MODERN ALUMINIUM SMELTING TECHNOLOGY AND FUTURE TRENDS : ALUMINA QUALITY IMPLICATIONS

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ABSTRACT

High performances have been achieved, over the last ten years, with modern smelting technology and new developments are being carried out. A quick review of Aluminium Pechiney technology is made.

With a high level of technical results consistently achieved, more stringent requirements are put on alumina quality. Aluminium Pechiney has carried out theoretical and applied studies, bench scale and industrial tests aimed at optimising the grade of alumina used on its modern pots. The results are condensed in the alumina specification, which sets thresholds for the main alumina characteristics. Chemical and physical characteristics are described in relation with the behaviour of alumina on the pots, in the dry scrubbing centers and in the handling systems.

An attempt is made to define the ideal alumina for modern and future pots.

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1.0 INTRODUCTION

Since the end of the 1970 s, important changes have taken place in Aluminium Pechiney smelting capacity culminating in 1991 with the shutdown of its Soderberg plant (Norgueres) and the start up of the new AP30 plant (Dunkoque) (264 pots, 300 kA, 220 kt/a).

In the 1980's, smelting capacity was rejuvenated via greenfield smelters in Australia, Canada and France the former two having been expanded in 1993 and 1990 respectively. (The technology used is AP18 -180 kA cells and AP28 - 280 kA cells). Technical results achieved in those new plants have been consistently high.

A summary of main results has been presented for the Canadian smelter (1) showing current efficiency at 94,9% and kwh/t at 13300 over 6 years for the 180 kA cell. With the development of its new cells since the late 1970s, a set of technology options have been defined :

- The new cells are characterized by a high amperage and an excellent magnetic and thermal balance ; they are fitted with automated operating procedures and automatic process control ; they are well hooded cells which operate associated to a fume treatment plant.
- Definite requirements have been established for the alumina feeding devices, the handling of alumina prior to reaching the cell, the cells operating set point and its associated process control.

A review of the technology is developed below.

2.0 ALUMINA HANDLING

If we consider all the alumina handling occurring in a smelter, we can identify three categories :

- supplying alumina to the cell,
- introducing alumina into the liquid bath,
- treatment of alumina in the fume treatment plant.

2.1 Alumina Feeding To The Cell - Advanced Design For Introduction Of Alumina Into The Bath

Modern cells (that is AP18/AP30) with prebaked anodes using central positive risers to achieve low magnetic fields have been designed to automatically feed alumina almost continuously under simple hoods which remain closed for this operation (2).

Each cell now has its own breaking and feeding equipment which can control the feeding of the small individual quantities of alumina necessary for efficient operations.

2.1.1 Functionality

When not introduced directly into the bath, alumina quality for the electrolysis deteriorates : high temperature water content decreases, alpha content increases under the effect of fluorides fumes and therefore solubility decreases.

Breaking and feeding functions have been separated which means that the breaker does not have to be operated each time the feeder operates and that the alumina is kept above the crust in a hopper before being dumped directly into the bath. As with small alumina doses (1 kg per dose), feeder operation is frequent, while breaker operation only need to keep the crust hole permanently open.

This development allowed large savings in compressed air consumption.

2.1.2 Equipment

Both pneumatic or gravity types of feeders are sufficiently accurate when associated with a suitable process control. However modern cells make extensive use of gravity feeders.

Alumina hopper

The alumina hopper placed in the superstructure allows alumina to be preheated to around 100°C by the pot before it is discharged into the bath. This reduces low temperature water content causing a smaller evolution of hydrogen fluoride by hydrolysis, less dusting on the bath surface and a more reliable introduction of alumina.

The heat required to dissolve the alumina is smaller since water is not vaporized.

AlF_3 point-feeder (reminder)

Point-feeders are also used for bath composition corrections and the most recent cells have been designed with the AlF_3 hopper integrated into the superstructure and a removable gravity feeder supplying AlF_3 into a hole kept open by a breaker shared with an alumina feeder.

2.1.3 Position and number of feeders for one cell

The number of feeders required not only depends on the reliability and characteristics of the breaker/feeder but also on :

- performance of the associated automated control,

- stability of the cell proceeding from the magnetic and thermal design and leading to metal and bath movements,

- size of the cell: the number of feeders required is not proportional to amperage. In a large cell with 4 breaker/feeders the automated process control is able to detect the operation of a breaker/feeder and compensate for it until the problem is corrected.

The position of the feeders in the central channel is determined to obtain the best compromise regarding constraints such as :

- velocity of the bath for alumina dissolution,

- accessibility of the breaker hole from the cell side,

- position of feeders relative to anodes to minimize,

- freezing of feeding holes when changing anodes,

- design of the superstructure.

