

WHICH METHOD TO CHOOSE FOR ALKALINE REDUCTION? EITHER IN THE POT ROOM CRUCIBLE OR IN THE CASTHOUSE?

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Abstract

Lithium, sodium, calcium and magnesium may all be reduced efficiently from molten aluminium to very low levels of ppm in the pot room crucible before transfer to the melter/holder furnace and this, within a few minutes; no chlorine is required, only the use of aluminium fluoride salt. Some removal, particularly of sodium, may also be obtained by simply transferring from one crucible to another whilst transporting or delivering molten aluminium, without the introduction of either gas or salt. On the other hand, these same elements may also be reduced in the holder furnace in the casthouse, using either salts or gases by various means including: manual additions of fluxes; or chlorine lances; or, more recently, rotary gas/flux injectors. Degassers may also be used as in-line treatment for removing alkalines with the use of argon and chlorine.

Introduction

For several reasons, alkalines have long been considered as undesirable elements in the processing and commercial use of aluminium. Sodium, for example (excepted when used as a modifier for casting foundry alloys) can lead to cracking during hot rolling, when levels are present as parts per million; lithium can accelerate corrosion of certain aluminium alloys, even when present in amounts as low as parts per million. The TAC process (Treatment of Aluminium in a Crucible) developed by Alcan and commercialised in the early 80's was mainly targeted to reduce lithium directly in the crucible at the smelter⁽¹⁾⁽²⁾ together with sodium and other alkalines.

More recently, the emphasis has shifted from the removal of lithium to the removal of sodium and calcium. Lower levels of sodium are demanded not only in smelter casthouses prior to casting but also in remelt and recycle operations. Traditionally, chlorine gas in the holder furnace (using lances or rotary gas/flux injectors – RGI/RFI) or with in-line degassing equipment such as the ACD (Alcan Compact Trough Degasser) has been the most common approach to reduce alkalines prior to casting into final slabs and billets.

However, the use of chlorine gas in casthouses is becoming less and less desirable for several reasons. Firstly, governments are legislating against its use for environmental reasons; and secondly, chlorine gas is a safety hazard which means high costs to maintain and operate a chlorine gas delivery system. Furthermore, chlorine gas is highly corrosive, and indirect capital and maintenance costs can be exorbitant. There are alternates to the use of chlorine, which can provide solutions to alkaline removal without substantially adding to costs.

For large companies who source metal not only from smelters but also from remelt and recycle operations, the choice of metal treatment without the use of chlorine, or at least to reduce its use, is not necessarily an easy one. This paper explores some of the pros and cons of the different

methods to reduce alkalines in molten aluminium, mainly with the TAC for pot room metal or in the casthouse using either the RGI or RFI and/or in-line degassers.

TAC

It is not the intention to discuss in detail each of the processes mentioned in this paper. Sufficient to say that the TAC process (Photo 1, Photo 2, Sketch 1) was originally developed to reduce lithium, sodium and other alkalines in the pot room crucible before transferring to melting/holding furnaces⁽³⁾.

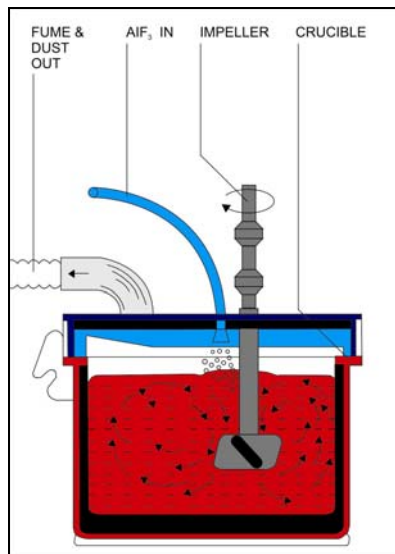


Photo 1



Photo 2

The TAC process does not use chlorine but adds aluminium fluoride as a salt flux to the molten aluminium directly into the crucible in which a vortex is deliberately developed using a rotating cast iron rotor. The rotation is eccentric, i.e., off-centre with the impeller positioned at the correct distance from the bottom of the crucible, whilst maintaining a suitable height of molten metal.



