

REMOVAL OF LITHIUM IN COMMERCIAL METAL

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An effective process to remove trace levels of lithium and other alkali impurities contained in aluminum tapped from electrolytic reduction cells has been developed by Alcan Smelters and Chemicals Limited.

In the process, metal is transferred directly from tapping crucibles and passed through a bed of particles of material containing active aluminum fluoride maintained continuously immersed in molten aluminum.

High removal efficiencies are achieved for lithium, sodium, calcium and magnesium.

The process has been operated by production personnel in Alcan Smelters and Chemicals Limited for over three (3) years in four production centers and has been found to be effective and practical.

The process will be described and its use will be discussed for the production of commercial aluminum.

Introduction

The growing use of lithium fluoride in aluminum electrolytic cells has increased the need for developing an efficient, cheap and environmentally acceptable process to solve problems during casting and fabricating attributed to the contamination of aluminum by lithium.

Literature surveys have indicated that most of the existing processes to remove trace lithium from molten aluminum (1) are based on physical or chemical reactions.

Because reactions involved in the former are generally limited to the molten bath/air interface, they are not acceptable for high productivity casting centers.

Chemical operations using either gases (chlorine/nitrogen, hydrocarbon halides), liquids (molten alkaline earth chlorides), or solids (carbon) are inevitably associated with environmental difficulties in the form of air pollution or reaction products disposal. On-line gaseous fluxing has recently been proposed as an attractive solution to these problems (2, 3). However, this technique is being preferably used in the final stage of alloy preparation, before casting, and does not eliminate the problems caused by long holding of alkali contaminated metal in furnaces (4).

Work has started in Alcan in 1974 to develop a process for removing lithium and other alkali contaminants from smelter metal prior to furnace transfer. The process also had to meet other operating conditions as given in Table 1.

Table I. Alcan Lithium Filter Process Criteria for Removal of Lithium for Primary Aluminum

I -	Efficient for Li and other contaminants, e.g. Na, Ca, Mg.
II -	Environmentally safe.
III -	Uses available chemicals which can be recycled on site.
IV -	Unaffected by electrolytic material, bath and high temperatures.
V -	Requires no extra or specialized manpower.

In this paper, basic principles and laboratory optimization will be outlined first. Secondly, typical smelter-casting plant installations which have been operating for more than three years will be described in detail.

Description of the System

The Alcan lithium Filter System is built around a submerged filtering layer of aluminum fluoride, held in place between two layers of porous refractory material (5).

The physico-chemical properties of Alcan's aluminum fluoride are given in Table II.

Table II. Alcan Aluminum Fluoride

Chemical Composition	Size Distribution		Void Fraction (%)
	Cumulative % Larg. Than	Size (mm)	
AlF ₃ : 86%	20	13.0	44
Al ₂ O ₃ : 9.0%	41	9.4	39
Na ₃ AlF ₆ : 2.8%	76.5	6.7	
SiO ₂ : 0.3%	97.0	4.7	38
Fe ₂ O ₃ : 0.05%	99.2	3.3	
	99.4	2.3	
Apparent Density	: 2.0-2.2 g/cm ³		
Modulus of Rupture	: 100 kg/cm ² (1422 psi)		
Shape	: Broken, egg-shaped granules		

These egg-shaped briquettes are obtained during high temperature fluorination of alumina trihydrate pellets. Since the sodium hydroxide used as a binder for the initial trihydrate agglomeration was transformed into sodium cryolite and chiolite during the fluorination process, it does not react with molten aluminum during filtration.

This material is sufficiently hard to resist crumbling and wear during handling and transportation. It also retains its physical properties even after heating in air to 800°C (1470°F) or to exposure to molten aluminum for several days.

The preferred particle size (experimentally found) was adopted for its high efficiency and low metalstatic head build-up. It also gives a uniform void fraction of between 38-44% over the entire size range of from 2 mm to 30 mm. This last characteristic, apart from the physical properties of the Alcan aluminum fluoride material, is the key factor for obtaining a filter packing with stable and uniform flow resistance. It is of prime importance for minimizing channel formation within the bed.

Chemistry of Filtration Reactions

Thermodynamics and phase diagrams of the compounds formed by reacting aluminum fluoride with alkali and alkaline earth metals have been discussed in the literature (6). As shown in Table III, a selection of reaction products can be expected. With the eutectic temperature for binary and ternary products with AlF₃ being relatively low (8), it is reasonable to expect that solid-liquid mixtures will be present at the filtration temperature of about 825°C (1520°F). To study the effects of these reaction products on filtration efficiency and to optimize the different process parameters, laboratory simulation experiments were first conducted using a 190 cm² test bed.

