

TAC - A NOVEL PROCESS FOR THE REMOVAL OF LITHIUM

AND OTHER ALKALIS IN PRIMARY ALUMINIUM

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A simple and economical process for the elimination of lithium and other alkali metal contaminants from primary aluminium has been developed by Arvida Laboratories, Alcan International Limited. The treatment is done directly in the crucible, before furnace transfer, and does not require additional operations or holding capacity. In the process, aluminium fluoride powder is intimately mixed with the metal, using a specifically designed rotor. High efficiency alkali removal occurs through the formation of stable fluoride compounds, without the use of toxic gases or formation of corrosive waste products. Routine production operations with the TAC system began in Arvida during mid 1982. The process is now successfully used in two Alcan Casting Plants.

Introduction

The increasing use of lithium as an additive to Hall-Héroult electrolyte is at the origin of work to develop new technologies to control alkali metal levels in smelter grade aluminium. Although the immediate concern of these developments was directed to the removal of lithium, 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 an on-line fluxing unit 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 Alcan active bed is an example in that second category (1).

These two lines of approach led to considerable improvements both in the hot metal treatment process and equipment manufacturing.

Both systems, however, still have some weak points as regards compatibility with existing hot metal installations, operating flexibility, or efficiency at high metal throughput, and this justifies the search for a more economical and flexible melt treatment system.

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 are its high flexibility and low operating and energy costs.

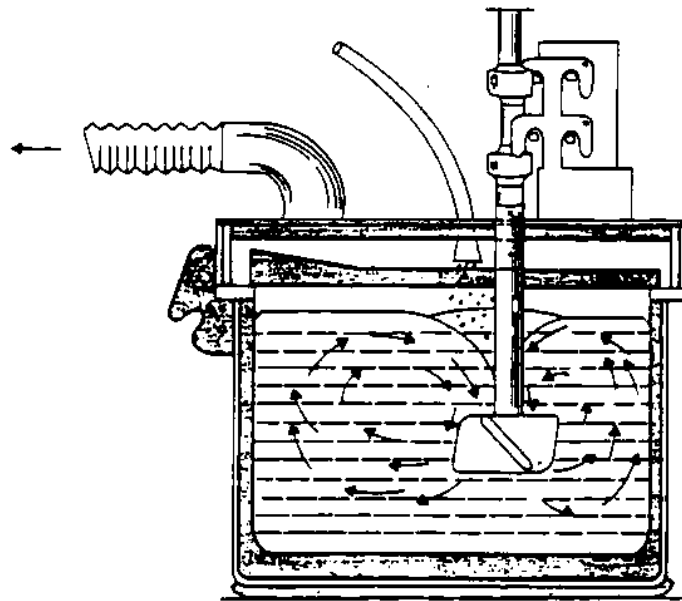
In this paper, the TAC process principles and performances will be presented first. A typical plant installation will then be described and operating results discussed.

Basic Principles

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

The vortex which is generated by a rotor ensures an intimate and continuous contact between molten aluminium and fluoride during the whole treatment (5-10 min.). Under the effect of forced metal circulation induced by the rotor, the aluminium fluoride is continuously recirculated from inside the metal to the melt surface. The penetration of fluoride in the metal is essential to ensure efficient and fast removal of alkalis through the formation of stable fluoride compounds. 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 chase flux particles at the melt surface during the treatment also has the secondary effects of preventing dross formation during mixing and improving metal cleanliness.

Figure 1 gives a schematic view of the TAC process equipment.



SCHEMATIC OF TAC PROCESS

FIGURE 1

The core of the TAC process is the 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 inside and at the melt surface.

The rotor and its drive system are mounted on a refractory-lined mobile cover. This cover also receives the aluminium fluoride powder pneumatic injection outlet and an exhaust for the dust released during the treatment. Rotor life expectancy is between 300-400 treatments (about six minutes each) and depends mostly on the metal temperature. The rotor is not affected by thermal and mechanical shocks nor by the presence of electrolyte. It does not contaminate the metal and can easily be replaced in an hour. Replacement cost is about \$0.10/m.t.

This basic equipment can be adapted for the treatment of aluminium in different types of siphoning and transfer crucibles. Because of its simplicity, a fully automated treatment station can easily be designed.

