

TAC: A NEW PROCESS FOR MOLTEN ALUMINUM REFINING

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In the electrolytic process for the production of aluminium, an equilibrium exists between the metal ions in the bath and the same metals in the aluminium. Hall-Héroult reduction cell electrolyte contains various fluoride compounds such as NaF CaF₂ and increasingly more so LiF. Thus, it is observed that molten metal tapped from electrolytic cell will always contain some traces of Na, Ca and Li. The presence of very small quantities of the alkali and alkaline earth metals in aluminium can cause significant problems in end use. For example, it is known that sodium at the parts per million level will cause hot shortness (cracking) when magnesium alloys are hot rolled. Equally, it is known that lithium at similar concentrations will cause surface corrosion and lead to staining and other problems.

Over the past 20 years in particular, new technologies to control alkali metal levels in smelter grade aluminium has been developed. Although the immediate concern of these developments was directed to the removal of Na, Li and Ca. Other objectives became increasingly important, such as the decrease in environmental pollution, improved efficiency and internal quality of cast metal as well as the economic aspect of overall metal treatment operations.

To reach this goal, two approaches were followed by research and production personnel; the first approach consisted in developing in-line fluxing processes to be used between the holding furnaces and casting station. There are various commercial systems which are examples in that category. The second approach involved the treatment of molten metal before furnace transfer.

The TAC process, "Treatment of Aluminium in Crucible", developed by Alcan that we are presenting here is based on the direct treatment of metal in crucibles to remove alkali and alkaline earth metal contaminants.

The main advantages of the TAC process over other technologies are its high flexibility and low operating and energy costs.

In this paper, the TAC process principles and performances will be presented first. A typical plant installation will then be described and operating results discussed.

BASIC PRINCIPLES

The TAC process is based on the reaction of alkalis and alkaline earth metals, molten aluminium contaminants, with a small amount of aluminium fluoride powder (between 1-2 kg/t), which is added either directly to the potroom crucible or to a transfer crucible.

The practical Success of the TAC process depends upon achieving an effective solid-liquid reaction between the AlF₃ reacting agent and contaminated molten aluminium. This is fully accomplished by the patented TAC rotor which is designed to generate a vortex with the right axial and radial flow components. This is essential to guarantee high reaction efficiency, minimize surface turbulence and prevent air ingestion in the vortex.

Using extensive water modelling, the design (diameter, height, number and inclination of blades) and operating (RPM, position in the crucibles) parameters were identified in order that the vortex reach a maximum penetration power, combined with a fast recirculation of particles throughout the melt. Continuous flowing of fluoride at the melt surface causes some agglomeration and leads to the formation of flux pellets, which are active agents for alkali removal. These pellets which are mainly made of chiolite, are formed by the reaction of aluminium fluoride with the electrolyte contained in the primary aluminium. The presence of these flux Particles at the smelt surface during the treatment also has the secondary effects of preventing dross formation curing mixing and improving metal cleanliness. After the treatment, these particles either agglomerate on crucible walls or float on the surface where they are recuperated to be recycled into reduction cells as bath additions.

PROCESS PARAMETERS

The following variables were identified to control the alkali and alkaline earth removal process:

- 1) Aluminium fluoride addition;
- 2) Reaction time;
- 3) Stirring rate;
- 4) Metal temperature;
- 5) Presence and type of electrolyte in crucibles.

Figures 1 and 2 describe the effects of the aluminium fluoride addition and reaction time on the removal of Li and Na. For conditions shown in Figure 1 and from an addition of 0.6 kg AlF_3 /t of Al, the removal rate increases almost linearly with the amount of AlF_3 added up to a level of about 2 kg AlF_3 /t of Al. In practice, a saturation point is reached at this level as only marginal improvement was gained when adding up to 3.2. kg AlF_3 /t of Al.

Given the logarithmic scale of Figures 1 and 2, the removal process is shown to proceed very rapidly and to follow an exponential decay as a function of treatment time. For example. Sodium concentration can be taken from 35 ppm down to 2 ppm in a 5-minute treatment time while a six (6) minute treatment time will bring lithium from 15 ppm down to 2 ppm. In practice, the effectiveness of small AlF_3 additions and short reaction times means that the TAC process can be carried out while molten metal is in transit between potrooms and casthouse. It also means that while no particular insulation or preheating of crucibles is required only marginal metal temperature losses occur.

