Light Metals 2011 *Edited by: Stephen J. Lindsay*
TMS (The Minerals, Metals & Materials Society), 2011

IN-LINE SALT-ACD^{TM}:
A CHLORINE-FREE TECHNOLOGY FOR METAL TREATMENT

Patrice Robichaud[1], Claude Dupuis[1], Alain Mathis[2], Pascal Côté[3] and Bruno Maltais[3]

[1]Rio Tinto Alcan, Arvida Research and Development Centre, P.O. Box 1250, Jonquière, QC, Canada G7S 4K8
[2]Rio Tinto Alcan, Aluval, 725 Aristide Berges – B.P. 27 - 38341 Voreppe Cedex - France
[3]Société des Technologies de l'Aluminium du Saguenay Inc. (STAS), 1846, Outarde, Chicoutimi, QC, Canada G7K 1H1

Key Words: Aluminum Processing, In-Line Treatment, Salt Fluxing, ACD

Abstract

A new generation of the Alcan Compact Degasser (ACD^{TM}), the Salt-ACD^{TM}, based on the utilization of salt fluxes in replacement of chlorine gas, was introduced to the aluminum industry [1]. This unique technology has been developed by Rio Tinto Alcan (RTA) since 2003 and in collaboration with La Société des Technologies de l'Aluminium du Saguenay (STAS). Its utilization in combination with the Rotary Flux Injector (RFI^{TM}) for furnace preparation and/or the Treatment of Aluminum in Crucible (TAC^{TM}) for aluminum pre-treatment eliminates the use of chlorine in casthouses. The Salt-ACD^{TM} technology has been successfully implemented and operated in RTA casthouses. It supports the objective of eliminating chlorine from the casthouse for health, safety and environmental reasons.

This paper presents recent developments in terms of equipment, key components and retrofittability to existing ACD^{TM} units. The operating experience and metallurgical performance are reviewed.

Introduction

In-line metal treatment of aluminum alloys is a key step to meet increasing customer's quality requirements for critical application products such as can stock, lithographic sheet, fine wire and micropore extruded tubes. Molten metal quality depends on the control of non-metallic inclusions, alkali/alkaline earth elements (Na, Ca, Li) and dissolved hydrogen. To maximize productivity, a casthouse must exploit every opportunity in the processing chain to treat the metal using the most efficient technology available. In a smelter casthouse, the three main time periods available for metal treatment are pre-treatment in the crucible for the removal of alkali elements and inclusions, treatment in the furnace after alloy preparation and in-line during casting of the product [2].

The evolution of metal treatment technologies over the years is a good reflection of the increasing demand in terms of quality, metal processing cycle time, investment and operational costs [3-7]. Another important priority of today's aluminum industry is the impact of our processes on the environment and worker safety. Chlorine is a reactive gas with a proven track record in the aluminum industry for molten metal fluxing, but it is also a toxic gas. Environmental pressure and increasingly severe legislation have pushed the industry and manufacturers to develop technologies based on the utilization of salt fluxes to replace chlorine.

A new chlorine-free technology, the Salt-Alcan Compact Degasser (Salt-ACD^{TM}), developed at the Arvida Research and Development Centre of Rio Tinto Alcan since 2003 and La Société des Technologies de l'Aluminium du Saguenay (STAS), has been introduced to the aluminium industry. This technology, composed of a Flux Feeder for Degasser (FFD^{TM}) combined with the ACD^{TM}, is considered as the last technological step required to achieve a 100% chlorine-free casthouse. The same principle of in-line salt injection has been applied to other technologies with positive results [8].

Since then, the deployment of the technology has been successfully completed in key Rio Tinto Alcan casthouses. From its original inception and prototype version, the FFD^{TM} has now evolved to a mature industrial design well adapted for easy implementation and ensures reliable and precise operation.

This paper presents recent advancements of the FFD^{TM} technology, its application with the ACD^{TM} and reports the metallurgical and operational performance.