Process Efficiency

The TAC process efficiency has been analyzed using the batch stirred tank reactor model, to determine the rate controlling parameters and optimize process performances.

Analyses of sodium and lithium removal rate vs reaction time for a given metal temperature have confirmed the validity of a first order reaction model:

$$-\ln\left[\frac{C_{Li}}{C_{Li}^0}\right] = \left[\frac{KS}{m}\right] \times \tau \quad (1)$$

where: C_{Li} = lithium concentration in Al at time t

C_{Li}^0 = initial lithium concentration in Al

K = reaction rate constant (function of metal temperature)

S = effective surface area between molten aluminium and solid aluminium fluoride

m = mass of aluminium in crucible

t = reaction time.

Figure 2 illustrates a typical Plot of $-\ln(C_{Li}/C_{Li}^0)$ and $-\ln(C_{Na}/C_{Na}^0)$ vs reaction time for an experiment carried out directly in a potroom crucible containing 3500 kg of aluminium at 800°C, with a 60 cm diameter rotor at 150 RPM, using 2 kg AlF_3 /m.t. Al. Sodium and lithium concentrations decrease exponentially with reaction time, according to Eq. (1).

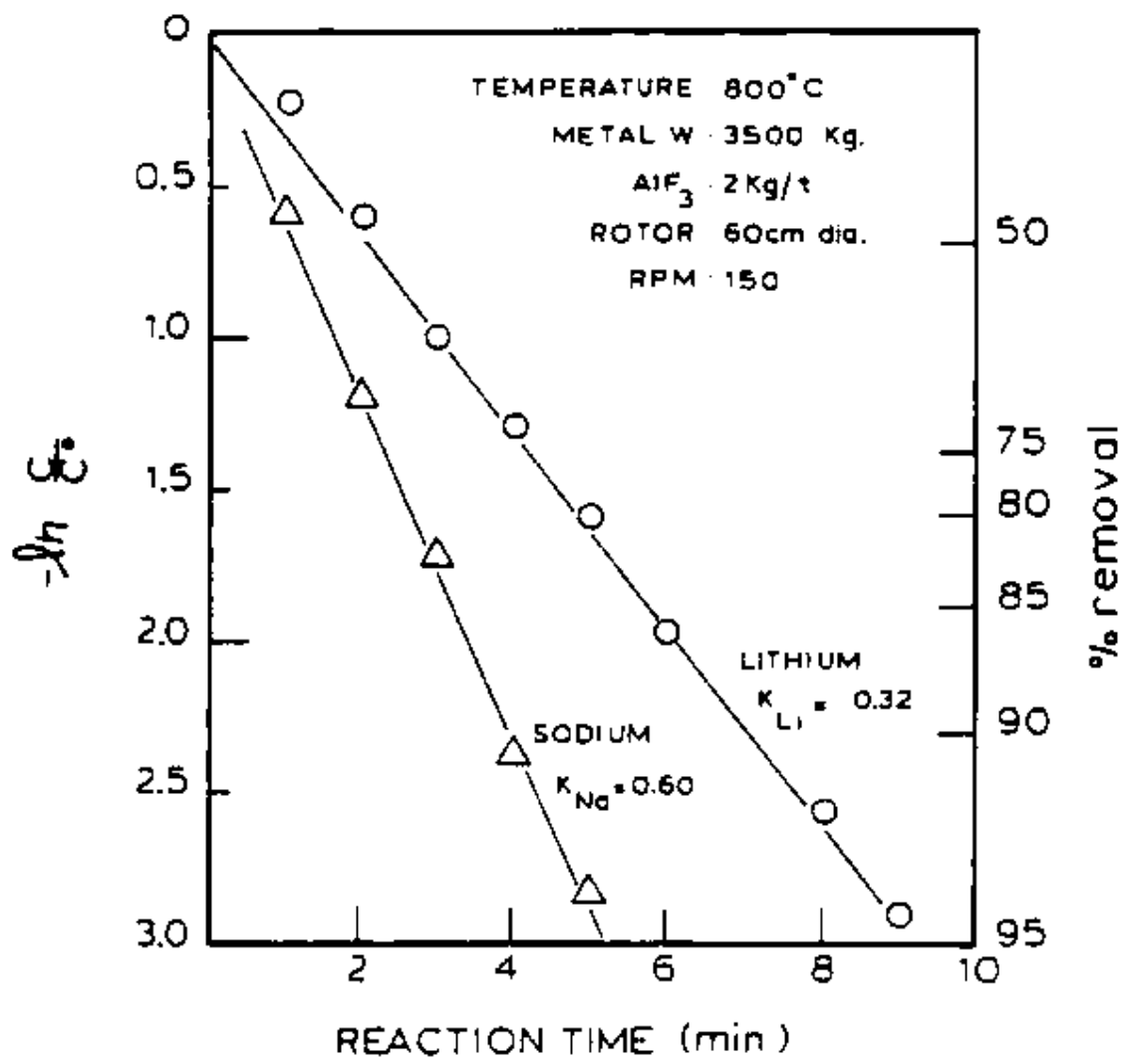
It is interesting to note that although aluminium fluoride has a higher Gibbs energy of reaction with lithium compared to sodium, in practice sodium removal is always more rapid than lithium's. This phenomenon may be explained by the much higher sodium vapour pressure, which assists sodium removal both by reaction with aluminium fluoride and oxidation at the metal-air interface.