Optimization of the position and number of feeders cannot be obtained by design only but also requires prototype testing with long and systematic development work.

When optimised, this alumina feeding structure allows optimal control of alumina introduction to the liquid bath.

2.2 Transport Of Alumina To The Cell

Alumina fed to the cell has been handled a very large number of times through different handling systems. The transport operations and handlings facilities of a modern smelter are :

- pneumatic lifter or vacuum unloader from the cargo ship,

- belt conveyor and pneumatic lifter to the plant silo,

- belt conveyor to the dry scrubber silo,

- airslides to the dry scrubber system,

- hyperdense phase transport to the cells for the final distribution.

As a result, alumina has been in and out four different silos, run along hundred meters of belt conveyors or airslides, subject to the dry scrubbing process and again along hundred meters of hyperdense phase transport. All this handling creates ways to degrade the quality of the alumina before it reaches the liquid bath in the cell.

Silo engineering, bulk handling design and dry scrubbing engineering are working on maintaining mechanical characteristics of the alumina through the system so as not to create too many quality variations damaging to cell feeding system and control procedures.

2.3 Fume Treatment Plant

The need for elimination of fluorine pollution made it necessary to develop an efficient hooding of the cell making pollution control an integral part of the production process. This leads to the development of the dry scrubber systems which use the alumina as absorbent for the fluorides in the pot gas effluent.

There are various systems in use but they all require certain characteristics for the alumina, mainly high adsorption to fluoride gas, strong mechanical property and low chemical impurity levels.

With high purity metal sections set up in potlines, some cells are fed with fresh alumina and only a reduced share of the alumina feed is used in the dry scrubber.

3.0 CELLS OPERATIONS

3.1 Process Set Point

Aluminium Pechiney has chosen a process set point for running its modern potlines which is characterised by :

- high AlF_3 excess bath,
- low alumina content in the bath,
- bath superheat around 10-15°C.

The advantages/drawback of this operational set point and the technical results associated has been well documented (3). The main constraint is that it requires a sophisticated control system since the alumina solubility is significantly lowered and anode effects can occur if alumina content becomes too low.

We outline below the importance of controlling the main operating parameters that are :

- bath composition, temperature and volume,
- alumina content in the bath.

3.2 Control Of Bath Operating Parameters

3.2.1 Bath temperature

Liquid bath temperature is very dependent on cell condition. It varies greatly with alumina content in the bath. In the case of cells with automatic control of alumina feeding and a narrow range of alumina concentration, the liquid bath temperature is closely related to the alumina feeding rate at the time. It also varies according to the operating procedures running at the time so it is advisable to always measure temperature when the operating conditions of the cell are steady or to take into account these operating conditions when interpreting the results.

Temperature provides useful information for checking the bath analysis made on a sample taken at the same time as the temperature as the estimated bath superheat is of particular interest.

3.2.2 Bath composition

Bath analysis is used for AlF_3 corrections which are carried out according to a systematic correction table. It also enables monitoring of CaF_2 content which is believed to stabilize AlF_3 content in the bath.

The bath composition of cells with automatic point feeding is very sensitive to instability and long anode effects. A good correction can only be made on the basis of an analysis which is recent enough to reflect the current cell condition. Keeping AlF_3 excess actual values as close as possible to a target optimum is difficult. However, it allows a check to be kept on the alumina solubility.

3.2.3 Bath volume

Bath composition of cells is directly correlated to the bath volume in the cell. Very strict controls are imposed on bath transfer in relation to work organisation for operations and measurements.

3.2.4 Optimisation of bath temperature

The optimum average temperature is the lowest temperature at which deposit on the cathode surface and excessive instability can be avoided. It can only be arrived at by experience and depends on :

- **cell design**
  - * type of alumina feed involving the range of alumina concentration,
  - * cathode thermal balance ;

- **bath composition** (additives)
  - * excess AlF_3,
  - * CaF_2,
  - * LiF ;

- **solubility of alumina**
  - * BET specific surface,
  - * LOI 300-1000°C.

3.3 Control Of The Alumina Content In The Bath

Pechiney's control strategy on cells with point feeding is centered around the facts that : operation in the area where resistance increases with alumina content (alumina content larger than 3%) eliminates anodes effects but increases the risk of sludge deposits on the bottom of the pots, poor cathode drop, uneven cell condition in the potline and large and rapid thermal changes.

- Operation in the area of minimum resistance eliminates the risk of sludge deposits, but is more difficult to detect because of the small variation of resistance with alumina content.

- Operation in the area where resistance clearly decreases with alumina content (2 to 2,5%) increases the risk of anode effects but, in spite of a slightly higher bath temperature, experience shows it is the best area for optimum current efficiency and energy consumption.

A sophisticated control system with many feeding parameters used to adjust the range of alumina content is used to maintain the cell around the chosen set points.