Key Technology Principles

Optimized Treatment Zone

Principles for optimizing the metallurgical performance of the Salt-ACD^{TM} have been well established since the development of the first FFD^{TM} prototype [1]. The key process characteristics are the interfacial contact area that is created between the metal and the dispersed salt droplets, the residence time of these salt droplets within the molten metal and the subsequent separation by flotation of the impurities to the metal surface [9].

Figure 1 conceptually shows how the FFD^{TM} is used in conjunction with the ACD^{TM} to provide a precisely controlled flow rate of salt-gas mixture injected in the molten metal.

The multi-stage design of the ACD^{TM} technology is a key feature to maximize the performance of the process. Injection of the salt-gas mixture takes place through the first rotor of the ACD^{TM} relative to the metal flow. The salt is dispersed into small droplets by the rotor and is further sheared by subsequent downstream rotors where the separation and flotation of impurities take place.

The standard FFD^{TM} comes as a volumetric controlled feeder system, which is sufficient to achieve the required dosing precision. As an option, it can be fitted with a weighing module to achieve Loss-in-Weight type control and positively record the amount of salt injected (in compliance with American EPA requirements, for example). With a controllable injection rate ranging from 1 to 30 g/min combined with the typical gas flow requirements of the ACD^{TM} technology, the FFD^{TM} capabilities cover a wide spectrum of process requirements in terms of aluminum treatment.

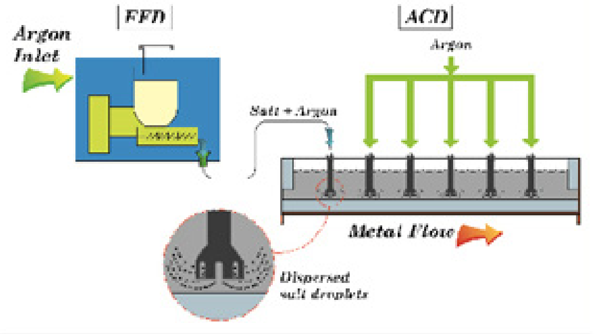

Figure 1. Optimized Treatment Zone

Optimized Reactant

A pre-fused salt mixture of $MgCl_2$ and KCl is preferably used. Adjustment of the chemical composition and granulation to a specific size distribution results in salt particles that are most suited to maximize the chemical kinetics of the reactions taking place in the Salt-ACD™.

It is well known that $MgCl_2$ is the chemically reactive agent in the salt flux responsible for removing the alkali impurities according to reactions 1 to 3 while KCl is used to reduce the melting point of the salt mixture [10, 11].

$$MgCl_2 + 2\,\underline{Na} \rightarrow 2\,NaCl + Mg \qquad (1)$$
$$MgCl_2 + 2\,\underline{Li} \rightarrow 2LiCl + Mg \qquad (2)$$
$$MgCl_2 + \underline{Ca} \rightarrow CaCl_2 + Mg \qquad (3)$$

Based on the KCl-$MgCl_2$ phase diagram generated using FactSage™ presented in Figure 2, it can be seen that working with $MgCl_2$/KCl mixtures close to one of the three eutectics at 36, 40 and 64% $MgCl_2$ allows injection of a salt flux that transforms to the liquid state below the molten metal processing temperature.

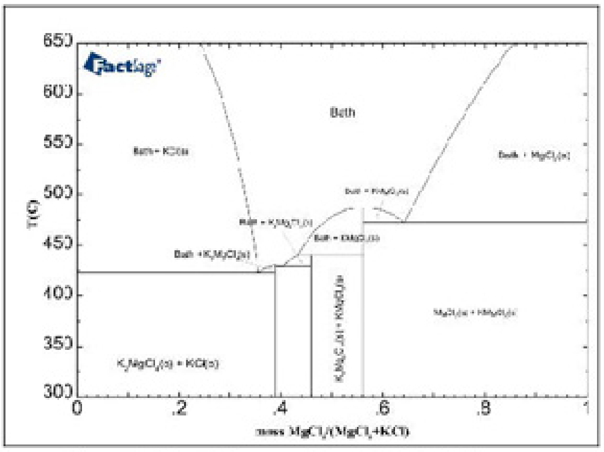

Figure 2. Phase Diagram of the $MgCl_2$ / KCl System

Production runs were performed to investigate if increasing the $MgCl_2$ content in the salt mixture above 60% could provide better metallurgical performance. Figure 3 shows that there is no significant difference in the alkali removal efficiency of the Salt-ACD™ obtained while using a salt flux mixture composed of 60% $MgCl_2$ compared to 75% $MgCl_2$.