In this test (Figure 2) sodium decreased from an initial 35 ppm to less than 2 ppm after 5 minutes and lithium from 15 ppm down to 2 ppm in a 6-minute treatment.

These residual levels measured in the crucibles are more than satisfactory to meet lithium cast product specifications due to further concentration decreases during metal transfer and batching operations.

The slope of the plot $-\ln C/C^0$ vs time makes it possible to calculate the product of the reaction rate constant (K) and solid/liquid interfacial area (S).

According to the first order reaction model, the overall reaction rate



LITHIUM AND SODIUM CONCENTRATION
 vs REACTION TIME
 FIGURE 2

can be increased by maximizing S and K. This can be achieved by using the optimum amount of AlF_3 per ton of Al, of the highest technical grade available. The interfacial area S can be significantly increased by using the highest possible degree of agitation and dispersion. To a more limited degree, the transport rate of the alkali atoms to the solid/liquid interface will also be improved by increasing the degree of agitation in the crucible.

In the following sections, the influence of these parameters (stirring rate, quantity and grade of AlF_3 , metal temperature. etc) on the reaction rate, $K \times S$ (kg/min.) of lithium and sodium removal will be discussed.

a) Effect of Aluminium Fluoride Concentration

Smelter grade aluminium fluoride powder containing between 90-93% AlF_3 gives a superior performance compared to a lower grade product (80-85% AlF_3). The particle size of the material is not critical provided a maximum of 20-25% does not exceed 150 mesh (105 microns). Much finer material (ex. -325 mesh) does not offer improvement in the alkali removal rate, probably due to a higher tendency to agglomerate and to less effective penetration into the aluminium.

b) Effect of Stirring Rate

The stirring rate, (and rotor design) controls the dispersion and the degree of circulation of AlF_3 into the molten aluminium and exerts a significant effect on the alkali removal rate.

Table I shows a typical RPM effect on lithium, sodium and calcium removal efficiency.