Table III. Standard Gibbs Energy for Formation of Alkali and Alkaline Earth Metal Fluorides from Aluminum Fluoride at 1000°K (7)

3/2 CaF ₂	=	-80.2 Kcal/mole AlF ₃
3 LiF	=	-74.4
1/2 Li ₃ AlF ₆	=	-42.0
3/2 MgF ₂	=	-41.8
3 NaF	=	-39.2
1/2 Na ₃ AlF ₆	=	-30.8

Laboratory Simulation

Figure 1 is a schematic view of the test bed.

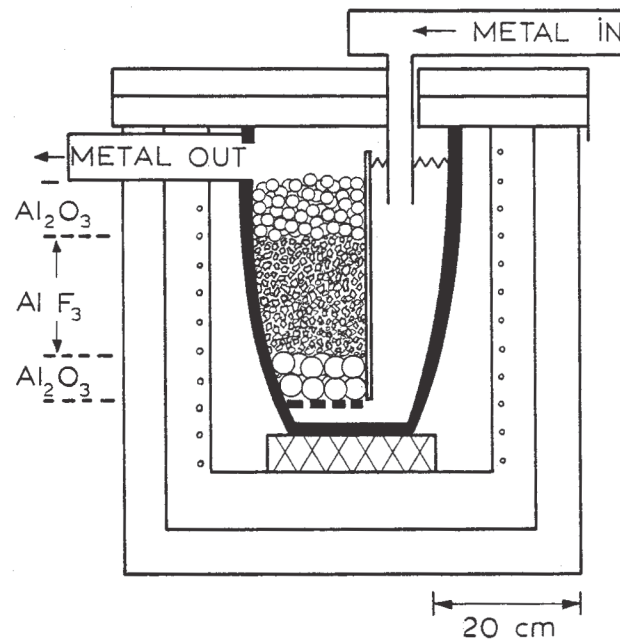


Fig. 1 - Aluminum Fluoride Filter Bed Laboratory Simulator

The crucible contained 4 kg (8.8 lb) of AlF₃ in variable height and surface ratios. The metal temperature was electrically controlled between 700° and 900°C (1300-1650°F).

Laboratory filtration tests were done using commercial aluminum (500 kg batch (1100 lb)) containing sodium, lithium and calcium. Metal was sampled before and after the filter and analyzed by optical emission spectroscopy. Each filtration test, with a specific bed packing, was performed over a period of between 5 and 7 days with the filter medium continually submerged in molten aluminum to simulate production conditions. Filtration efficiency is defined as $\left[\frac{C_{in} - C_{out}}{C_{in}} \right] \times 100\%$.

After having established that with between 20 and 300 ppm of Na, Li and Ca that the filtration efficiency was almost independent of the inlet concentration, C_{in} (it increased by 5% with an increase in C_{in} from 20 to 200 ppm), it was decided to run the laboratory tests at a concentration 5 times higher than plant concentrations. This was desirable not only to accelerate the saturation of the filter but mainly to increase the analytical precision of the outlet concentrations - particularly at the early stage of the filtration run.

Effect of Metal Temperature

Since the temperature of metal originating from potrooms can vary between 750°C (1380°F) and 900°C (1650°F) and possibly even higher depending on crucible preheating and delays, the efficiency of the filtration process was determined between these temperatures for sodium, lithium and calcium under the following operating conditions:

- Metal flow : 11.7 kg/sec. m² (1 lb/in.² min.)
- AlF₃ quantity : 4 kg (8.8 lb)
- Size distribution:
 - 25% > 14 mm (0.55 in.)
 - 25% > 9 mm (0.35 in.) ≤ 14 mm (0.55 in.)
 - 25% > 6 mm (0.24 in.) ≤ 9 mm (0.35 in.)
 - 25% ≤ 6 mm (0.25 in.)
- AlF₃ thickness : 18 cm (7 in.)
- Void fraction : 39%
- Inlet metal concentration:
 - Li : 30 ppm
 - Na : 100 ppm
 - Ca : 10 ppm

Figure 2 illustrates the strong influence of metal temperature on alkali removal efficiency, particularly between 700 and 800°C (1300° and 1470°F).