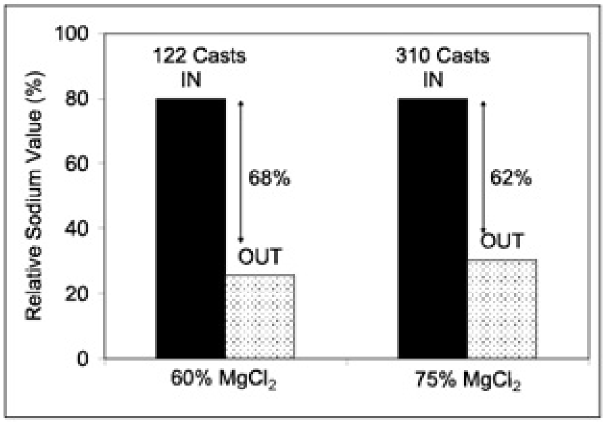

Figure 3. Sodium Removal Efficiency
for two $MgCl_2$ Concentrations in the Salt Flux Mixture

Production lots of salt are stringently controlled to ensure that residual moisture is always kept at minimum. The $MgCl_2$ is a deliquescent salt, meaning that it will absorb moisture from the air. The deliquescence relative humidity of the $MgCl_2$ under typical workplace conditions is approximately 33% [12, 13]. At humidity levels above this, any contact with the salt will result in water contamination [14] and could potentially affect the performance of the salt-ACD™.

Technology Presentation

A considerable effort has succeeded in the development of a compact salt flux feeding system that can easily be added to a new ACD™ system or retrofitted to an existing unit. Economical aspects have also been considered in order to obtain an affordable package. Moreover, the retrofit was proven operational and efficient on all existing ACD™ configurations including sealed, non-sealed, and while employing a controlled atmosphere in the ACD™. The controlled atmosphere ACD™ consists in adding a small air flow in the ACD™ to produce a controlled atmosphere above the molten metal having about 2%-4% oxygen.

The FFD™ system comes as a stand-alone unit which includes the gas and electrical distribution panels as well as its own human machine interface. The gas distribution panel precisely doses the gas volume to efficiently convey the salt and gas mixture to the ACD™ rotor no. 1 relative to the molten metal flow. The salt dosing system, adapted with an optimized screw design, is secured in a hermetically sealed cabinet kept under dry atmosphere to prevent any humidity pickup by the salt. Figure 4 shows a perspective view of the unit.

Figure 4. 3D View of the Flux Feeder for Degasser (FFD™)

A system for continuous casting applications is also available. Integration of an airlock with the flux reservoir allows salt refilling without interruption of the process.

A specific design of the ACD™ Rotor no. 1, where salt is injected, completes the system. A thermally insulated tube, placed inside the graphite shaft of the rotor maintains the salt mixture below its solidus until it enters a temperature zone above its liquidus thus preventing partial melting.

The FFD™ can be installed in the vicinity of the ACD™, either on the ACD™ structure or floor-mounted on the shop floor, as shown in Figure 5. This arrangement allows for easy refilling of the unit at an ergonomic level without the use of platforms. It also provides direct access to the local controls of the feeder, as they are conveniently located directly on the unit.