Table I. RPM Effect on Lithium, Sodium, and Calcium Removal Efficiency

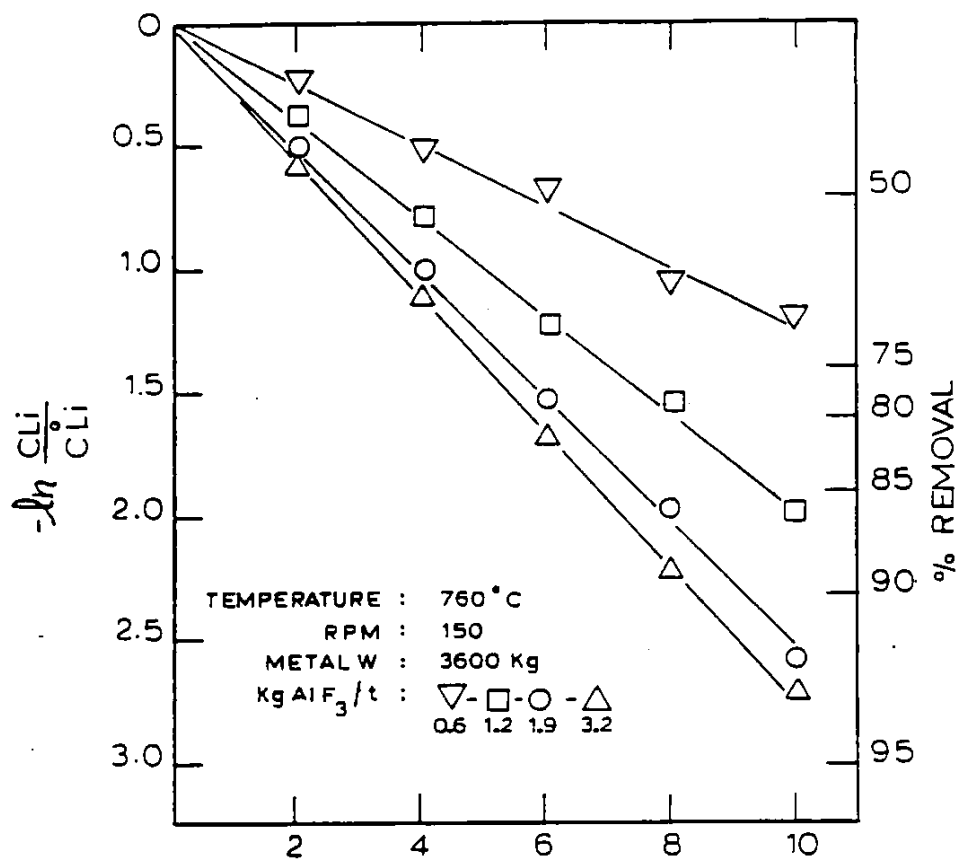
RPM	% REMOVAL *		
	Lithium	Sodium	Calcium
100	76	89	90
130	85	95	>95
165	89	97	>95

* Reaction time 6 min., 2 kg AlF_3 /m.t. Al

Although from Table I it appears desirable to operate at maximum RPM, practical considerations also have to be taken into account in selecting the optimum RPM. For instance, too high a rotation can cause air ingestion into the metal, increasing the risks of projection and dross formation. Freeboard distance, metal depth and crucible shape also influence the optimum RPM.

c) Effect of Aluminium Fluoride Addition

Figure 3 illustrates the influence of aluminium fluoride addition per ton of aluminium on lithium removal rate vs reaction-time, measured at 760°C.



REACTION TIME (min.)

LITHIUM REMOVAL RATE vs
ALUMINIUM FLUORIDE ADDITION AND
REACTION TIME

FIGURE 3

Initially, the removal rate increases almost linearly with the amount of aluminium fluoride and reaches a saturation level of almost 2.5 kg $\text{AlF}_3/\text{m.t. Al}$. This saturation effect can be explained by the agglomeration of powder limiting the effective contact area with aluminium rather than by a decrease in the efficiency of the dispersion system.

In practice, an addition of the order of 1.5 to 2.2 kg $\text{AlF}_3/\text{m.t. Al}$ is adequate to obtain sufficiently low residual lithium levels in the crucibles to meet cast product specifications.

The choice of the amount of aluminium fluoride to be added in order to obtain a desired residual level does not depend only on the efficiency curves given in Figure 3, but also on several operating conditions specific to each aluminium reduction plant.

Some of the conditions are:

- a) the temperature of the metal,
- b) the amount of bath in the crucible during the treatment,
- c) the frequency of utilization of the TAC process.

Each one of these factors affects the TAC process efficiency independently, and also in combination.

For instance, a high metal temperature ($\sim 850^\circ\text{C}$) during the TAC treatment without or with a small quantity of bath will have little or no effect on alkali removal efficiency. However, a high metal temperature combined with a large amount of bath in the treatment crucible will affect severely the removal efficiency. In this last case, this condition will have to be compensated for by an increase in treatment time and/or a larger addition of fluoride.

d) Effect of Consecutive Treatments

Figure 4 illustrates the effect of four consecutive TAC process treatments using the same potroom crucibles to treat 14,000 kg of smelter metal.