Sketch 1

One of the main advantages of the TAC is that the flux material is readily available in the smelter and can be recycled to the pots when the crucible walls are cleaned with a crucible cleaning machine. The time of treatment is typically of the order of a few minutes but is a function of the alkaline to be reduced (e.g. Li or Na); a total cycle time can be less than 15 minutes and allows up to 150,000 tonnes per year to be treated with a single station.

Recently, a modified version of the TAC (different flux is used) has been developed for the pre-treatment of metal in the casthouse of a remelt plant to remove not only calcium but also inclusions in the charge crucible.

RFI/RGI

The RGI/RFI is now accepted as an efficient alternate for replacing lancing and porous plugs for injection of chlorine and manual additions of flux. Although the RGI uses chlorine gas, the total quantity per furnace batch treatment is reduced significantly compared with lancing.

The RGI is a gas-only model employing nitrogen as a carrier gas and chlorine as the reactive agent. The RFI is a design in which nitrogen is used as the carrier gas, but a solid flux (often a magnesium-potassium chloride flux) is used to replace the chlorine gas and is therefore more environmentally friendly. The RGI/RFI has been modified and much improved of late, to be used mainly in the holding furnace of various shapes and sizes to reduce alkalines. These injectors rotate as high as 500 rev/min and are designed to be either fixed to the furnace, fixed to the floor adjacent to the furnace or as a mobile unit able to treat more than one furnace in the casthouse(see Photo 3, Photo 4, Photo 5).



Photo 3: Typical RFI – Mobile

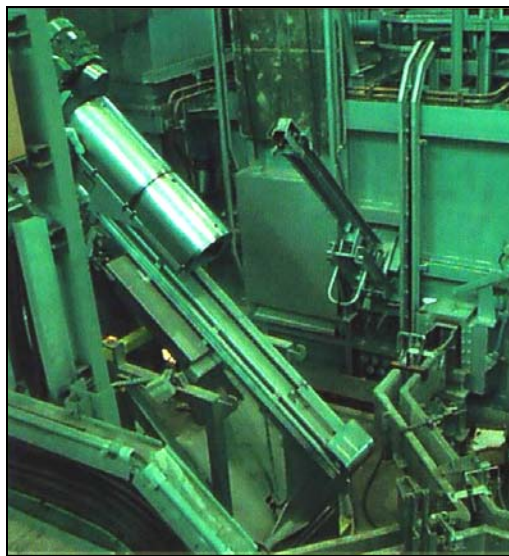


Photo 4: Fixed RGI for 2 Furnaces

It is critical that the injector is positioned correctly in the furnace whilst maintaining a proper height of metal above and below the impeller. These injectors using graphite rotors can treat up to 150 tonnes of metal in the furnace with a single machine. Much research work using modelling and practical evaluations has been carried out ^{(4) (5)} to ensure the optimum reduction of alkalines can be achieved.



Photo 5: Typical RFI – Fixed

In-line Degassing

The ACD is the latest development for in-line degassing. Being a modular system, 2 rotors per module, it is ideally suitable to treat flow rates from a few kg/min to as high as 1500 kg/min. It is designed to use spinning rotors with up to 8 rotors (Photo 6) immersed in the molten aluminium directly in the trough, so that there is no loss of metal during alloy changes. The number of rotors is a function of the flow rate, alloy type, as well as the desired reductions of hydrogen, inclusions and alkalines and so on.

Argon and chlorine gas is injected to the spinning rotors; and with stoichiometric additions of chlorine gas, alkalines can be reduced by up to 90% with typically between 65 and 75% being obtained⁽⁶⁾. Where chlorine gas is not available, the ACD can be operated successfully without its use. In fact, there are several units now operating world-wide without chlorine gas.