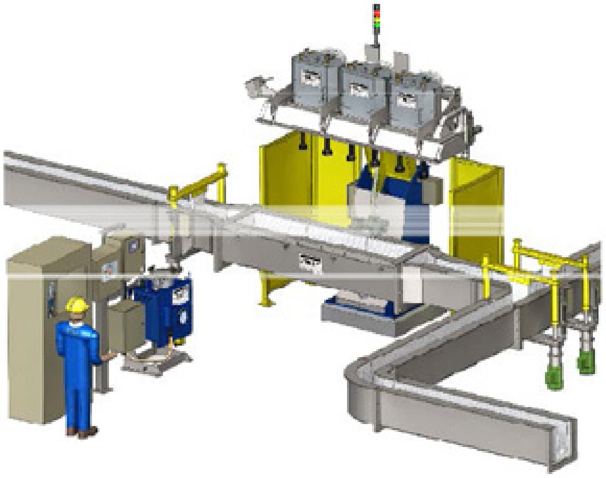

Figure 5. Floor-mounted FFD™ Installation

From a control point of view, benefits are achieved by the use of a dedicated local controller. The stand-alone configuration reduces the work required to link the FFD™ to the control panel of an existing ACD™. Specifically, hardware and software modifications are minimized in case of retrofits. However, expansion capabilities for connections to sophisticated level 2 systems are possible, including complete integration to the casting pit controls.

The self-contained control panel includes all the necessary elements for reliable process control such as pressure monitoring, gas flow control, and a sophisticated motor controller for precise salt flow control in a very compact design.

Industrial Experience

The FFD™ has been implemented and operated for production in key Rio Tinto Alcan casthouses. The process is qualified for the production of numerous products with many customers.

Operation of a FFD™ has proven to be stable with no problems related to salt accumulation (with sealed, non-sealed and controlled atmosphere ACD™).

The consistency of salt injection is monitored by measuring the pressure inside the flux feeder. To convey the salt mixture through the injection line, a nominal pressure is maintained within the unit during treatment. This pressure depends on many parameters such as the injection line dimensions, the salt flow rate, the rotor immersion depth in liquid metal, etc. Changes in pressure will indicate abnormal conditions such as line blockage. Figure 6 shows the typical pressure variation inside the injection line during the casting period while Figure 7 shows the initial pressure at cast start for 50 consecutive casts. As illustrated, the pressure of Cast no. 1 is very similar to that of Cast no. 50, indicating stable and reliable performance.

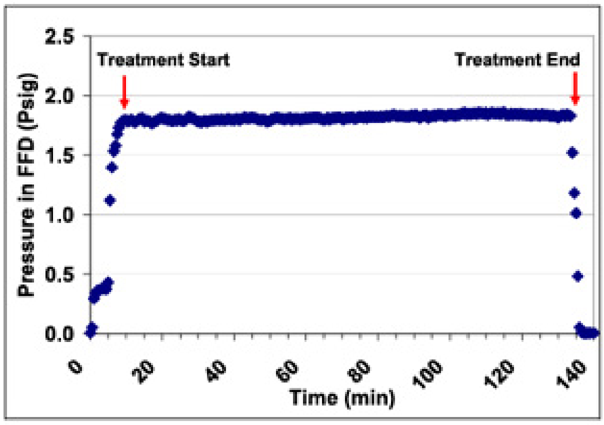

Figure 6. Process Stability during a Cast

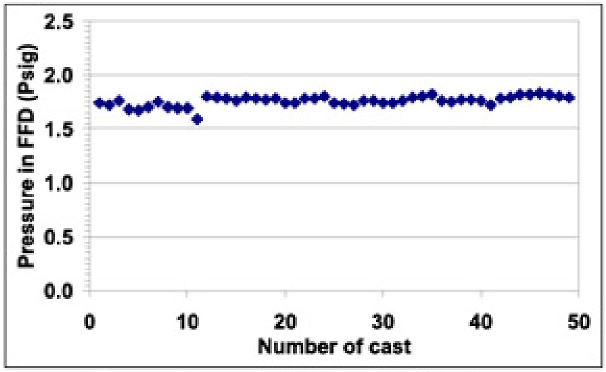

Figure 7. Process Stability over Multiple Casts

Metallurgical Performance

Characterization of the metallurgical performance of the Salt-ACD^{TM} was done by taking measurements and comparing the impurity levels at the inlet and outlet. Hydrogen concentration was measured using AℓSCAN^{TM}[1]. Alkali removal was measured using Optical Emission Spectroscopy measurements from horizontal disks, while inclusion concentration was measured using PoDFA.^{TM}.