3.3.1 Process control procedure

Automatic control routines are carried out through cell voltage (U) and potline amperage (I). Cell control procedures are based on the calculation of a pseudo-resistance (R).

$$R = \frac{U - E}{I}$$

where E is a constant value.

These procedures are designed to :

- maintain the resistance close to a target value,
- manage the alumina point feeding,
- adjust operations to operating procedures (anode changing, tapping...).

On cells with automatic point feeding, the alumina feeding programs have priority over the conventional regulation of the pseudo-resistance (2).

Briefly, the point-feeding program controls the variation in cell resistance over time and initiates an overfeeding period when this variation exceeds a given value (the basic procedure is alternate of overfeeding and underfeeding periods).

$$\frac{dR}{dt} = \frac{dR}{d(Al_2O_3)} x \frac{d(Al_2O_3)}{dt}$$

A given value of $\frac{dR}{dt}$ combined with a fixed alumina underfeeding

rate $\frac{d(Al_2O_3)}{dt}$ corresponds to a given slope of the bath profile
(R versus Al_2O_3).

Continuous calculation of $\frac{dR}{dt}$ during underfeeding, at constant anode cathode distance makes it possible to initiate an overfeeding period when the alumina content reaches a low threshold (critical slope). If it is not reached the resistance is forced back to the no-adjustment zone.

This method gives access to a quantified value of alumina concentration (the slope) which allows operation with a reduced alumina concentration range around a low target percentage.

3.3.2 Conditions for a successful alumina feeding regulation procedure

Bath volume should be as constant as possible since for a given over

and under-feeding the variation of alumina content with time $\frac{d(Al_2O_3)}{dt}$

depends on bath volume.

Slight variations in bath temperature should be limited to those caused by variations in alumina content.

Dissolution of alumina must be rapid and complete so that required feeding rates have an immediate effect on alumina content in the bath.

Alumina must be very soluble.

The feeder system must be reliable.

The anodic surface must remain as even as possible.

Experience shows that this point-feeding program is flexible and sensitive to the needs of the cell, an therefore capable of adapting to sudden changes in the thermal balance of the cell or the alumina characteristics.

As a safety measure and also as an additional control, it is possible, on a systematic basis to stop feeding the cell every day or two. No order is given to the cell so as to keep a constant anode cathode distance and the resistance is observed. Overfeeding is initiated when the resistance has increased by a given value.

This procedure of tracking is used to control the alumina content operating range. It drains excess alumina from the cells which have had problems (anode effect, instability) and gives valuable information on the entire potline through average tracking time and standard deviations.

4.0 REQUIREMENTS ON ALUMINA QUALITY

Having outlined the equipment and process control implemented in a modern smelter, there remains one very important factor in order to achieve best potline performances: to optimise the alumina specification to meet its specific operation requirements. The discussion encompasses the impact of physical and chemical characteristics of the alumina. Table 1 summarises the main operating constraints and requirements arising from the technology chosen and therefore narrowing the range of alumina to be used in each case. Their relative importances depends greatly on the cell technology (4).

For example, centre-worked pots are more sensitive to dissolution phenomena than side-worked pots, which can even be operated on floury alumina. Against this, dust emission in the potroom when feeding with the hoods open can be a problem with sidebreak cells.

The main requirements are further defined below for cells with point feeding and prebake anodes operated with a dry fume treatment plant.

These are :

- speed of dissolution,
- excellent collection and treatment of hydrogen fluoride,
- good and controlled feeding,
- no volcano formation, no dust during feeding,
- good anode cover and stable crust,
- high metal purity, no bath impurity.

TABLE 1 - POT OPERATION CONSTRAINTS

Consistent and regular alumina quality is fundamental to satisfactory pot operation.

Acceptable limits on variations in alumina specification will depend on the reduction technology employed

