

## METALLURGICAL PERFORMANCE OF SALT AND CHLORINE FLUXING TECHNOLOGIES IN CASTING FURNACES

Mark Badowski<sup>1</sup>, Stephen Instone<sup>1</sup>, Markus Hagen<sup>2</sup>

<sup>1</sup> Hydro Aluminium Rolled Products GmbH, Research and Development Centre, Georg-von-Boeselager-Str. 21, 53117 Bonn, Germany  
<sup>2</sup> Hydro Aluminium Rolled Products GmbH, Aluminiumstr., 21129 Hamburg, Germany

Keywords: Salt, chlorine, gas fluxing, alkaline metals, dross

### Abstract

Gas fluxing with the addition of chlorine or salt is widely used in the Aluminium industry to remove soluble impurities and non-metallic inclusions and to produce a dry dross with lower Aluminium content. In particular the removal of alkaline metals Na, Ca and Li is important to achieve the appropriate product quality. The metallurgical performance of this furnace treatment process determines the treatment time required. This can have a significant effect on the furnace cycle time and subsequently overall cast house productivity.

This paper presents the results of an extensive production scale study conducted by Hydro Aluminium Rolled Products into the performance of furnace salt and chlorine fluxing technologies. Emphasis is placed on the following metallurgical aspects, alkaline removal kinetics, reduction rate of non-metallic inclusions and dross formation. Safety aspects and the effect of the treatment process on the furnace cycle time is also reviewed.

### Introduction

The concentration of impurities is a key factor determining the quality of cast products for rolling applications. The alkaline metals Sodium, Calcium and depending on the process chain Lithium are introduced into the metal during the production of primary Aluminium in the electrolysis cells, while secondary Aluminium tends to contain higher concentrations of Calcium. It is known, that an elevated concentration of dissolved alkaline metals can cause various product defects, like Na induced edge cracking in AlMg-alloys. Undissolved impurities in the form of non-metallic inclusions can be generated along the whole process chain, but the liquid metal production step also has a significant influence. Potroom metal is generally high in Aluminium carbides, while remelt metal often contains larger amounts of inclusions like oxides, especially in case of organic contamination of the re-melted material.

Both types, dissolved and undissolved impurities have to be reduced to low levels for production of high quality rolled products. Partly this can be done inline during the degassing and mechanical filtration steps, but often an additional melt treatment in the casting furnace is necessary.

### Gas and salt fluxing in casting furnaces

Gas fluxing with a chlorine-nitrogen-mix using a lance has long been a common practice for the treatment of the melt in the casting furnace and is still widely used in cast houses around the world. The metallurgical performance of the chlorine fluxing step was recognised as a key parameter which could contribute to a reduction in the furnace cycle time and boost the production volume. Studies by Celik & Doutré [1] as well as Béland et al. [2]

identified a concentration of 10% Chlorine as sufficient to achieve best alkaline removal performance for lance fluxing. Higher concentration of chlorine in the gas-mixture led to acid gas emission due to incomplete reaction of chlorine. Large bubbles and limited metal circulation resulted in a low process efficiency. Additionally the large bath surface to volume ratio (shallow metal depth) of casting furnace produced a short contact time between reactive gas and the melt. The resulting large diffusion distances resulted in limited alkaline removal and emission of unused molecular chlorine.

The limitations of the metallurgical performance initiated studies to replace the lance fluxing process by alternative processes like flux wands, porous plugs or furnace impellers of which the later one was proven to have the best performance [3],[4],[5],[6]. Various types of furnace impeller with spinning rotor heads have been developed and successfully implemented in the cast house process, such as Pyrotek HD2000 [7], the Pechiney IRMA [8] or the STAS Rotary Gas Injector (RGI) [9].

The environmental aspect of the furnace fluxing process was also continuously in focus during the optimization of the furnace treatment procedure and led to the replacement of chlorine by fluxing salts [5],[6],[10]. DeYoung & Lavesque reported on a detailed comparison of the environmental and metallurgical performance of an RGI unit operated with 250 l/min of a N<sub>2</sub>-10%Cl<sub>2</sub>-mix and a Rotor Flux Injector (RFI) operated with a flux salt (MgCl-40%KCl) at 1 kg/min in AA5052 charges [6]. They concluded that both showed the statistically equal alkaline removal kinetics. The RFI salt fluxing process produced higher emissions of particular matter and hydrochloric acid, while the RGI chlorine fluxing showed higher emission of molecular chlorine. The study additionally confirmed that the emission of molecular chlorine was dependent on the utilization of the chlorine for the alkaline removal.

