The sensible variations are mainly result of deliberated modification of particle size distribution target to obtain a coarser seed, for anticipation of a low performing classification period when the classification system is partially out of order for cleaning and maintenance.

As it was above mentioned, classification allows particle size distribution adjustment of product hydrate according to the target value on calcined alumina.

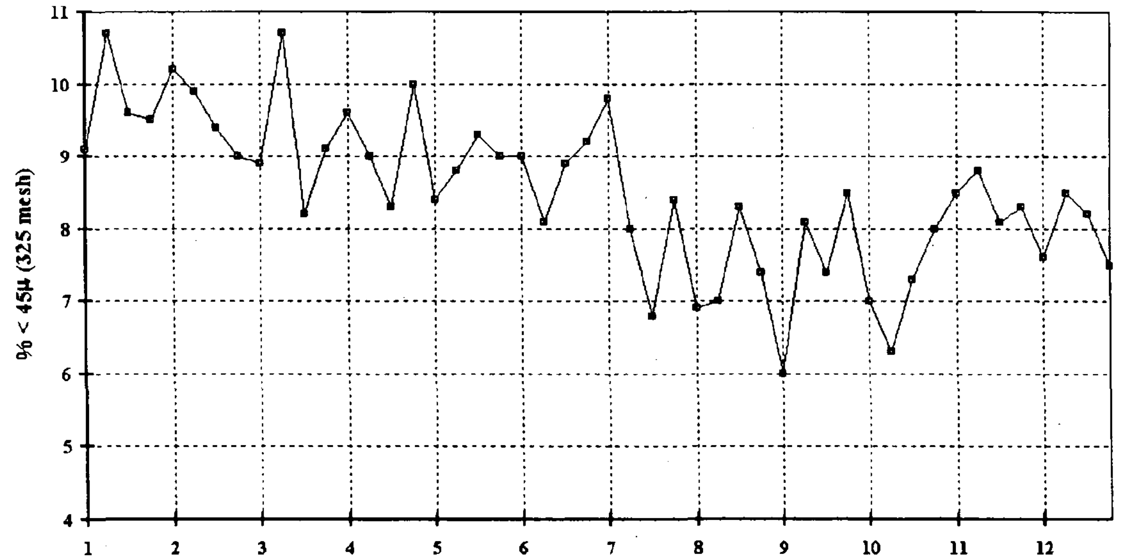
FIGURE 6 : EVOLUTION OF SEED PARTICLE SIZE DISTRIBUTION



3.2.2. Minus 45μ ROTAP on calcined alumina

As it is shown in figure 7, capability of process control allows to adjust minus 45μ of calcined alumina at the desired value more or less 2%.

FIGURE 7 : CALCINED ALUMINA : EVOLUTION OF MINUS 45μ (325 mesh)



As a result, according to what is shown in data evolution, one may distinguish two parts in figure 7, as follows:

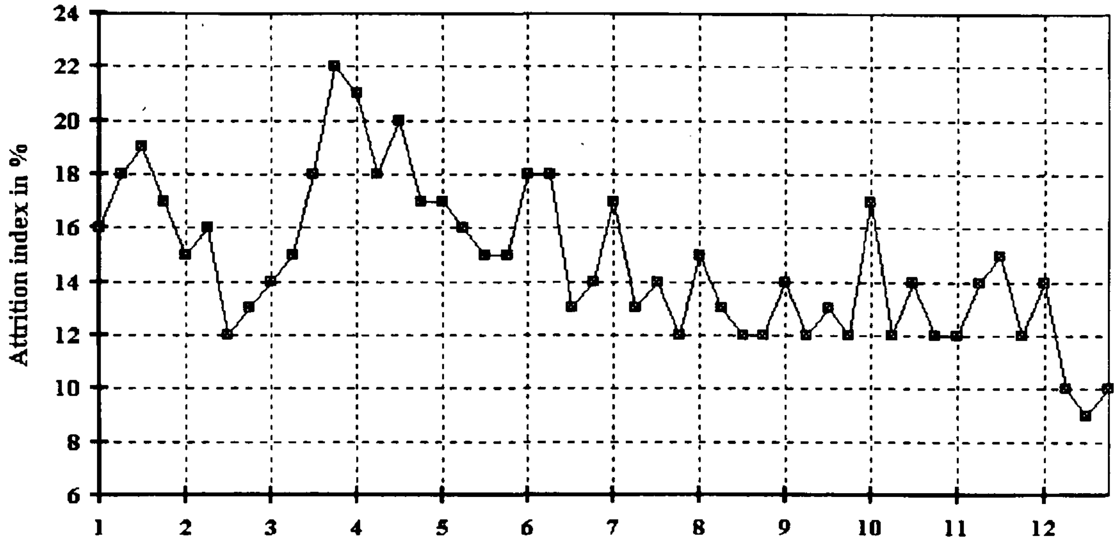
- A first period of seven months with an average value slightly superior to 9%.
- A second period with an average value of about 8% corresponding to a new objective (8±2%) desired by the main consumers of ADG alumina.

This last result is achieved thanks to the flexibility of the process allowing different particle size distribution to be obtained on the seed and therefore on the calcined alumina.

3.2.3. Attrition index

Attrition index given in figure 8 varies from 9 to 22%, with a typical value of 14%. This typical value of 14% is seen satisfactory by ADG customers.

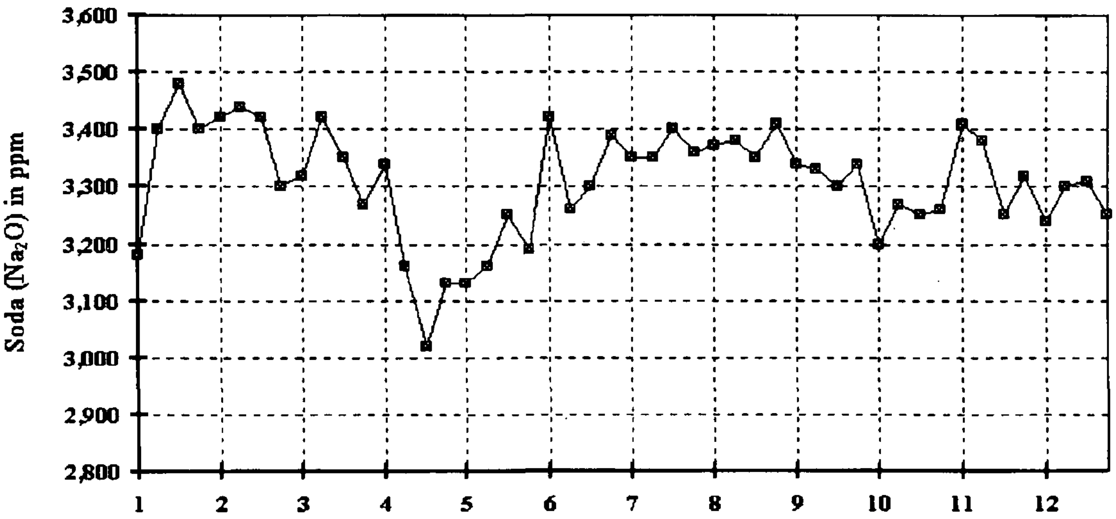
FIGURE 8 : EVOLUTION OF ATTRITION INDEX (ALCOA)



3.2.4. Content in soda

Although supersaturation control in the head of precipitation is mainly achieved by temperature adjustment, fluctuations of soda in calcined alumina are not significant. The concentration of bound soda is in the range 3,100 - 3,500 ppm Na_2O (figure 9).

FIGURE 9 : EVOLUTION OF SODA CONTENT



As it was above mentioned (2.1.4), this steadiness is achieved by suitable addition of crystal growth modifier into seed tank.