Table 1 shows how variations in rotor speed for a particular design affects the rate of removal of lithium, sodium and calcium.

It is apparent that increasing the rotor speed increases the rate of removal. The Maximum rpm which can be tolerated, however, will depend upon the freeboard available, the metal depth, and the crucible Shape. If the rotor speed is too high, air may be ingested into the metal with consequent dross formation.

TAC production units are operated at constant AlF_3 addition, impeller rpm and reaction time. Crucibles are treated immediately upon arrival at the station in order to minimize disruption of hot metal delivery for furnaces.

Under these conditions, TAC process performances will only be affected by metal temperature and amount of bath in crucibles (not taking into account variation in metal level).

Figure 3 describes the effects of metal temperature and bath on residual lithium concentration after TAC.

Under similar treatment conditions, the lithium removal rate is inversely proportional to metal temperature. Removal efficiencies varied from 90 to 80% in the normally encountered metal temperature range of 750 to 840°C.

The results illustrate the importance of metal temperature distribution in the determination of process parameters.

Close monitoring of the TAC process performances also showed that the presence of large amounts of bath in crucible during the treatment is responsible for variations and decrease in the removal process efficiencies. Metal temperature distribution and conditions of crucibles with regard to bath at the TAC treatment station depend on the hot metal delivery system from potrooms to casting, on siphoning practices in potrooms and on crucible cleaning

practices. When frequent treatments at high temperatures and in presence of large amounts of bath have to be performed, a larger addition (in excess of 2 kg/t of Al) of AlF_3 cannot alone provide satisfactory results. In this case, the AlF_3 powder would readily react with cryolite (Na_3AlF_6) to form chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$), thus reducing the effective AlF_3 concentration for alkali removal. This situation might also lead to unacceptable difficulties in crucible cleaning operations.

A solution was found and demonstrated in production whereby metal is first transferred into a designated treatment crucible and then TAC processed (TAC II). Metal temperature drops after transfer from about 850 to 810°C while most of the liquid bath stays in the original crucible or solidifies and floats on the surface of the metal in the treatment crucible. Lithium residual levels obtained with the TAC II method are shown in Figure 4 and compared to the original TAC process.

The TAC II method led to substantial improvement in the efficiency and reliability of the process. For example, from an initial Li content of 20 to 25 ppm, a 3 ppm residual lithium level was reached with less than 0.5 kg AlF_3 /t aluminium while 2.5 kg/t had been needed previously. Furthermore, very low Li contents (0.5 to 2 PPM) could be obtained with the TAC II only. Lithium residual contents after TAC II were also more consistent from one treatment to another.

Associated advantages are reduction in operating costs due to reduction of AlF_3 addition, extended rotor life and easier crucible cleaning operations.

STANDARD ELECTROLYTE

The TAC Process was further evaluated under plant conditions using standard electrolyte (6-7% excess AlF_3 , no LiF) with the objective of optimizing the process with respect to sodium removal. Dissolved Na in smelter metal ranged from 40 to 60 ppm upon arrival at the cast house. All crucibles coming from one potline were treated during a 10-day trial period using a portable demonstration TAC unit. Results are shown in Figure 5.

Figure 5 demonstrates the effectiveness of the TAC process with regard to sodium removal. Treatment parameters set at 6 min. and 0.5 kg AlF_3 /t Al reduced sodium concentration down to 1 ppm. Lower sodium concentration could easily be obtained by increasing the AlF_3 addition up to 1.0 kg/t without increase in treatment time.

It is interesting to note that although aluminum fluoride has a higher energy of reaction with lithium compared to sodium, in practice sodium removal is always more rapid than lithium's. It is believed that the higher sodium vapour pressure assists sodium removal both by reaction with aluminium fluoride and oxidation. It is also likely that the high (6-7%) excess AlF_3 in the electrolyte present in the crucibles during the treatment assists sodium removal.

METAL CLEANLINESS

Certain products require very clean metal. Metal inclusions are of various types. Many of them being generated during the alloying and casting operation. There is one inclusion,

however, which comes from the Hall-Héroult cell, that is, aluminium carbide.

It has been shown that the TAC process substantially reduces the aluminium carbide content of metal. In this case, the amount of aluminium carbide was measured by attacking the metal by sodium hydroxide solution and analyzing by gas chromatography the methane generated. As Table II shows, the average aluminium carbide content was reduced from 14 ppm to 3 to 4 ppm after the TAC treatment.