Hydrogen Removal

Hydrogen removal occurs as a result of diffusion mass transfer between the liquid metal and the dispersed gas bubbles that are generated by the rotary injectors [7]. The concentration gradient between the gas and liquid phases is the driving force. Parameters such as the interfacial gas-liquid contact surface area (the size and number of micro-gas bubbles) and residential time of the bubbles in the melt, affect the hydrogen removal rate. However, these are independent whether chlorine or salt is being injected with the gas.

When injecting an anhydrous salt, hydrogen removal performance remains essentially unchanged as compared to operation with chlorine. Figure 8 shows plant measurements which exemplify the transparency of converting from chlorine to salt use in the ACD^{TM}. As illustrated, H_2 levels (mL/100 g) and variation at ACD^{TM} outlet are similar.

Figure 9 shows the hydrogen removal performance during in-line salt treatment. With hydrogen inlet levels ranging between 0.21 to 0.29 mL/100 g, the removal performance varied between 51 and 68%.

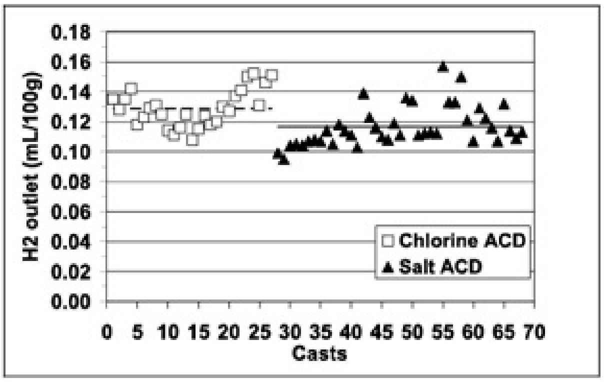

Figure 8. Hydrogen Content at ACD Outlet

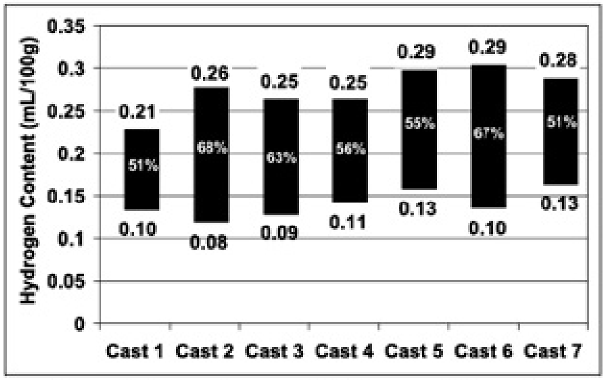

Figure 9. Hydrogen Removal Efficiency with Salt-ACD

Alkali Removal

Alkali elements are removed by reaction with $MgCl_2$ according to equations presented earlier.

The kinetic factors affecting the alkali removal rate have been documented elsewhere [15]. It is generally accepted that the controlling mechanisms are directly dependent on the salt-melt interfacial area generated. Increasing the contact surface is achieved by optimizing salt droplet dispersal.

Figure 10 shows the sodium removal performance when using stoichiometric ratios of 1 and ratios of 1.5 to 3 respectively. With a ratio of 1.0, the sodium removal efficiency is approximately 40%, while at stoichiometric ratios, the sodium removal performance increases to approximately 50%.