Constraints	Operating Requirements	Importance of Requirements				Alumina Properties Concerned
		Soderberg	Prebake			
		No Dry Process Treatment	No Hoods, No Dry Process Treatment	Hoods And Dry Process Treatment	Point Feeding Dry Process Treatment	
Physico-Chemical	Speed Of Dissolution	+	+	+	+++	Rate Of Dissolution
	Little Hydrolysis Of Bath	++	++	++	++	Moisture Content
	Satisfactory Protection Of Anode System (Against Air Burn Of Carbon And Corrosion Of Steel Pins)	0	++	++	+	Impermeability To Air And To The Bath
	Low Heat Of Dissolution	0	0	0	++	Crystal Structure
	Low Overvoltage	++	++	++	++	Lattice Water
Thermal	Effective Heat Insulation (Anode Cover)	+	++	++	++	Thickness Of Layer Thermal Conductivity Of Layer
Mechanical	Good Stability Of Alumina Cover	++	++	++	++	Stability Of Layer
	Formation Of A Stable Crust	++	++	++	++	Wettability Of Alumina
	Crust Easy To Break	+	+	+	+	Wettability & Reordering Of Alumina Crystal Structure
	No Formation Of Volcanos	0	0	0	+++	Behaviour Of Grains (Absence Of Hydrate)
	Good Penetration Of Alumina Into Bath	++	++	++	++	Wettability & Dispersion In Bath
	Good Feeding	0	0	0	+++	Free-Flowing
Environmental And Work Condition Related	Minimum Dust Emission (Geyser Effect And Fly-Up) : When Not Carrying Out Tending	+	+++	+	+	Little Susceptibility To Entrainment By Air Or Pot Fume
	Operations When Carrying Out Tending Operations	+++	+++	+++	+	Ability To Outgas
	Minimum Emission Of Fluorine Products (At Given AlF_3 Excess)	++	++	++	++	
	Good Gas-Tightness To Pot Fume	+++	+++	+	+	Formation Of Gas-Tight Cover
	Satisfactory Collection/Treatment Of HF	+	+	+++	+++	Adsorption
	Minimum Retention Of SO_2	0	+	++	0/+	Adsorption
Production	Maximum Reduction Current	++	++	++	++	

RANKING ORDER REQUIREMENTS :

0	=	Not Important
+	=	Slightly Important
++	=	Important (Particularly As Regards Economics)
+++	=	Fundamental

The main related alumina characteristics are :

- water content,
- specific surface area,
- crystal organisation (alpha content),
- grain size distribution and attrition,
- chemical purity,
- mechanical properties (angle of repose, flowability, crust hardness, segregation, dissolution).

4.1 Operating Requirements

4.1.1 Speed of dissolution. With the development of the alumina centre-point feeding technology, the bulk of the Aluminium Pechiney research effort has concentrated on this point and includes : tests carried out on microcells, infrared spectroscopic determinations, X-ray scattering, electronic micro-diffraction analysis and potentiometric determinations on chlorofluorinated baths (4).

An understanding of the mechanism of the process of dissolution, the degree of organisation of the crystal structure and the part played by water makes it possible to set rules for obtaining a soluble alumina.

Mechanism of dissolution. The introduction into the liquid bath of a grain of alumina gives rise to two conflicting phenomena, namely:

I) exothermic restructuring of the transition phases (recrystallisation of large crystals in the alpha phase) assisted by the pre-existence of organisable crystallites and the absence of defects to be eliminated (lattice water);

II) endothermic destruction of the crystal lattice, with preferential attack at sites of defects. Dissolution is assisted by the existence of a crystal structure exhibiting a high degree of disorder, a substantial interfacial area available for liquid/solid interaction (mass transfer) and a sufficient reserve of heat in the vicinity of the interface.

Crystal organisation. This will be determined by the kiln technology employed in the calcination of the hydrate. Thus:

- slow decomposition leads to the formation of large crystals of organisable phases (chi, kappa and alpha) and elimination of defects ;

- sudden decomposition (involving thermal shock), characterised by the in-situ formation of a boehmite phase, leads to the formation of phases which are less readily organised (gamma and delta) unless they can be held for extended periods at high temperature (theta and alpha).

Part played by lattice water. Residual water is "stabilised" by the presence of lattice defects. It is lost when slow and extended recrystallisation occurs on calcining. It therefore provides a useful picture of the degree of disorder of the crystal structure. The sudden volatilisation of water on contact with the liquid bath brings about disruption of the grains and dispersion of the alumina/bath magma, which is favorable to dissolution.

Implications for calcination technology. These considerations point to the desirability of :

I) subjecting the Bayer hydrate to thermal shock,

II) very short residence time at high temperature for all the constituent particles. Calcining in the rotary kiln gives a product of mixed composition. A soluble alumina can be obtained only by aiming at high surface area and avoiding over-calcination of fines.

Fluidised bed calcination gives a more uniform product and is carried out at lower temperature. Extended residence times should nevertheless be avoided since they give rise to a theta phase which is highly ordered and therefore not very soluble.

The gas suspension calcination technologies now being developed combine the two requirements of thermal shock and short residence time and yield a soluble alumina. Experience to date points to promising results towards improved solubility.

It should be emphasized that the correlations observed between crystal organisation, moisture content and specific surface differ to a fair extent as between technologies.

Implications for particle size distribution. The process of dissolution takes place via the transfer of mass across the solid/liquid interface. The greater the area and the reactivity of the interface, the faster the rate of exchange. Hence, for a given quantity by weight, the smaller the particles the greater the surface area and the faster the rate of dissolution. The presence of large grains has a negative effect. A further requirement is that the interfacial area should be not greatly different from the surface area of the alumina and this will not be the case if the bath solidifies around the particle because of the heat absorbed on dissolution.