The mechanism of metal cleaning by TAC has been demonstrated to be flotation of nonmetallic inclusions by the recirculated aluminium fluoride rich flux granules. This also explains the residual level of 3-4 ppm aluminium carbide always present in the solid metal, the solubility of carbon in aluminium at the treatment temperature being in the order of 1 ppm.

PRODUCTION EXPERIENCE

Since the first TAC process implementation in 1982, several units have been installed in Canada [1-2], U.S.A. [3] and Japan. In 1986, more than 525,000 tons of primary aluminium will be processed with TAC and TAC II. Being fairly simple in principles and equipment, the TAC process has been easily engineered for various types of hot metal delivery systems be they with overhead cranes, transport vehicles or lift trucks. It has also been adapted to a variety of crucibles, from 2 to 6 tons capacity with cylindrical or oval shapes.

Typical TAC stations consist of:

- A rotor, complete with support structures and drive unit (electric or hydraulic) and optimized in design and position for specific potroom crucibles.
- An AlF_3 pneumatic feeding system.
- A dust collection system to remove effluents generated during treatment.

These emissions consist mainly of aluminium fluoride and alumina dusts, with small quantities of cryolite and chiolite. Materials collected from bags can be returned to potrooms.

- A programmable controller, which enables the station to be activated and operated automatically through the various process steps. This key feature, common to all existing TAC stations, has largely contributed to a low operating and maintenance cost. TAC stations of capacity in excess of 100,000 t/yr have been implemented in production without additional manpower requirements.

The implementation of TAC in existing operations was facilitated by the fact that it can be installed almost anywhere on the route between potrooms and cast house with a small floor space requirement. Contrary to alternative methods, TAC units can service any number of casting furnaces. Following treatment, no other operation is required and the crucibles are immediately transferred into furnaces. Since crucibles are in a rapid

transit at the station, no extra energy is expended. No material other than regular reduction grade aluminium fluoride powder is required for the process. Excess aluminium fluoride and reaction products adhering to crucible walls are scraped off during regular crucible cleaning operations and returned to the potrooms for recirculation. Process economics are therefore extremely attractive due to this inherent material recycling.

PERFORMANCE

A) Alkali removal:

Lithium and sodium concentrations at various stages of production are given in Table 1:1 for remelt and fabrication ingots (Trilock and D.C. cast). It can be seen that with residual levels in crucibles after TAC of the order of 1.5 to 3.0 ppm, final product lithium and sodium levels can easily be met. This is especially true for alloyed materials which allow a more pronounced alkali reduction after TAC treatment due to longer batching time.

B) Metal cleanliness:

After four years of production experience, the TAC process has proven not to generate any dross or particular inclusions during treatment. Moreover, the special action of the fluoride fluxes on aluminium carbides collection and flotation has made TAC a valuable process tool in the production of critical products such as container sheet and thin foils.

COMPARISON WITH ALTERNATIVE PROCESSES

Most alternative processes for the removal of alkali contaminants in Al more or less rely on the use of chlorine and can be classified as being carried out in furnaces or by in-line fluxing units.

Fluxing in furnaces has been a general practice over the years to remove sodium, calcium, lithium. Gas mixture of N_2 , Ar and Cl_2 or freon is blown into the melt for chlorine to react with alkali elements. Although still widely used, this technique is characterized by poor efficiency and very long process time especially for Li removal. Moreover, environmental regulations in various countries have severely limited and even prohibited the use of Cl_2 in furnace fluxing.

In-line fluxing and degassing units located between furnaces and casting machines have increased the chlorine reaction efficiency mainly by generation of very fine gas bubbles through the use of mechanical dispersers. Still, the process is limited to only about 50-70% lithium removal efficiency. On the other hand, these units are fairly expensive to purchase and to operate. Also, they can service only one casting machine per unit, therefore making this option prohibitive where several DC pits are used. In some cases too, particularly in nonrecent installations, the required floor space between furnace and casting machines may not be available.

The TAC process is the only competitive process to give complete flexibility in the design

and the installation of equipment. It also has the advantage over the above methods to carry out the removal process before furnace transfer. Furnace wall buildup and excess dross formation associated with handling Li contaminated aluminium are therefore eliminated with the TAC process.