The nature and properties of the reaction products which build up at the AlF₃ particle surface account for this temperature effect. A "post mortem" analysis of spent AlF₃ particles clearly showed that a thick recrystallized solid layer had completely coated the original AlF₃ particles. An XRD analysis of this layer showed the presence of cryolite (Na₃AlF₆) chiolite (Na₅Al₃F₁₄) and cryolithionite (Li₃Na₃Al₂F₁₂) with traces of CaF₂ and LiF. It was also observed that the density inside the AlF₃ particles gradually decreased during filtration, i.e. eventually an empty shell was formed while

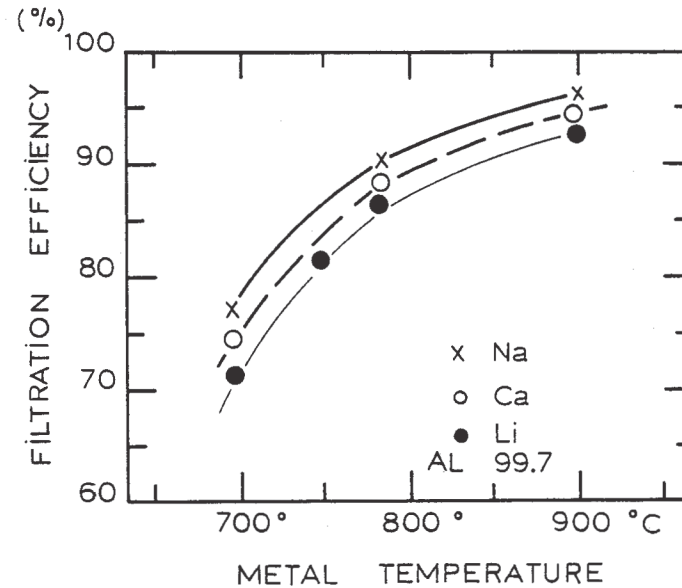


Fig. 2 - Filtration Efficiency vs Metal Temperature retaining the initial AlF₃ shape (Fig. 2).

This shell reduces the AlF₃ concentration at the solid/liquid interface and gradually decreased the alkali removal efficiency. Increasing the operating temperature in particular from 700° (1300°) to 800°C (1470°F) yields two significant effects which have an impact on process efficiency. First, it significantly increases solid aluminum fluoride vapour pressure, 0.003 mm Hg at 723°C (1333°F), 0.08 at 823°C (1510°F) and 1.12 at 923°C (1693°F). Secondly, the formation of liquid phases containing an excess of aluminum fluoride, e.g. chiolite, will be promoted. The high reactivity of such compounds with alkali metal was probably responsible for the marked increase in filtration efficiency at higher temperatures (9). It was also observed that the temperature effect becomes even more pronounced with filter utilization. This can be explained through the presence of a thicker reaction product layer which insulated the fresh aluminum fluoride from molten aluminum.

Effect of Filtration Rate

Having established through testing that a bed of 18 cm (7 in.) thickness constituted the best compromise between premature obstruction, filtration efficiency and quantity of filter media per unit area of surface, then the effect of the filtration rate on alkali removal efficiency was studied.

Figure 4 shows the change in filtration efficiency for sodium and lithium with increasing filtration rates - filtration conditions are similar to those of Figure 2. The calcium removal efficiency which is not shown on Figure 4, is similar to that of sodium. It can be seen that filtration efficiency in the order of 90-95% can be easily achieved at 800°C (1470°F) for a flow rate as high as 11 kg/m²/sec. (1 lb/sq. in./min.) which is acceptable for plant operation. This filtration rate was then adopted during the continuation of laboratory studies.

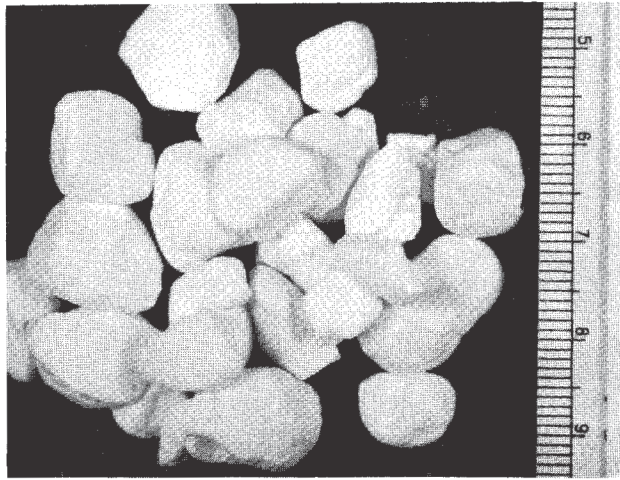


Fig. 3 - a) Alcan Aluminum Fluoride Pellets Ready for Utilization in Aluminum Filter (scale in mm).