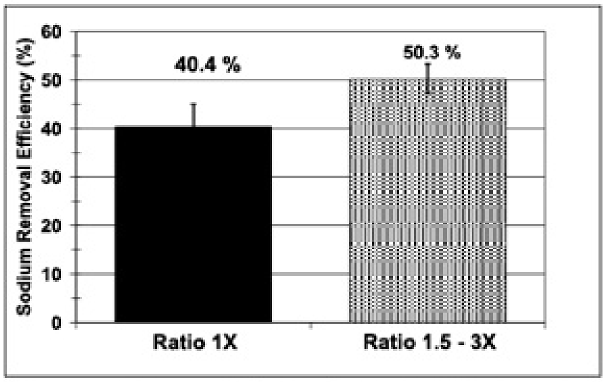

Figure 10. Na Removal Efficiency for Two Salt Injection ratios

Inclusion Removal

The inclusion removal efficiency of the Salt-ACD^{TM} varied between 69 and 88% over all industrial conditions tested as shown in Figure 11. This performance is the result of a good balance between the dispersal, dewetting and flotation mechanisms achieved in the multi-stage treatment approach of the Salt-ACD^{TM} process [16, 17].

---

[1] AℓSCAN is a registered trademark of Rio Tinto Alcan Inc.

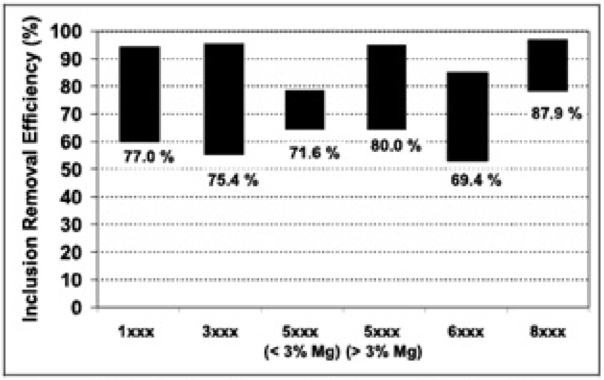

Figure 11. Inclusion Removal Efficiency for Different Alloy Families

Cumulated experience indicated that the inclusion removal efficiency achieved using the multi-stage Salt-ACD™ is equivalent or better than the ACD™ operated with chlorine gas.

Dross Generation

No differences were observed regarding dross condition or quantity when comparing the Salt-ACD™ process with the ACD™ operated with chlorine. The dispersed salt is found to be a good dewetting agent to keep the dross dry and non-reactive.

Impact on Downstream Operations

The in-line injection of salt using the Salt-ACD™ was observed to have no impact on the performances of downstream filtration technologies such as Ceramic Foam Filters and Deep Bed Filters. Figure 12 compares the metal cleanliness measured downstream of the filtration unit using LiMCA II™ [2], before and after the retrofit of a FFD™ to an existing ACD™ .

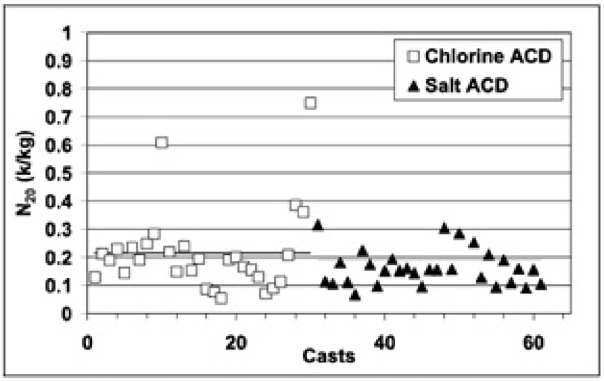

Figure 12. Metal Cleanliness after Filtration

Conclusions

The Salt-ACD™ process has been successfully implemented in key Rio Tinto Alcan casthouses. A thorough understanding of the critical process parameters and a detailed process monitoring allowed reaching metallurgical performance equivalent to the utilization of chlorine.

The FFD™ technology integrating key features for controlling the key parameters for ensuring a reliable injection of salt flux, has proven to be retrofitable to existing ACD™ units.

Together with in-crucible treatment, as achieved with the TAC™ system, and the in-furnace treatment using the RFI™, the Salt-ACD™ technology completes the technology port-folio allowing for a complete elimination to the utilization of chlorine for metal treatment with no compromise on final metal quality for critical product applications.