3.2.5. Minus of 20μ Laser

The level of ultrafine particles is quite low. It is permanently less than 2% w/w.

This is due, in a great part, to alumina strength and performance of classification systems.

3.2.6. Evolution of alumina main characteristics.

In table 2 evolution of ADG alumina main characteristics since 1992 is presented.

For all physico-chemical characteristics one may note a significant amelioration of alumina steadiness as shown by decrease of standard deviations over the years.

Table 2

Main characteristics of ADG alumina

			1992	1993	1994	1995
Specific surface area (B.E.T.)	average	$m^2 \bullet g^{-1}$	75	71	70	70
	standard deviation	$m^2 \bullet g^{-1}$	2.3	3.7	2.2	2.0
< 45μ ROTAP (325 mesh)	average	%	10	9.0	8.6	8.4
	standard deviation	%	1.9	1.7	1.4	2.2
Attrition index	average	%	18	17	14	14
(test ALCOA)	standard deviation	%	4.6	3.1	2.3	3.0
Na_2O	average	ppm	3,250	3,290	3,255	3,210
	standard deviation	ppm	252	163	159	142
Fe_2O_3	average	ppm	127	97	100	101
	standard deviation	ppm	7	9	8	6.1
SiO_2	average	ppm	102	96	104	99
	standard deviation	ppm	20	31	17.2	13.9
CaO	average	ppm	286	206	193	190
	standard deviation	ppm	61	61	30	24

4.0. ALUMINA BEHAVIOUR ON SMELTER POTS

4.1. Main smelters requirement

B.ALLAIS (5) and P.HOMSI (6) have recently shown the six main requirements of smelters operations having direct incidence on the alumina quality. These are as follows:

- A satisfactory speed of dissolution: dissolution of alumina in bath is favoured by a strong crystal disorganisation (low alpha content) and a narrow distribution of particle size, in the area of 45 to 100μ.
- A good and controlled feeding: a steady flow is necessary for good control of pots' feeding in case of centre point feeding cells (reproducible filling and emptying of the feeder). The latter is disturbed by the fine particles of alumina and fluoride dusts. Industrial experience indicates that the electrolysis doesn't tolerate an alumina entering pots with more than 20% minus of 45μ, resulting in requirement of an alumina with few fine and strong particles.
- Chemical purity: the main impurity is soda that is fully responsible for the consumption of AlF_3. The correct control of bath composition in particular, in the modern pots requires an alumina with regular Na_2O content of about 3,000 ppm.

  The other impurities (Fe, Si, Ti, V etc.) except for phosphorous which is considered as a poison for electrolysis, have mainly an influence upon the metal purity.

- An excellent collection and treatment of hydrogen fluoride: in fact, the current legislation imposes an absorption efficiency of hydrogen fluoride greater than 99.99% in the fume treatment plant. Consequently, a minimum specific surface area is required. The latter must vary with pot technology, since emissions are dependent on AlF_3 excess in the bath.
- Good anode cover and crust stability: with the point feeding system on one hand, a stable crust is imperative to be established to avoid overfeeding phenomena and, on the other hand, a good anode cover to avoid oxidation and to limit heat losses from the pot top. Both these requirements are taken away with an under-calcined alumina with low content of alpha alumina.
- Avoidance of volcanoes and dust emission: the appearance of volcanoes accompanied by dust emission is mainly due to the presence of residual hydrate in quite high quantity, corresponding to a lake of calcination.

4.2. Main specifications of calcined alumina

From the above mentioned requirements, the standard specifications of alumina for electrolysis, in particular for Pechiney pots AP 18 and AP 30, have been defined (5) (6).

In table 3 these specifications are compared with the main characteristics of ADG alumina.