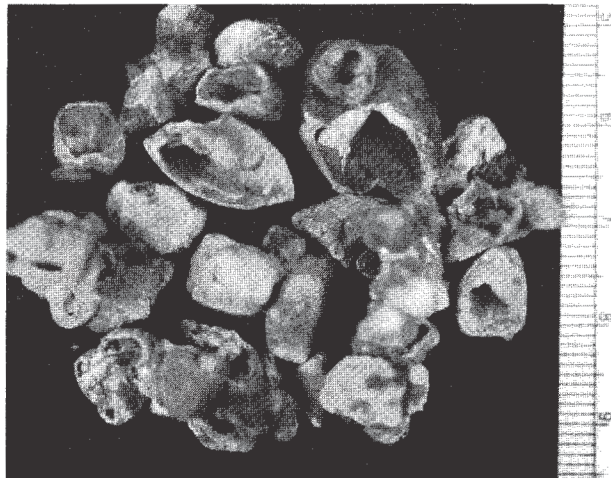


Fig. 3 - b) Spent Aluminum Fluoride Filter Bed Material (scale in mm).

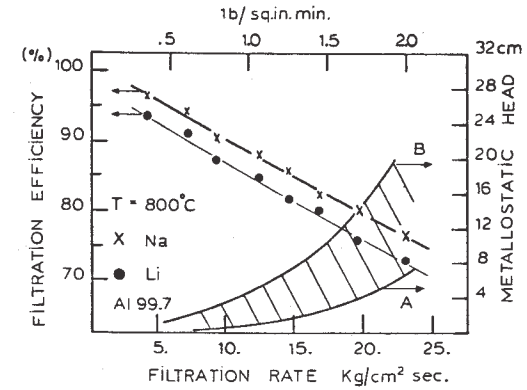


Fig. 4 - Filtration Efficiency and Head Build-up vs Metal Flow Rate.

It was also observed that the metallostatic head over the filter increased significantly during the filter's life, i.e. the head changed from curve A to B of Figure 4 from the beginning to the end of filter life. As discussed previously, the accumulation of reaction products on the aluminum fluoride particles gradually reduces the porosity of the filter bed and so accounts for this phenomenon.

Effect of Aluminum Fluoride Particle Size

To measure the effect of fresh aluminum fluoride particle size on filtration efficiency, head build-up and useful filter life, three filter beds of different AlF_3 particle sizes were compared (see Table IV for aluminum fluoride characteristics). Liquid aluminum at 780-800°C (1430-1470°) containing sodium at 100-150 ppm, lithium at 30-50 ppm and calcium at 10-15 ppm, was filtered at a flow rate of 11 kg/m²/sec. (1 lb/sq. in./min.) through three filters in batches of 500 kg (1100 lb). Filtration efficiency and head build-up through each filter were monitored. Typical results for lithium are given in Figure 5.

Table IV. Aluminum Fluoride Particle Sizes

Number	Particle Size	Void Fraction	Quantity
A (▲)	>13 mm ≤20 mm	44%	4 kg
B (△)	> 6 mm ≤13 mm	40%	4 kg
C (○)	> 3 mm ≤ 6 mm	39%	4 kg

Filter A, with the lowest specific surface, showed very low alkali removal efficiency even at the beginning of filtration. Filters B and C gave an equivalent performance at the start, however as metal throughput increased, the finer filter (packing C) showed a steeper decrease in efficiency in conjunction with the appearance of a significant metallostatic head. This filter became plugged after filtering 12 000 kg (26,400 lb) of aluminum. Contrarily, lithium filtration efficiency of packing B stabilized for approximately 5 000 kg (11,000 lb) before declining very rapidly. No filter plugging was experienced with this medium-size packing.

The abrupt decrease (<50%) in filtration performance corresponds to the chemical life of the filter for a ratio of 0.25 kg AlF_3 per m.t. of Al (50 lb/ton) filtered (containing 20 ppm Li, 40 ppm Na). In practice, the theoretical chemical life of a filter bed will never be achieved.

The AlF_3 consumption will be determined by the lowest filtration efficiency acceptable. It can be approximated from Figure 5 that an aluminum fluoride consumption in the order of 0.8 kg AlF_3 /m.t. Al (1.6 lb/ton) seems to be possible for a lithium filtration efficiency cut-off at 80%. Equivalent consumption figures can be calculated for sodium.