The need is either for substantial local superheating of the bath, which will be favoured by a disordered crystal structure, or for each grain to be surrounded by a large enough volume of bath ; this is obtained if the alumina grains fed to the cell are well separated and is assisted by the volatilisation of water, leading to further separation of the individual grains.

Two of these requirements (no coarse grains and sufficient spacing of particles) add up to the need for a narrow distribution of particle size within the range 45-100 μm.

4.1.2 Collection and treatment of hydrogen fluoride

The many variants of the dry treatment process all rely on the adsorption of hydrogen fluoride on alumina. Briefly :

- current legislation effectively imposes an efficiency of better than 99.99% for the adsorption of hydrogen fluoride on the alumina in the fume treatment plant ;
- the gas/alumina contact time in the state-of-the-art systems can be very short, so that the rates of diffusion of the hydrogen fluoride into the pore system and adsorption have to be high ;
- the alumina has to adsorb and retain the totality of pot fume emission and the pots have to be able to digest the totality of the alumina treated in the fume treatment plant.

As a result, a minimum will have to be set for the alumina specific surface area according to the process set point since emissions are very much dependent on AlF_3 excess in the bath.

Note : Under certain operating conditions, the pots have a tendency to give off more fume, whereupon the natural reaction of management is to look for an alumina offering a larger surface area. This is the wrong reaction insofar as such an alumina will generally contain more moisture, the effect of which, as a result of hydrolysis of the components of the bath, is to boost hydrogen fluoride emission very substantially.

4.1.3 Good and controlled feeding

The virtually continuous alumina feed from an automatic volumetric feeder requires filling and emptying under reproducible conditions which in turn call for a free-flowing alumina (i.e. one with minimum internal friction). The presence of alumina fines and fluoride dust has a strongly negative effect on flow properties. The angle of repose may not be a sufficient criterion and Aluminium Pechiney habitually uses a special procedure to determine flow characteristics. Industrial experience shows that centre-point feeding cells can generally accommodate an alumina containing, after attrition at the various process stages, up to 20% of fines passing the 45 μm.

4.1.4 Avoidance of volcano formation and dust

With alumina centre point feeding, residual hydrate leads to the formation of spurts or "geysers" of ultrafine material, as a result of vapour blanketing and disruption of particles at the bath surface. The geysers, in turn, can result in the constitution below the crustbreakers of "volcanos" with walls consisting of alumina ex-hydrate which recrystallises in contact with fluorine fume.

In addition to the problems of interference with crustbreaker operation and poor control of alumina feed (with alumina falling onto the outer slopes of the mounds or expelled from the feeder hole), collapse or deliberate breaking-up of the mounds leads to the formation of a low-solubility granular magma below the crustbreaker at the centre of the cell.

Although a small quantity of residual water is tolerable for centre-point feeding, the proportion of hydrate has to be kept low. Aluminas of very high specific surface give rise to the same problems.

Industrial-scale tests have been carried out by Aluminium Pechiney at different smelters on various batches of alumina which showed that materials brought into suspension in the air are very finely divided and that particle size at the pot is not determined solely by that of the alumina as supplied to the smelter. Analysis showed that the principal factors of importance are :

I) the impact of local and operating conditions,

II) the size history of the alumina (i.e. particle size at the cell),

III) water content.

Impact of local and operating conditions. The differences in behaviour of one particular alumina in two smelters, or even in two adjacent potlines can highlight the influence of ventilation (wind exposure, natural draught, scrubber blowrate, etc.) and of the operation such as different handling stages before the cells.

Alumina size distribution on the cell. The qualification "on the cell" is of high importance, given that particle size will to some extend be affected by the various stages through which the alumina has to pass on the way to the cell, with attrition in airlifts and, particularly, in the dry treatment process, and segregation in storage silos. To what extend, exactly, can be determined only via a method of analysis which is not itself attritive and which can detect and measure the smallest particle sizes (e.g. wet sieving or the laser analyser).

It can thus be shown that particle size at the cell depends on :

a) the susceptibility of alumina to attrition, as evaluated by the standard attrition index test [or modified version in order to simulate actual behaviour in industrial practice] ;

b) the severity of the effects of handling, particularly at the dry treatment stage ; very considerable progress has been made in this respect (in terms of gas flow and distribution of alumina in the gas stream) and certain dry processes which are only mildly attritive (e.g. the Air Industrie process used at Saint-Jean-De-Maurienne & Dunkoque makes outstanding resistance to attrition less imperative) ;

c) possible segregation phenomena, a problem which has now been effectively resolved thanks to systems employing rotating feeding systems and multiple discharge points or honeycomb silos.