Table 3

	Average values of ADG alumina	Pechiney specifications for AP 18 and AP 30 pots
B.E.T. surface, $m^2 \bullet g^{-1}$	70	65 - 75
% < 45µ (325 mesh)	8	< 10
Attrition index, % (ALCOA)	14	< 15
Na_2O, ppm	3,200	3,000 to 4,000
Fe_2O_3, ppm	100	< 165
SiO_2, ppm	100	< 130
CaO, ppm	200	200 to 400

One may verify that ADG alumina is well accordant with the modern smelting technology requirements. (It should be noticed that the B.E.T. surface and the silica are not linked with the precipitation process).

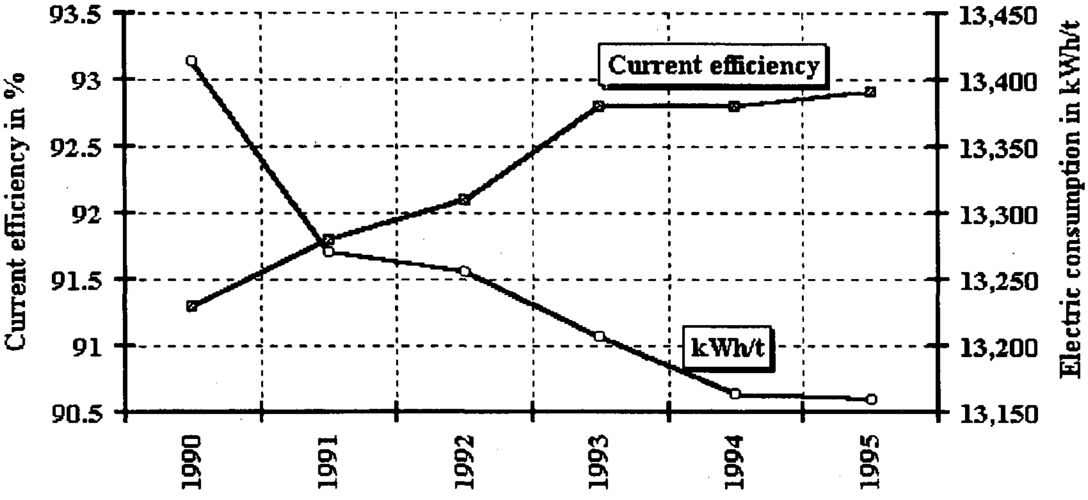
4.3. Utilisation of ADG alumina in "Saint-Nicolas" plant

ADG electrolysis is composed of 3 pot lines, of 70 and 90 kA, with hooded and prebaked pots and point feeding.

Apart from highly satisfactory quality of metal, the main performances of the electrolysis are good in particular taking into consideration the age of this technology.

It has been accepted that improvement of alumina quality, especially steadiness, has contributed to the improvement of technical results, as shown in figure 10 where evolution of current efficiency and electric consumption are shown.

FIGURE 10 : EVOLUTION OF CURRENT EFFICIENCY AND ELECTRIC CONSUMPTION



4.4. <u>Utilisation of ADG alumina in pots of new technology in "Saint-Jean-de-Maurienne"</u>