Acknowledgment

The authors wish to thank Rio Tinto Alcan for permission to publish the present paper. The authors also want to acknowledge the collaboration obtained with key Rio Tinto casthouses during the deployment of the technology.

References

[1] Leboeuf, S. et al. "In-Line Salt Fluxing Process: The Solution to Chlorine Gas Utilization in Casthouses", *Light Metals 2007*, (The Minerals, Metals & Materials Society, 2007), 623-627.

[2] Le Brun ,P. "Melt Treatment – Evolution and Perspectives", *Light Metals 2008*, (The Minerals, Metals & Materials Society, 2008), 621-626.

[3] Maltais, B. et al. "Metal Treatment Update", *Light Metals 2008*, (The Minerals, Metals & Materials Society, 2008), 547-552.

[4] Gariépy, B. et al."The TAC Process: A Proven Technology", *Light Metals 1984*, (The Minerals, Metals & Materials Society, 1984), 1267-1279.

[5] Rasch, B. "Refining of Potroom Metal Using the Hydro RAM Crucible Fluxing Process", *Light Metals 1998*, (The Minerals, Metals & Materials Society, 1998), 851-854.

[6] Dupuis, C. et al. "Rotary Flux Injection: Chlorine-Free Technique for Furnace Preparation", *Light Metals 1998*, (The Minerals, Metals & Materials Society, 1998), 843-847.

[7] Waite, P.et al "The Alcan Compact Degasser: A Trough-Based Aluminum Treatment Process Part I: Metallurgical Principles and Performance" *Light Metal 1996*, (The Minerals, Metals & Materials Society, 1996), 1001-1005.

[8] Chesonis, C. et al "Chloride Salt Injection to Replace Chlorine in the Alcoa A622 Degassing Process" *Light Metals 2008*, (The Minerals, Metals & Materials Society, 2008), 569-574.

[9] Waite, P. "A Technical Perspective on Molten Aluminum Processing", *Light Metals 2002*, (The Minerals, Metals & Materials Society, 2002), 841-848.

---

[2] ACD, Salt-ACD, FFD, TAC, RFI, LiMCA II, PoDFA are trademarks of Rio Tinto Alcan Inc.

[10] D.H. DeYoung, "Salt Fluxes for Alkali and Alkaline Earth Element Removal from Molten Aluminum," *Aluminium Cast House Technology* (Proceedings of the 7th Australian Asian Pacific Conference, 2001), 99-113.

[11] T.A. Utigard et al., "The Properties and Uses of Fluxes in Molten Aluminum Processing" *JOM*, 50 (11) (1998), 38-43.

[12] Lietai Yang, et al., "Experimental Determination of the Deliquescense Relative Humidity and Conductivity of Multicomponents Salt Mixtures" *Materials Research Society*, 713. (2001), JJ11.4

[13] Greenspan L., "Humidity Fixed Points of Binary Saturated Aqueous Solutions", *J. Res. Nat. Bur: Stand. (US.)*, 81A,1, (1977), 89-96

[14] G.J. Kipouros, and D.R Sadoway, "A Thermochemical Analysis of the Production of Anhydrous $MgCl_2$", *Light Metals* (Elsevier Science Ltd, 1, 2001), 111-117.

[15] Bilodeau, J-F. et al. "Modeling of Rotary Injection Process for Molten Aluminum Processing", *Light Metals 2001*, (The Minerals, Metals & Materials Society, 2001), 1009-1015.

[16] R. R. Roy. et al. "Inclusion Removal during Chlorine Fluxing of Aluminum Alloys", *Light Metals 1998*, (The Minerals, Metals & Materials Society, 1998), 871-875.

[17] R. R. Roy. et al. "Inclusion Removal Kinetics During Chlorine Fluxing of Molten Aluminum", *Light Metals 2001*, (The Minerals, Metals & Materials Society, 2001), 991-997.