However, particle size at the cell is not the whole explanation for the variations in dust emissions observed on one potline. The moisture content has to be taken into account :

<u>Influence of water content</u>. There are four "categories" of water to be found in alumina :

I) physically adsorbed water; this is removed at the dry treatment stage,

II) chemisorbed water; this is bonded to the surface and is partially stable up to 300°C,

III) water of constitution (residual hydrates); this comes from the admixture with the alumina of low-calcined dust,

IV) lattice water; this is stabilised by defects in the crystal lattice and is an accurate reflection of the degree to which the crystal structure is ordered.

Chemisorbed water: the more or less abrupt volatilisation of a substantial quantity of water entraining fines when alumina is introduced into the bath.

Residual hydrate: leading to the formation of geysers of ultrafine material.

In short, the need is to ban hydrate and curtail the area available for chemisorption.

4.1.5 Stable crust and anode cover

With alumina point feeding there is a strong need for a stable crust in order to prevent overfeeding of the pot and to help overall gas collection efficiency. (A well tended pot with only the feederholes open will have a better collection efficiency).

Also required is a good anode covering mixture to reduce oxidation and heat losses from the top of the cell.

The cover will have a better gas-tightness if a solid crust develops. This is achieved with under-calcined aluminas, which are subject to a restructuring of the transition phases, leading to large crystals of alpha phase.

Nevertheless, experience shows that on the other end of the range, if alpha content is too low (below 5%), problems may occur with excessive crust hardness, leading to operational difficulties on the cells (anode beam motorisation, anode changing procedure).

4.1.6 Chemical purity

Na_2O content gives way to a net bath production in the cell which explains nearly all of the AlF_3 consumption. Efficient control of excess AlF_3 in the bath greatly depends on its regularity over time. In modern pots, the equilibrium value seems to be around 3000 ppm of Na_2O.

As environmental considerations on bath handling and storage outside plants grows and as developments of sophisticated bath composition and volume strategy are being developed smelters seek to have the minimal content of Na_2O required.

Li_2O content: Mediterranean alumina contains around 100-150 ppm Li_2O which increases the LiF content of the bath to values around 1,5-1,7%. This leads to increased difficulties in alumina dissolution on normal cell operations.

P_2O_5: regarded as a poison to the electrolysis process, the phosphorus content of the alumina should always be minimal.

Other chemical impurities: the main impurities of concern are those that cause problems for casthouse product castability or metal purity. The impact of the recovery of these impurities in the fume treatment system has been shown but quantifying it remains difficult. Impurities such as Titanium, Vanadium, Zinc and Silicon are considered.

5.0 MAIN ALUMINA CHARACTERISTICS

5.1 Water Content

Three parameters are monitored in relation to water content :

- L.O.I.: 0-300°C with commercial implications as to how much water is sold as alumina.
- L.O.I.: 300-1000°C linked to the calcination process and to the resulting crystal structure. Its accuracy is questionable and it is affected by the presence of hydrate.
- Water content increase in 44% humidity atmosphere, after drying at 300°C.

Ideally, thermobalance determinations should be used. A simplified test, consisting of measuring the total water content, after exposure for 24 hours to a 44% humidity atmosphere, gives good indications on the behaviour of alumina in the cells.

5.2 Specific Surface Area (S BET)

During the thermal treatment of alumina, a crystal intergranular network is formed and restructured. The specific surface area is the area of this porous network. It is related to the type of calcination and final temperature achieved during calcination. HF and SO_2 adsorption are directly linked to this parameter.

5.3 Crystal Organisation (Alpha Content)

The alpha crystal phase represents the ultimate stage of calcination of the hydrate. It constitutes the most organised of all the phases appearing successively during the calcining process. It is determined by X-ray diffraction.

There is a correlation between BET, alpha content, total water content, specific to each of the three calcination technologies.

5.4 Grain Size Distribution And Attrition

Several determination methods are used :

Dry sieving (TYLER) where the particles are sorted on a pile of successive screens (square section holes). This method slightly breaks the grains.

Wet sieving (VECO). The particles are dispersed in a liquid, are sorted on separate screens with round section holes. The screens are slowly shaken with an alternate movement.

Laser grain size distribution. The particles are dispersed in a wetting liquid and are exposed to a laser beam. The diffraction diagram is analysed using a mathematical model, based on a number of assumptions : spheric or cubic shape for the particles, gauss distribution, etc.

Differences between methods are essentially explained by the actual shape of the particles or attrition due to the method.

Alumina properties affected by grain size distribution are essentially dust emission and speed of dissolution.

5.5 Mechanical Properties

Angle of repose. This property depends on the shape of the grains and on the spread of the grain size distribution.

It provides interesting information on the flowability, and the capacity to form a stable layer of the alumina. Its value varies when dust particles are added to the alumina.