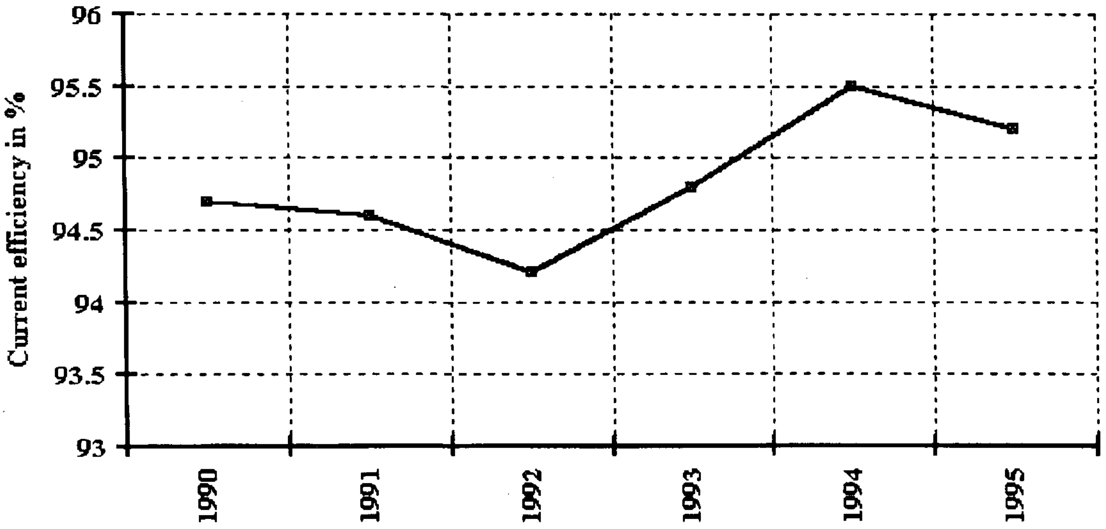
The electrolysis of "Saint-Jean-de-Maurienne" (France) is composed of two modern pot lines:

- the pot line F started in 1979 with pots of AP 18 technology operating at 180 kA.
- the pot line G started in 1986 with pots of AP 28 technology, operating at 290 kA.

Since 1989 the pot line G has been fed with ADG alumina. Utilisation of this alumina and amelioration of its quality have contributed to very good technical results (95.5% of current efficiency in 1994, figure 11) with limitation of fluorine emissions at 0.55 kg•t^{-1} of aluminium. Furthermore, transport of this alumina from fume treatment plant to pots by hyper-dense phase system (7) takes place in excellent conditions.

ADG alumina's usage in "Saint-Jean-de-Maurienne" indicates that this alumina has been perfectly adapted to the pots of new technology.

FIGURE 11 : EVOLUTION OF CURRENT EFFICIENCY



5.0. CONCLUSION

The classic european process of precipitation adapted by Pechiney based on the control of nucleation density at 1.5µ ($N_{1.5\mu}$) allows an alumina of SANDY type to be regularly produced with a minimum investment.

The initial adaptation (1) resulted in a significant loss of yield (more than 10%) with direct influence upon operating cost and/or production rate.

The developments carried out in ADG (additive of precipitation, interstage cooling in continuous precipitation, optimum process control) have allowed to compensate this loss and even to push yield till 91 $g \bullet l^{-1}$.

Alumina produced by Pechiney process (6 to 10% less than 45µ, 3,000 to 3,500 ppm of Na_2O) responds to the requirements of the electrolysis especially for pots of new generations (AP 18 and AP 30).

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REFERENCES

(1) Cristol, B and Mordini, J. (1988) Alumina production for modern smelting technologies by high solid content precipitation. First international alumina quality workshop. Gladstone (Australia).

(2) Roe, W.J., Owen, D.O. and Jankowski, J.A. (1988) Crystal growth modification: practical and theoretical considerations for the Bayer process. First international alumina quality workshop. Gladstone (Australia).

(3) Denaxas, N. and Zervos A. (1992) Saving energy in alumina - aluminium plants. International congress on energy efficiency in process technology. Athens (Greece).

(4) Papadakis, A. and Leredde, J.P. (1994) Interstage cooling in continuous precipitation of aluminium hydroxide in "Aluminium de Grèce" alumina plant. Rapport technique final à la communauté européenne.

(5) Allais, B. (1993) Modern aluminium smelting technology and future trends: alumina quality implications. Third alumina quality workshop - Hunter Valley - New South Wales (Australia).

(6) Homsi, P. (1995) Alumina requirements for modern smelters. Fifth australasian aluminium smelter technology workshop. Sydney (Australia).

(7) Martin, O., Crapart A. and Gérard P. (1992) G line in St-Jean-de-Maurienne, 6 operating years. AIME 1992, San Diego (USA).