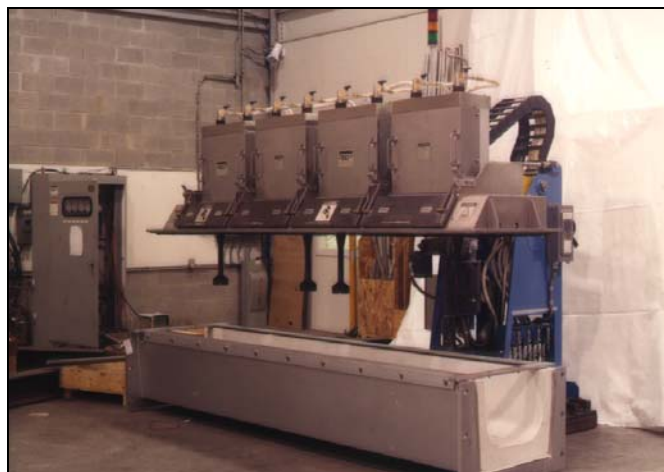


Photo 6: 8-Rotor ACD

Applications

TAC Applications

Based on experience over the last 20 years, there are several factors used today to design and operate a TAC station. Obviously, the specific alkaline and volume of metal to be treated need to be targeted to calculate the time of treatment and quantity of flux. One or more stations may be required.

Other factors also play a role in the design stage:

- ◇ *Metal temperature:* Need to avoid fires in the dust extraction system.
- ◇ *Location of the station(s):* In the pot room, or in a separate building, or in the casthouse.
- ◇ *Skimming:* Need to avoid bath material, which, if present, may stop the rotor and also may lead to pick-up of unwanted elements in the holding furnace. Skimming may also be required after treatment.
- ◇ *Rotor:* The rotor size, configuration and position in the crucible are determined for a given application. The rotor impellers are of cast iron with a life expectancy of up to 500 treatments. Iron pick-up has been studied and is found to be negligible. There is a slight build up of flux material on the rotors, which retards its abrasion.
- ◇ *Crucible transport:* The transport method determines the type of station; for example, a drive-through station is preferred, if there is no lid to be removed, where the operator stays with the "transporter" and operates the TAC by remote control.

Need For Sodium Removal

When the first papers were presented by Alcan to describe the TAC technology, the emphasis was on lithium removal; but more recently, as higher and higher amperages are used in the electrolytic cells, sodium levels are increasing to as high as 100 ppm or more in the molten metal after siphoning, and sodium removal is the focus.

No chlorine is used and therefore the process is considered environmentally sound. Typical results have previously been published ⁽²⁾ and are as per Figure 1.

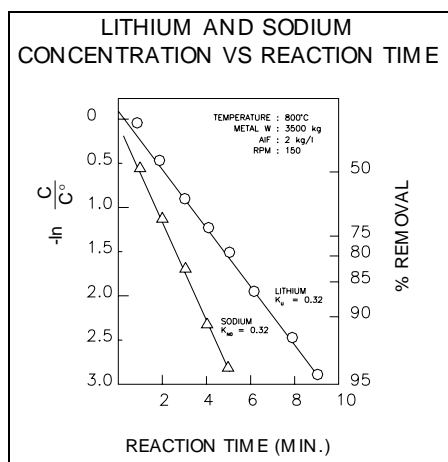
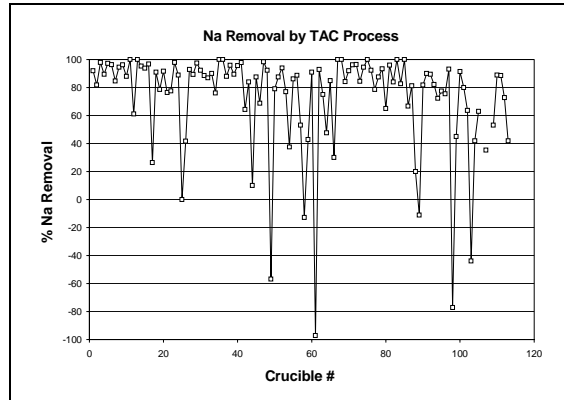