Flowability. Tests have been developed by some companies using point-feeding technology. Results make it possible to predict variations in the feeder shot weight.

Crust hardness. The formation of hard crusts is linked to structural changes in the alumina with a reorganisation to stable crystal phases.

Segregation. Some fractions of the alumina powder tend to segregate. It is still difficult nowadays to predict and overcome such a phenomenon.

Dissolution. Various tests have been developed in order to qualify the capacity of alumina to dissolve.

5.6 Chemical Purity

Sodium content. Internal investigations have shown a difference of Na content between the various fractions in the same alumina. It provides a chemical explanation to the thermal balance changes occurring when reaching the bottom of an alumina silo : the fines, which segregate, have a different sodium content compared to the bulk of the material.

Other elements. Routine laboratory test.

6.0 SPECIFICATIONS

The determination of the optimum choice of alumina for centre-worked, hooded, prebaked pots employing an automated, virtually continuous, point-feeding system and associated with a dry-process fume treatment plant is imposed by the following basic constraints.

- Collection and treatment of hydrogen fluoride.
- Speed of dissolution.
- Good controlled alumina feeding.
- Avoidance of volcano formation.
- Metal purity.

6.1 Technical Recommendations

The alumina feeding technology requires holes to be kept permanently open in the crust at the points of operation of feeders.

As explained Aluminium Pechiney seeks to operate at fairly high excess of AlF_3 which raises the cell emissions.

With the fume treatment system operating at full efficiency at all times the dry treatment process has to adsorb an average 18 kg of hydrogen fluoride per tonne of aluminium, with peaks at 25 kg/t.

The adsorption kinetics are such that the alumina has to have an accessible surface area of not less than 55 m^2/g. It is therefore possible to work with aluminas which are not highly calcined. However in the case of some cells being dedicated to the production of high purity metal, the lower limit will be significantly different in the ratio of the % of such cells to the total number of cells in the potline.

Speed of dissolusion
This is the major consideration. Should dissolution be incomplete, then sludge will form under the crustbreaker, the process control system will order the injection of a further quantity of alumina to compensate for the fraction not dissolved and this will in turn contribute to the production of more sludge. The adverse effects are even more pronounced in the case of cells operating with a high excess AlF_3 bath.

Highly-ordered crystal phases are to be avoided. Hydrate should be kept low, less than 0,5%. A narrow particle size distribution within the range 45-100 μm favours the dissolution in the bath.

Good and controlled alumina feeding
This requirement results not only in a specified angle of repose but mainly in a grain size distribution with a limited amount of fines.

Avoidance of volcano formation
Experience shows that specific surface should be limited to 80 m^2/g and the proportion of hydrate to less than 0,5%.

Aluminium purity
Of main concern are elements that lead to difficult levels for the casthouse end products or too high levels for purity ingots. This leads to limits on Titanium, Vanadium, Zinc and Silicon content of alumina.

Bath composition
Optimal Na_2O content is sought to minimize net bath production. Low levels of Li_2O are preferred to keep alumina solubility within an acceptable range. With a CaF_2 bath content maintained around 5%, the CaO content in the usual alumina is not a problem.

To sum up, the fundamental factors to be considered in the case of modern cells are to do with the regularity of the introduction and dissolution of alumina. A wide range of surface areas is tolerable (55 to 80 m²/g) but the objective of a degree of disorganisation of the crystal structure means that we prefer a narrower range centered on 70 m²/g and, where possible, the use of a gas suspension calciner.

6.2 Specification To The Smelters

On all these grounds, Aluminium Pechiney recommend, for modern cells, the use of alumina of the following specification (see full specification in Appendix).

BET surface area	:	65 to 75 m²/g
L.O.I. 300-1000°C	:	0,6 to 0,9%
Hydrate	:	0%
Fines (- 45 µm)	:	< 20% at the cell
Coarse (+ 150 µm)	:	< 5%
Na_2O	:	3000 - 4000 ppm

6.3 Out Of Specification Alumina

Alumina specification outlined by Aluminium Pechiney shows where the essential parameters lie in order to achieve best performance with its modern cells.

However commercially available aluminas often have to be accepted even if they are not in the optimal parameters range, provided the resulting performance degradation is kept within limits. This is the aim of the column named "acceptable". One should nevertheless be careful of cumulative effects which can lead to severe performance penalty.

7.0 TREND IN ALUMINA QUALITY

At the moment alumina quality as described in the technical specification is measured by an average value on essential parameters. This average value can be the monthly average of the alumina plant, the quarterly average or the cargo ship average, or the daily sample value before introduction to liquid bath.

The producer uses weekly and shipment averages while the user's references are its shipments and days/week of its production.