SUMMARY

The TAC process, developed to remove alkali metal impurities from aluminium without the utilization of chlorine gas, has proven to be effective, simple and practical to use. The TAC process requires minimum space and capital investment. It is characterized by the following advantages:

- low operation and maintenance cost
- freedom from environmental contamination
- negligible manpower requirements
- minimum training demands
- ease of incorporation into existing installations
- easy recycling of spent chemicals, no waste products
- improved metal cleanliness
- reduction of C_{12} usage in cast house

Several TAC systems are currently in use in Canada, U.S.A and Japan, and large tonnages of metal have been processed successfully through them.

[1] Dubé, G., Newberry, V.J.: TAC - A Novel Process for the Removal of Lithium and other Alkalis in Primary Aluminium, AIME, Light Metals, 1983.

[2] Gariépy, B., Dubé, G., et al.: The TAC Process: A Proven Technology. AIME. Light metals. 1984.

[3] Freudenberger, W.: Intalco's Experience with the Alcan TAC System. AIME. Light Metals, 1986.

[4] U.S. Patent No. 4,470,846.

TABLE II - TAC PROCESS: EFFECT ON NONMETALLIC Al_4C_3

Location	Arvida		Isle-Maligne	
AIF ₃ Addition	1.5 kg / t		2 kg / t	
Treatment Time	6 minutes		10 minutes	
Metal Weight	3.6 t		5.6 t	
Al_4C_3 Concentration	Before	After	Before	After
	9	2	14	4
	17	3	16	3
	14	6	16	4
	16	2	16	5
	14	3	14	4
% Eff.	79 %		71 %	

TABLE I - EFFECT OF ROTOR SPEED ON LITHIUM, SODIUM AND CALCIUM REMOVAL EFFICIENCY

RPM	% Removal*		
	Lithium	Sodium	Calcium
100	76	89	90
130	85	95	> 95
165	89	97	> 95
* Reaction time 6 min., 2 kg AIF ₃ /t Al			

The TAC process is patented in Canada, U.S.A. [4] and in other countries.

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REFERENCES

TABLE III – TAC PROCESS PERFORMANCES UNDER PRODUCTION CONDITIONS

Alloy	LITHIUM (PPM)			SODIUM (PPM)		
	Before In-crucible	After TAC		In-crucible	After TAC	
		In-crucible	Final Product		In-crucible	Final Product
Commercial Metal (23kg)	19	2.5	< 1.5	32	2.0	< 1.0
Commercial Metal (T ingot)	20	2.7	< 1.5	34	1.5	< 1.0
AA 1350	17	2.6	< 1.0	28	1.8	< 1.0
AA 5154	17.5	2.4	< 1.0	36	1.8	< 1.0
AA 3003	16.2	2.5	< 1.0	34	2.0	< 1.0