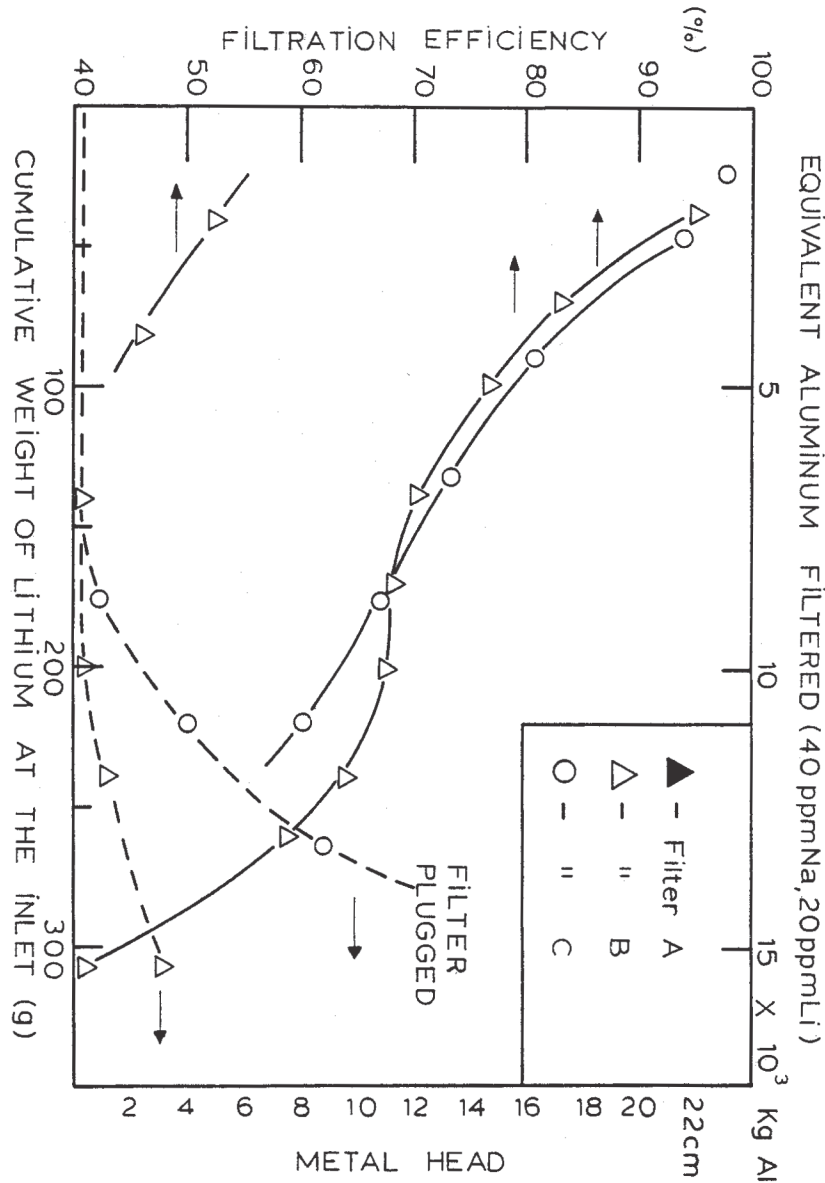
Based on these promising laboratory results, it was decided to continue the experiments on a larger scale.

Plant Equipment and Procedure

A typical Alcan Lithium Filter is shown in Figure 6. It is comprised of a refractory lined rectangular steel box measuring approximately 2.9 m (116 in.) long by 2.3 m wide (89 in.) by 1.3 m high (53 in.) and divided into two sections, i.e. entry and reaction chambers. Molten metal is introduced into the entry chamber by siphoning. Entrained heavy sludge particles settle out in front of a weir over which the aluminum passes to enter a downward passageway. Note that some bath electrolyte tends to remain as a supernatant layer at the top of the entry chamber. From the passageway, aluminum passes under a baffle into a space below a support grid of refractory concrete bars. This grid supports a layer of refractory particles which, in this case, is formed of tabular alumina balls 19 mm (0.75 in.) in diameter. This 20-50 mm (1-2 in.) thick layer absorbs non-metallic liquid and solid particles still present in the metal passing under the baffle and also has the effect of distributing metal flow to the layer of finer aluminum fluoride above it.

The molten, low density products resulting from the contact of the contaminated aluminum with the aluminum fluoride will tend to be washed through the layer of aluminum fluoride particles by the upward flow of metal. The effect of the reaction products is to gradually reduce the activity of the aluminum fluoride and to plug the filter bed's interstices. On the other side of the aluminum fluoride layer, there is a second layer of tabular alumina balls which trap the bed's molten reaction products. This upper layer of alumina balls also holds down the aluminum fluoride bed and acts as a heat distributor during preheating, thus preventing direct contact between the aluminum fluoride and an open flame. The depth of the different layers can be adjusted within limits in relation to the interdependent parameters of metal flow rate and of removal efficiency (typical conditions are shown in Table V). Finally, the treated molten metal leaves the Alcan Lithium Filter box through the exit port which is located above the upper layer. The entire bed remains submerged at all times under the molten aluminum.