Figure 1

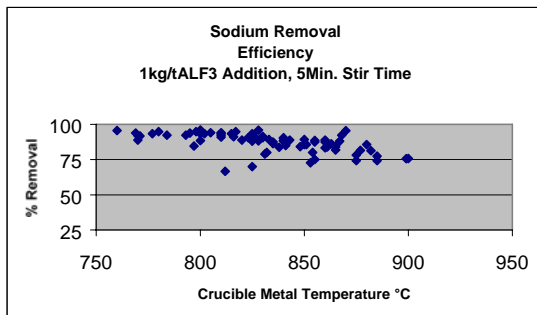
Confirmation of the efficiency of the TAC process has been more recently obtained:

- a) At an Alcoa plant where sodium reductions averaging between 80 and 100% have been obtained (Graph 1).

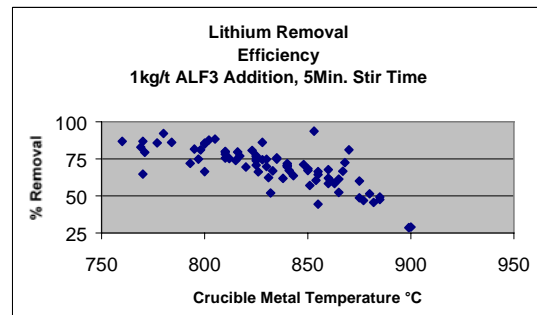


Graph 1

- b) One where molten metal is delivered to a nearby client's casthouse with tight restrictions on maximum permitted sodium levels. Although an average of approximately 60% reduction was required with two TAC stations able to treat 140,000 tonnes per year for a cycle time of 7.5 min, a much higher reduction has been obtained. An even shorter time is possible to meet the requirements.
- c) One installation which illustrates the influence of metal temperature on the reduction of sodium and lithium (Graph 2 and Graph 3): the higher the temperature, the lower the reduction.

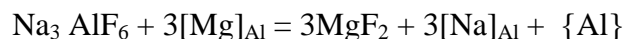


Graph 2



Graph 3

On the other hand, pick up of sodium can occur in the presence of bath material in the holding furnace when the charge material includes scrap or alloy remelts as well as pot room metal. For aluminium magnesium alloys, the benefit of sodium reduction by the TAC process ⁽⁷⁾ is nullified. Removal of the bath material is therefore critical not only as mentioned above to avoid rotor stoppage in the crucible but also to avoid risking picking up alkalis according to the following equation:



Should this occur, then two solutions might be considered. The first solution might be to treat only in the holder with an RFI (no chlorine gas) followed by treatment in an in-line degasser. In this case, there would be no TAC treatment. The second would be to skim all bath material and to consider siphoning of the molten metal into the melter/holder furnace so that the TAC treatment is the right alternate.

It is to be noted that sodium is highly reactive and is removed during transfer of molten metal and even during holding periods in the crucible. For example, in some of the older pot rooms, siphoning of a one-tonne quantity into a holding crucible of, say, five tonnes before transporting to the casting centre allows some of the sodium to be removed, due to its high vapour pressure. Or when transporting molten metal to a casting centre several kilometers away followed by transfer to a furnace, some sodium removal is obtained.

RFI Applications (No Chlorine Gas)

Typical coefficients for reductions of alkalis are given by Béland, Dupuis and Riverin⁽⁴⁾ using the RFI in a holding furnace. Depending upon the incoming levels, sodium for example can be reduced by up to 70% or more for a 20-25 minute fluxing period. A simple calculation will show that for starting levels in the holder of 20 ppm sodium, it can be reduced typically to 5 ppm with the RFI.