Even more than by the past, consistency in the quality is essential to optimal performance. This means tighter range on average values but also agreed limits on individual dispersion for each particular smelter.

On critical parameters such as the minus 45 μm fraction and Na_2O content cooperation between producers and users is increasing so as to be able to put a cap on the maximum differences acceptable on two shipments to the smelter. Such an approach will be widened to take into account the specific surface area (especially for smelters which run high purity metal cells) and its related characteristic alpha content and LOI and some chemical impurities which are Iron and Silicon.

This quantitative quality also mean that the analytical and sampling procedures used to characterise and certify alumina need to be accepted by producers and users if only for contractual purposes. Cooperation work is being done in this area between laboratories.

It will be necessary to standardise well-known analytical methods and to also improve on the tests for to measurement of properties such as mechanical resistance and dissolution which lack standard methods.

These developments pave the way to a "branded" commodity alumina tailored to the specific needs of a smelter technology. While this may be seen as contradictory to some trends to "buy at a low price attitude" and "short term supply contracts", it appears that most modern smelters, that is high capacity potline around 460 kt of alumina per year on one potline -need above all alumina consistency to avoid parameters adjustment detrimental to their top performances. This means an alumina with excellent average values and very narrow range of deviation.

While smelters may have to change their alumina source from time to time, they will require alumina in the commodity alumina range and request extra data on deviation. They will therefore be in a position to analyse the technical and economic consequence of any change. Provided the required criteria are met, the "commodity alumina" will be accepted. However alumina with characteristics that are out of range from this "commodity alumina" will not be accepted.

8.0 CONCLUSION

While we have seen that alumina quality needs to be optimised to allow for potline best performance, it should be noted that the ideal alumina, despite the best efforts of the producers is rarely found in smelters. Compromise is often the rule and if the levels of performance achieved in potlines required an alumina within the specification, of the utmost importance are the consistency in the quality of the supplied alumina and the adequate knowledge of variations occurring in the alumina delivered to the potline.

These two prerequisites allow potline management to select the right process control parameters based on the alumina "critical parameters" and the characteristics of the cells they operate.

Also of importance are the thresholds that shall not be transgressed in order to maintain good operation of the cells. This is generally well-known by potline operators who are often reluctant to accept any alumina change once they have reached an operational equilibrium.

Periodic meetings between users and producers are most fruitful when long term relationship (that is 3-5 years) is sought so that both sides clearly understand their respective specific interferences/trade-off/relationships on the parameters used by them to characterize "their optimal alumina".

REFERENCES

(1) M. Deshaies, Light Metals 1992, 337-341

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APPENDIX

ALUMINA

Pechiney specifications for continuous feeding cells (AP18 and AP30)

Physical characteristics

		Unit	Recommended (average value of the lot)	Acceptable (average value of the lot)	Deviation on individual value
Bulk density		g/cm³	0,90 min	0,90 min	-
BET Surface	Rotary kiln	m²/g	65-75	60-80	< 10
	Flash or fluidized Kiln	m²/g	65-75	55-80	< 10
Alpha content		%	5 min	5 min	-
LOI 300-1000°C		%	0,6-0,9	0,5-1,0	< 0,2
Hydrate content		%	0	0-0,5	-
Grain size distribution > 150 µm (100 mesh)		%	0 - 5	0 - 10	-
< 45 µm (325 mesh)	Before attrition test*	%	0 - 10	0 - 15	< 10
	After attrition test*	%	0 - 20	0 - 30	< 10

* Attrition test par Alcoa method

ALUMINA

Pechiney specifications

Chemical characteristics

Element contents are expressed in ppm.

ELEMENTS (I)		Alumina not acceptable for one of these elements will lead to degrated technical results			
P		< 5	P_2O_5		< 12
Ca	Recommended	150-300	CaO	Recommended	200-400
	Acceptable	0-400		Acceptable	0-600
K	Acceptable	< 160	k_2O	Acceptable	< 200
Na	Recommended	2000-3000	Na_2O	Recommended	3000-4000
	Acceptable	1500-4500		Acceptable	2000-6000
Li	Recommended	< 40	Li_2O	Recommended	< 90
	Acceptable	< 80		Acceptable	< 170
ELEMENTS (II)		Alumina not acceptable for one of these elements will lower metal purity			
Fe	Recommended	< 120	Fe_2O_3	Recommended	< 165
Si	Recommended	< 60	SiO_2	Recommended	< 130
Ti	Recommended	< 30	TiO_2	Recommended	< 50
V	Recommended	< 20	V_2O_5	Recommended	< 35
Zn	Recommended	< 100	ZnO	Recommended	< 125

If the anode baking furnace is provided with an alumina dry scrubbing process, the carbon content in the alumina fed to the electrolytic cells must be lower than 5000 ppm.