Fig. 5 - Effect of Aluminum Fluoride Particle Size on Lithium Filtration Efficiency



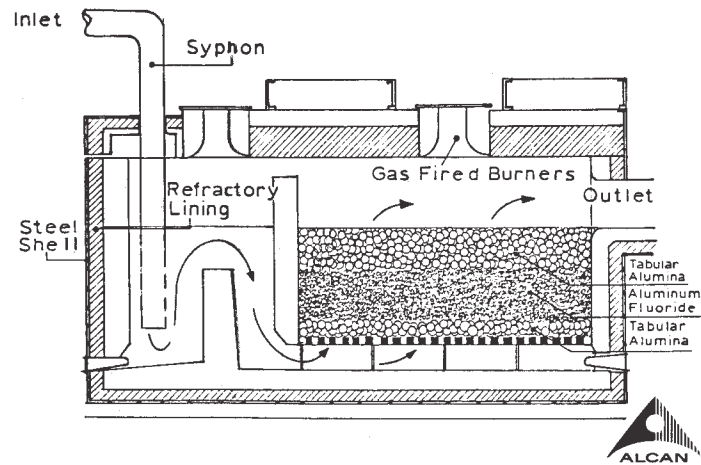


Fig. 6 - Alcan Lithium Filter System

Open flame gas burners are provided to automatically maintain the system at working temperature as well as to preheat the bed prior to start-up. Typically, the bed is maintained at 825°C (1500°F) during the process while the incoming metal's temperature usually varies from 825°C (1500°F) to 900°C (1650°F).

Table V. Combination of Conditions for an Alcan Lithium Filter System

	INNER PREFERRED LIMITS	OUTER PREFERRED LIMITS
MESH SIZE OF ACTIVE PARTICLES	100% 5-30mm (.25-1.2 in.)	90% 5-30 mm (.25-1.2 in.)
THICKNESS OF ACTIVE BED	125-225 mm (5-9 in.)	50-600 mm (2-24 in.)
CROSS-SECTIONAL AREA OF BED	1-2.5 sq. m (1550-3875 sq. in.)	0.1-3 sq. m (155-4650 sq. in.)
MESH SIZE OF REFRACTORY PARTICLES	100% 20-40 mm (0.75-1.6 in.)	90% 15-50 mm (0.6-2 in.)
THICKNESS OF REFRACTORY BED (UPPER)	25-50 mm (1-2 in.)	0-100 mm (0-4 in.)
THICKNESS OF REFRACTORY BED (LOWER)	125-225 mm (5-9 in.)	50-400 mm (2-16 in.)

In order to retard heat loss, an insulating lid covers the top of the filter box. Access is provided for skimming of the entry chamber.

General Layout

For maximum flexibility, the Alcan Lithium Filter System (Figures 7 and 8) typically is comprised of two filter boxes in parallel to permit continuous operation with a common trough to bring metal to either a furnace or a transfer crucible.

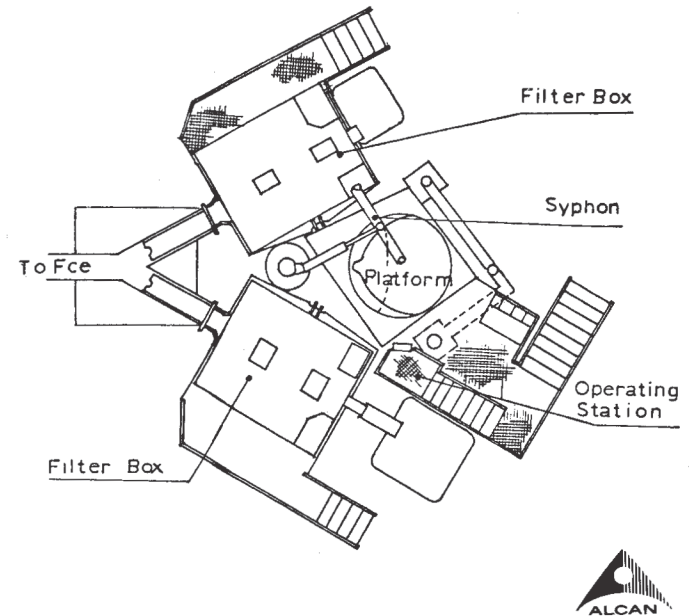


Fig. 7 - Alcan Lithium Filter System Arrangement

Results and Discussion

In a typical installation, the conditions were as follows:

- Bed area: : 2.6 sq. m (4000 sq. in.)
- Metal flow rate : 9.37-11.72 kg/m²/sec. (0.8-1.0 lb/in.²/min.)
- Metal throughput: 525 metric tons/day (580 tons/day)

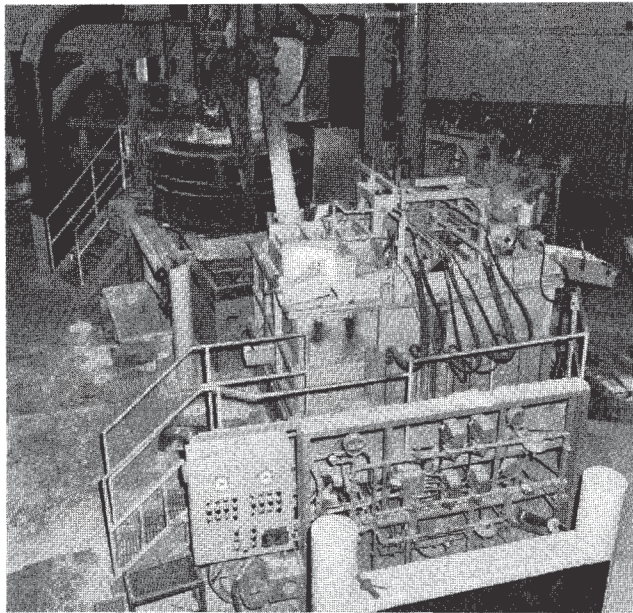


Fig. 8 - Alcan Lithium Filter System
Typical Plant Installation

Bed thickness:

Lower layer (Al_2O_3 : 50 mm (2 in.) or 227 kg (500 lb))
 Active layer (AlF_3 : 240 mm (9.5 in.) or 820 kg (1800 lb))
 Upper layer (Al_2O_3 : 525 metric tons/day (580 tons/day)
 Grade of AlF_3 : 68% AlF_3 - 10% Al_2O_3 approx.
 Size distribution of AlF_3 : 100% 6-20 mm (0.25-0.75 in.)
 Size distribution of tabular alumina: plus 20 mm mesh
 Average crucible capacity: 4.3 m.t. (4.75 tons)
 Average filtration cycle duration: 3 minutes
 Metal temperature: 825-900°C (1500-1650°F)

The results are given in Table VI.

Lithium removal efficiency varies with the quantity of metal passed through a bed (Figure 9). It also varies on the cleanliness of the crucible metal and on the utilization rate of the filter. Life expectancy of a filter bed can be predicted and its replacement scheduled relative to the required output lithium concentration.

After a bed is pulled out of service, the filter box is emptied, cleaned and prepared for the next run. Figure 10 shows a typical filter bed after having filtered 1400 m.t. (1540 tons).

Table VI. Alkali and Alkaline Earth Metal Removal Results

	Av. Before Filtration	Av. After Filtration	Average Removal
Lithium	22 ppm	2.2 ppm	90%
Sodium	35 ppm	3.5 ppm	90%
Calcium	4 ppm	1 ppm	75%
Life expectancy for 3 ppm residual Li:			1200-1400 m.t. (1320-1540 tons)

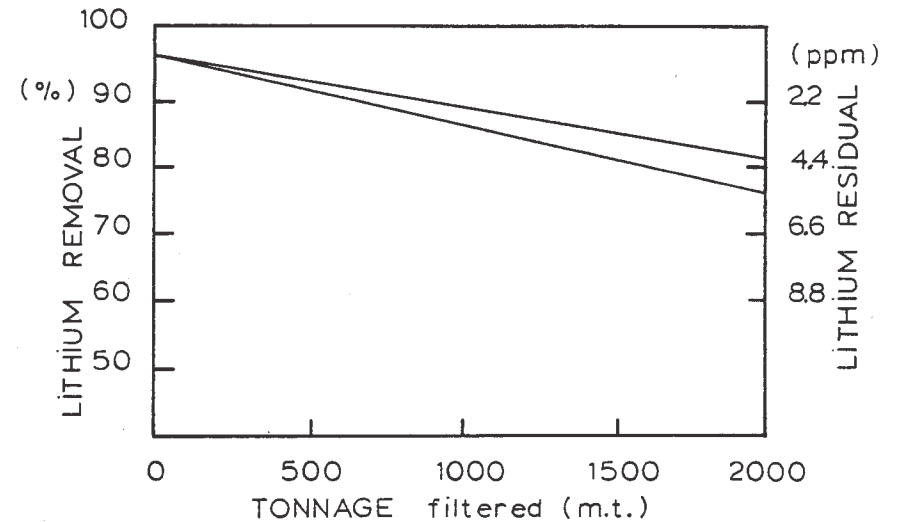


Fig. 9 - Variation of Lithium Removal vs Tonnage Filtered

Recycling

An attractive feature of the process is that the bed materials can be readily recycled. This is achieved by processing spent bed material through an autogeneous mill from which separation and classification of the fluoride rich fraction and refractory fraction is readily achieved. The fluoride rich material typically contains about 5% of lithium fluoride in the form of Li_3AlF_6 and is returned to the reduction cells. The approximate analysis of spent active material as follows:

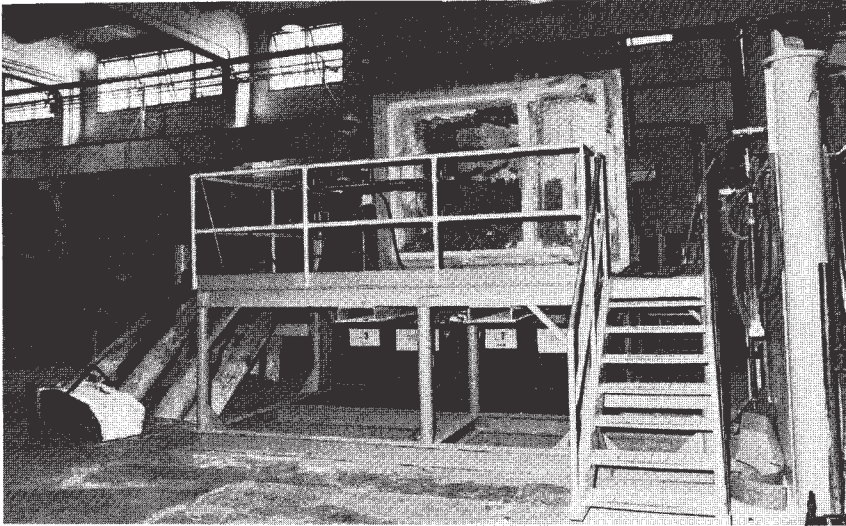


Fig. 10 - Cleaning of a Filter Bed After Usage

Al_2O_3	:	35%
CaF_2	:	0.2
Li_3AlF_6	:	12.2%
MgF_2	:	0.83%
Na_3AlF_6	:	8%
AlF_3	:	44%

The recovered tabular alumina is re-used directly in the filter bed. During the recycling process, recoveries of 90-95% for the tabular alumina and 85-90% for the active material are obtained. Recycling enables us to reduce operating costs and maintain a healthier environment.

Environmental Conditions

No fumes or fluoride dust are generated during operation since the filter bed is always submerged by molten aluminum. Only combustion products may be present around the filter box during operation. During draining and cleaning, minor quantities of fluoride gas and dust are generated, however, these operations are periodic and involve relatively small quantities released.

Heat exposure is comparable with regular operations in a casting center.

Environmental studies have shown that the Alcan Lithium Filter System is in compliance with governmental regulations.

Conclusions

The Alcan Lithium Filter System for removal of alkali and alkaline earth metal contaminants from aluminum has been proven effective and reliable without requiring additional manpower and is free of environmental problems. The process has been used for over three years with good acceptance and credit for the treatment of a large tonnage of molten aluminum drawn from electrolytic cells.

References

- (1) M. Bick, M. Markworth, Metallwissenschaft und Technik, 34(1980) pp. 1095-1098.
- (2) R.E. Miller, et al. "In-line Fumeless Metal Treatment", *Light Metals*, (1978), Vol. 2, pp. 491-505.
- (3) A.G. Szekely, "Apparatus and Process for Refining Molten Aluminum". Can. Patent 981912.
- (4) K. Buxmann, et al. "Process for Lowering the Concentration of Sodium in Aluminum Melts", U.S. Patent 4,138,246.
- (5) L. Montgrain, "Apparatus and Method for Removal of Alkali and Alkaline Earth Metals from Molten Aluminum. U.S. Patent 4,277,280.
- (6) K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky and J. Thonstad, Aluminium Electrolysis, The Chemistry of the Hall-Heroult Process, Aluminium-Verlag GmbH, Dusseldorf (1977).
- (7) JANAF Thermochemical Tables, Second Edition, U.S. Department of Commerce, National Bureau of Standards, June 1971.
- (8) M.L. Saboungi, P.L. Lin, P. Cerisier and A.D. Pelton, Metallurgical Transactions B, 11B (1980) pp. 493-501.
- (9) E.W. Dewing, Metallurgical Transactions, 3 (1972) pp. 495-501.