Bilodeau, Lakroni and Kocaefe⁽⁵⁾ reported the results of extensive modelling of the rotary fluxing technology with the objective of optimising the process. The work established that the furnace mixing achieved with the RFI was highly effective (see Figure 2 for an example of stirring efficiency when measured with thermocouples for the surface and furnace bottom). It was stated that the RFI process performances are governed by the dispersal efficiency of the rotor.

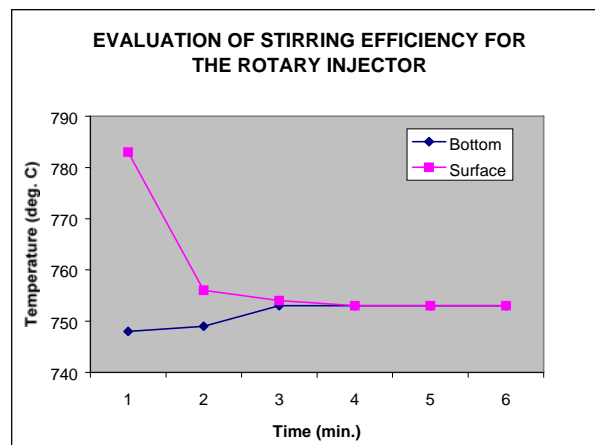


Figure 2

Alkalines are removed according to the "first order" for which the K constant characterises the removal kinetics. This type of reaction is also used for the TAC, RGI, RFI and the ACD.

There are various fluxes on the market, environmentally friendly substitutes for chlorine fluxing, many of which are based on a fully fused Magnesium chloride/Potassium chloride composition.

Successful applications of fused fluxes have shown good reductions at a remelt plant and at a smelter.

Case 1 – A Remelt Plant

Table I presents typical results obtained with the RFI. The results show excellent sodium and calcium removal even at low starting levels.

Table I: Alloy Grade 3XXX

	Average	
	Ca	Na
Furnace before RFI treatment	10.7	3.1
Furnace after RFI fluxing	4.2	0.8
Efficiency(%)	60%	75%
Removal rate, Kinetic, K (min-1)	0.037	0.054

Case 2 – Smelter

Table II: Alloy Grade 6XXX

Na (ppm)	Na (ppm)	(%)	K (min-1)
30	8	73	-0.05

Figure 3 shows simply how alkalines are removed according to the first order reaction for which the experimental results fit well with those calculated.

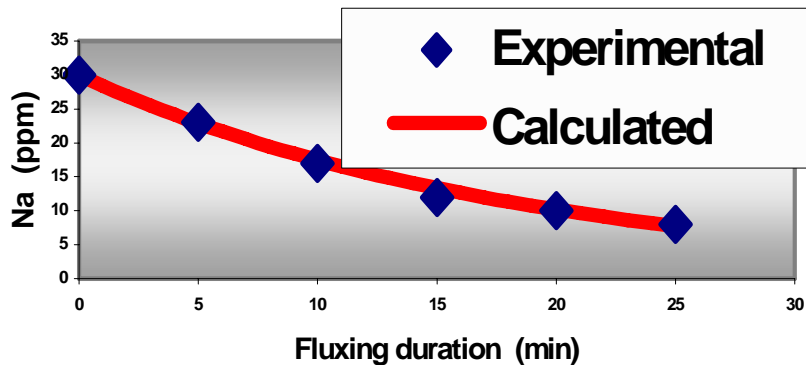


Figure 3

RGI Applications

In one example, there has been a shift away from the TAC to reduce lithium to be replaced by the RGI. Table III shows how the alkalines are all reduced to varying concentrations just by handling

of the crucibles, waiting time before treatment and the transfer of metal from pot crucibles to transfer crucibles in the cast house (up to 25% for sodium and even 10% for lithium). Once transferred to the furnace, there is another reduction of the alkalines; and once fluxing with an RGI is completed, another 70% reduction in lithium is obtained, for sodium 90% and calcium by 90%.