As shown in Table II, lithium and sodium levels before treatment decrease by approximately 40% after four consecutive treatments. This effect is due to the excess aluminium fluoride which mixed with bath material, forms a buildup on crucible refractory linings. During the electrolytic cells siphoning, this material containing excess aluminium fluoride reacts with the alkali elements. It also increases process efficiency by maximizing aluminium fluoride contact area with aluminium during the treatment.

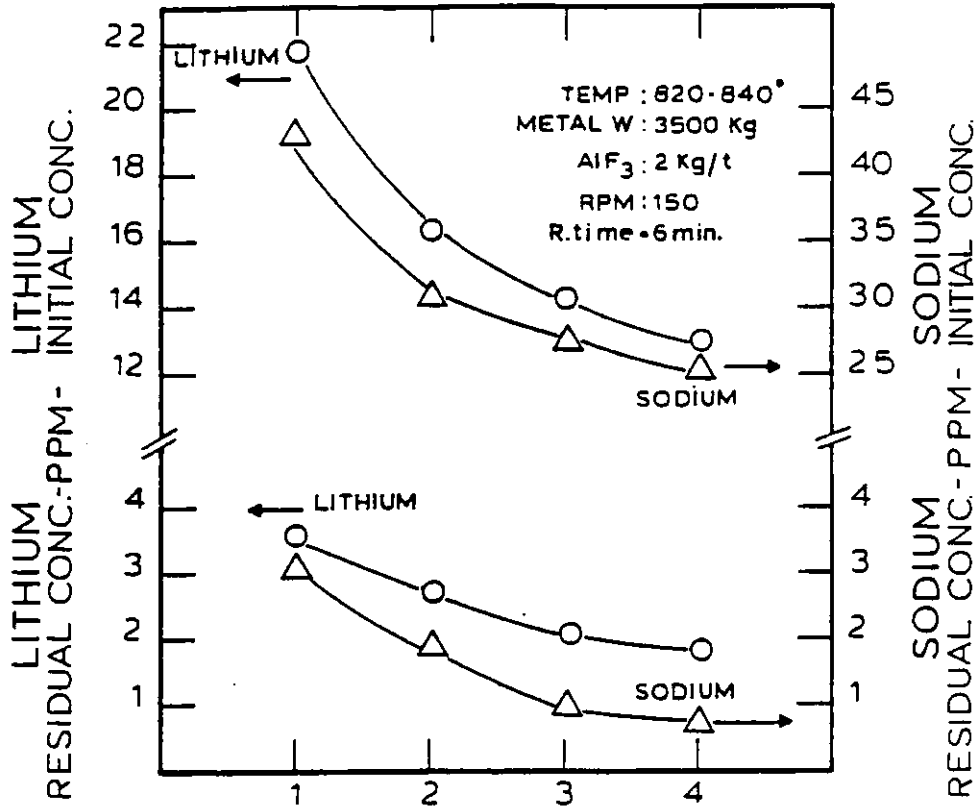
Plant Experience

1. Equipment

A typical automated TAC station is shown in Figure 5.

It consists of

- a rotor, complete with drive unit (electric or hydraulic), adjustable in position and elevation in relation to potroom crucibles,
- a refractory lined lid, to cover the crucible during the treatment,



NUMBER OF CONSECUTIVE TREATMENTS
 IN SAME CRUCIBLE
 FINAL LITHIUM AND SODIUM LEVEL AS
 FUNCTION OF CONSECUTIVE TREATMENTS

FIGURE 4

Table II. Effect of Consecutive Treatment in the Same Crucible on Reaction Rate, KS (kg/min.)

	Number of Consecutive Treatments			
	1	2	3	4
C_{Li}^0 (ppm)	21.8	16.3	14.2	13.0
C_{Li}^{10} (ppm)	3.6	2.7	2.0	1.8
KS_{Li} (kg/min.)	0.30	0.30	0.32	0.33
C_{Na}^0 (ppm)	43.0	31.0	27.0	25.0
C_{Na}^{10} (ppm)	3.2	1.8	1.0	0.8
KS_{Na} (kg/min.)	0.43	0.46	0.55	0.57



AUTOMATED TAC TREATMENT STATION, ONE CRUCIBLE (ON THE RIGHT)
BEING TREATED, THE OTHER CRUCIBLE IS READY FOR TREATMENT

FIGURE 5

- a fume extraction system to remove effluents generated during the early stage of the treatment. These emissions consist mainly of aluminium fluoride and alumina dusts, with small quantities of cryolite and chiolite. They can be collected by local (potrooms or cast house) scrubbing systems,
- a programmable controller, which enables the station to be operated automatically in sequence through the various process steps. The treatment sequences can be easily modified.