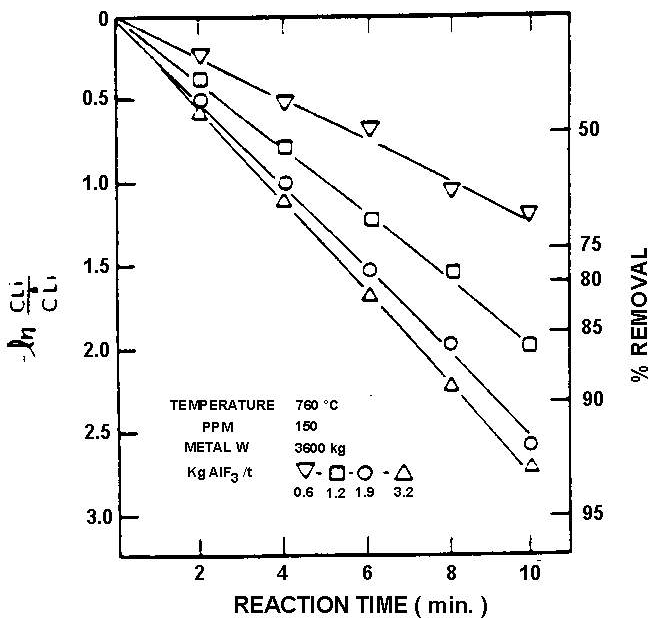


Figure 1 - Lithium Removal Rate vs Aluminium Fluoride Addition and Reaction Time

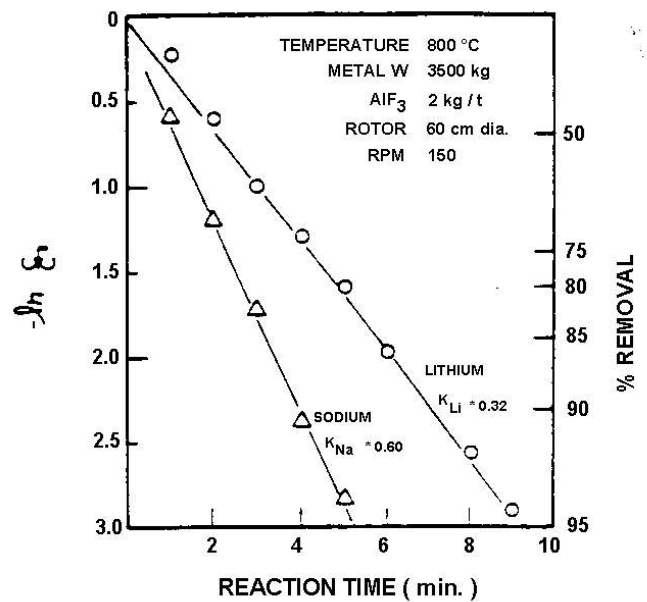


Figure 2 - Lithium and Sodium Concentration vs Reaction Time

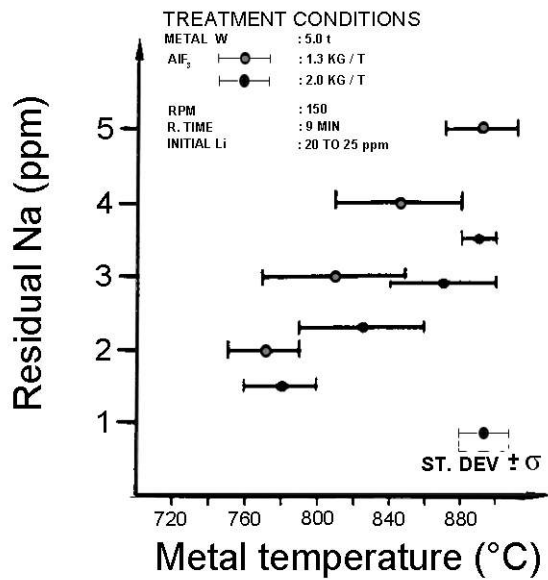


Figure 3 -Residual Lithium Concentration (After TAC) vs Metal Temperature

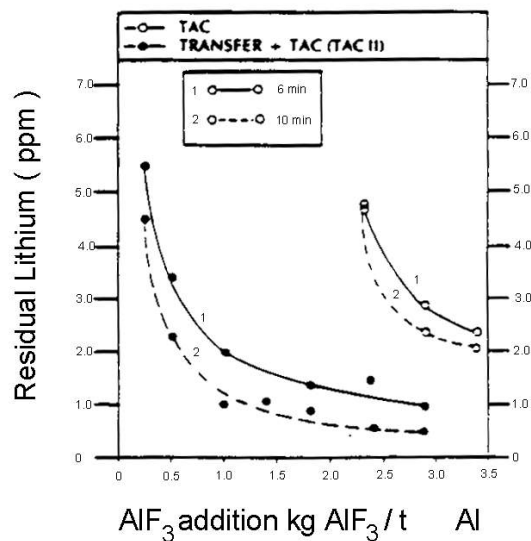


Figure 4 – Residual Lithium Concentration vs AlF₃ Addition, TAC vs TAC II (Transfer + TAC)

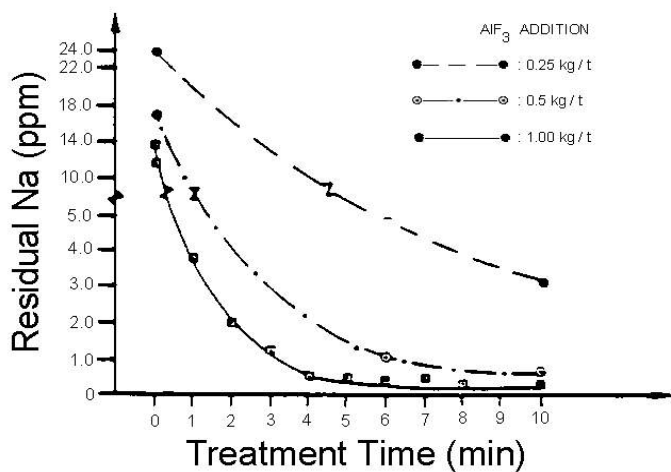


Figure 5 – Sodium Concentration vs TAC Treatment Time, Standard Electrolyte