Table III

	Average, A356 alloy		
	Li	Na	Ca
Before crucible transfer (pot room)	0.0011	0.0036	0.0004
After transfer (cast house)	0.0010	0.0027	0.0002
Furnace before RGI fluxing	0.0007	0.0009	0.0008 *
Furnace after fluxing	0.0003	0.0001	0.0001

* Pick-up was due to alloy additions in the furnace.

Overall, due to handling and furnace treatment with an RGI, the lithium is reduced by more than 72%, the sodium by 97% and the calcium by 75%, even allowing for calcium pick up during alloying in the furnace.

ACD Applications

Based on predictions for alkaline removal and the levels of near stoichiometric chlorine (up to 1.0 l/min), the efficiencies were as expected (Table IV), with sodium removal up to 90%. Calcium removal was lower at between 10% and 25%, but slightly higher volumes of chlorine gas would be necessary to near stoichiometric for calcium removal, if higher removals were required.

Table IV: Alkaline Samples

AA Type Alloys	Nb of Rotors	Cl ₂ (ml/min)	Na "pre" (ppm)		Na "post" (ppm)		Ca "pre" (ppm)		Ca "post" (ppm)		Removal Efficiency	
			1	3	2	4	1	3	2	4	Na (%)	Ca (%)
6262	6	483	7,6	7,9	2,1	1,5	36,2	35,5	37,6	34,3	76,8	-0,3
6262	6	1000	5,3	4,6	1,8	1,2	14,6	14,1	11,8	10,8	69,0	21,2
7075	4	670	8,5	8,2	4,3	4,3	28,9	28,3	25,4	26,1	48,5	10,0
7075	4	1000	9,2	8,0	1,0	0,6	46,7	47,0	36,9	37,6	90,7	20,5
2030	4	1000	10,1	9,9	1,5	0,4	33,1	33,9	23,7	27,3	90,5	23,9

The degasser is able to complete the alkaline reduction to customer's specification. Further reduction can be obtained in an in-line compact degasser to an average of 70% ⁽⁶⁾.

As an interesting example of overall process efficiency, it is noted that whilst average sodium levels in the holding furnace were 20 ppm, these dropped to less than 2 ppm after degassing in the holder and the ACD.

Summary/Conclusion

The TAC process is still very much an option for reducing alkalines for pot room metal at the smelter. It is not only efficient but also chlorine free. Sodium is present as high as 100 ppm or more as smelters use higher and higher amperage. It is becoming more and more unusual for final product specifications not to demand maximum sodium values, often below 1 ppm. Therefore, the TAC process is regaining a certain amount of popularity to reduce sodium in the crucibles as well as retaining its usefulness to reduce lithium where required.

Using a TAC can reduce considerably the amount of time needed to reduce sodium in the melter/holder furnace. On the other hand, for certain alloys no bath material can be allowed to be carried over into the holder whereby sodium pick-up can reoccur.

The RGI reduces the amount of chlorine used in holding furnaces compared with chlorine lancing, and it can reduce alkalines quite efficiently whilst providing an homogenous melt. It has been shown that even lithium can be reduced as well as sodium and calcium, particularly where there is extensive metal handling between the pot room and the furnace.

The RFI is chlorine free and not only reduces efficiently alkalines but also provides an excellent stirring to provide a homogenous melt. Results are in close agreement with predicted values using sophisticated modelling ("K" factor).

Alkaline removal can now be efficiently obtained in the casthouse with a combination of rotary injectors and a degasser. Results have shown that at starting levels of 20 ppm, for example, sodium in the holding furnace reductions to less than 2 ppm can be obtained after the degasser. It has been shown that reductions of up to 75% or more can be achieved in the holding furnace with further reductions of between 65 and 75% in the in-line degasser.

Acknowledgement

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