As shown, the equipment is fairly simple and can be modified to suit local conditions such as type of hot metal transport, volume and shape of crucibles. In the latter case, rotor design is optimized to best fit crucible geometry.

In a specific installation at Alcan Smelters and Chemicals Limited, Arvida, the potroom tapping crucibles containing approximately 3600 kg of aluminium skimmed in the potroom and brought directly by an overhead crane to the TAC treatment station located inside the cast house. Crucibles are handled through the TAC station using a two-position reciprocating platform. This allows treatment to proceed during crucible changeover.

Total time required for treatment will vary with plant operating conditions (metal temperature, desired alkali removal, crucible volume, etc.). In this case, total contact time averages 7-8 minutes for a 6-minute treatment period (see Table III).

Table III. Sequence of Operation for Automated
TAC Treatment Station

- CRUCIBLE POSITIONING	10 SEC.
- CLOSE LID, START ROTOR	40 SEC.
- ALUMINIUM FLUORIDE ADDITION	60 SEC.
- STIRRING	300 SEC.
- STOP ROTOR	10 SEC.
- OPEN LID	40 SEC.
- CRUCIBLE OUT	10 SEC.
TOTAL	470 SEC.

Following the treatment, no other operation is required, and the crucible is immediately transferred to the batching furnace. On an eight-hour basis, this station can handle up to 40 crucibles, or 150.000 metric tons per year.

No material other than regular reduction grade aluminium fluoride powder is required for the process. No extra energy is expended either. No significant melt loss is observed during the treatment. 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.

Table IV. TAC Process Performance Under Production Conditions

Test No.	Alloy	Metal Treated (kg)	LITHIUM (PPM)			SODIUM (PPM)		
			Before In-crucible	In-crucible	After TAC Final Product	In-crucible	After TAC In-crucible	Final Product
I	Commercial Metal (23 kg)	450,000	19	2.5	<1.5	32	2.0	<1.0
II	Commercial Metal (T ingot)	700,000	20	2.7	<1.5	34	1.5	<1.0
III	AA 1350	200,000	17	2.6	<1.0	28	1.7	<1.0
IV	AA 5154	100,000	17.5	2.4	<1.0	36	1.8	<1.0
V	AA 3003	50,000	16.2	2.5	<1.0	34	2.0	<1.0

Process economics are therefore extremely attractive due to this "automatic" material recycling.

2. Performance

a) Alkali Removal. Lithium and sodium removal efficiency measured under production conditions are given in Table IV for the production of remelt and fabrication ingots (trilock and D.C. Cast). It can be seen from these results that final product lithium and sodium levels can easily be met, with residual levels after TAC measured in the crucible of the order of 1.5 to 3.0 ppm. This is especially true for alloyed material which allows a more pronounced alkali reduction after TAC treatment due to longer batching time.

b) Metal Cleanliness. No dross generation occurs in the crucible during the TAC treatment.

It has been observed that metal cleanliness is also improved during the treatment, due to the fluxing action of the recirculated aluminium fluoride granules.

Conclusions

The TAC process for the removal of alkali and alkaline earth metals in primary aluminium has been proven very effective. simple and practical to use. A TAC installation can be incorporated into existing hot metal treatment installations without major modifications. Floor space requirements are very limited.

Operating costs are substantially lower compared to other alternative processes mainly due to the absence of energy costs, easy recycling of spent chemicals and high unit productivity.

The process is readily adopted by operating personnel.

Several TAC systems are currently in use throughout Alcan Smelters and Chemicals, Ltd, and large tonnages of metal have been processed successfully through them.

Patent applications on the TAC process are pending in the U.S.A. and elsewhere.

Reference

- (1) Pierre Achim, Ghyslain Dubé, "Removal of Lithium in Commercial Metal", Light Metals, (1982), pp. 903-918.