At the Hydro Aluminium Rolled Products cast house in Hamburg, Germany lance chlorine fluxing with N<sub>2</sub>-10%Cl<sub>2</sub>-mix has been the standard furnace operation applied for all charges. Increasing product demands regarding dissolved and undissolved impurities resulted in extended fluxing periods with negative effect on the furnace cycle time. Therefore the cast house considered the replacement the existing lance chlorine fluxing procedure with an alternative method.

This paper reports on an extensive on-site evaluation of the metallurgical performance of salt and chlorine fluxing with lances and furnace impellers in terms of the alkaline removal kinetics, the reduction of non-metallic inclusions, the formation of dross and reviews the influence of the metallurgical performance on the furnace cycle time.

## Procedure

The evaluation of the metallurgical performance of alternative furnace treatment options was performed at a production line of the Hydro Aluminium Rolled Products cast house Hamburg. This casting was dedicated to the production of 5000 series alloys and the alloy AA5754 (AlMg3) was exclusively monitored within this evaluation. Fig. 1 shows a schematic figure of the process steps at this casting line during standard operation and within the monitored charges with alternative furnace treatment options.

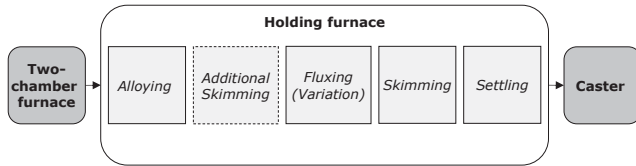


Figure 1: Furnace operation steps during standard production and during trial campaigns with additional skimming after melt transfer and alloy adjustment

The charge preparation including alloying was performed in a 145 mt two-chamber melting furnace based on a constant mix of cold metal, pre-consumer and post-consumer scrap. Batches of 45-50 mt representing the typical casted volume were transferred in one push into the holding furnace of 65 mt capacity.

The process steps at the melting furnace were performed according standard operational procedure and included:

- **Alloying:** A minor alloy adjustment according to the specific requirements of the individual charge
- **Fluxing:** Lance gas fluxing with a mix of  $N_2$ -10% $Cl_2$  depending on the initial level and the requirements for alkaline metals
- **Skimming:** Skimming of dross according local standard procedure
- **Settling:** A 1h settling period before cast start

In order to accurately monitor the furnace treatment, following adjustment to the furnace the following steps were introduced for these trials:

- **Additional skimming:** An additional skimming of the dross on melt bath surface was performed to provide a dross free surface prior to the fluxing trials

- **Variation of the furnace treatment procedure**

The furnace fluxing process was varied using the following four equipment setups:

1. **Lance Chlorine Fluxing** with the standard cast house equipment and a  $N_2$ -10% $Cl_2$ -mix
2. **Lance Salt Fluxing** with a Pyrotek FIM-S5 salt feeder [7] attached to the standard lance fluxing equipment without chlorine addition
3. **Impeller Chlorine Fluxing** using a mobile STAS RGI unit [9]
4. **Impeller Salt Fluxing** using the mobile STAS RFI unit plus a STAS salt feeder [9]

Table 1 shows the main process parameters applied for the furnace fluxing process and some aspects will be discussed in more detail:

- The RGI equipment was operated in a large and small setup with a 7 inch rotor head and 16 feet shaft at 210 rpm or 6 inch rotor with 13 feet shaft at 400rpm. This resulted in a 55% higher radial velocity of the small setup compared to the large setup. The RFI salt fluxing was only performed with the larger of the two setups.
- The  $Cl_2$  flow rate was kept constant for lance and impeller chlorine treatment by adjustment of the  $N_2$  flow rate to the recommended total gas flow rate for RGI processing. This resulted in a higher  $Cl_2/N_2$ -ratio for RGI chlorine trials than for lance trials
- Fused  $MgCl/KCl$  salt was applied for salt fluxing. PROMAG SI with 40%  $KCl$  close to the first eutectic point in the  $MgCl-KCl$  binary phase diagram [10] was applied for the lance salt fluxing trails, while Refinal 352XR based on the ternary system  $MgCl-KCl-NaCl$  [11] was applied for the RFI Salt Impeller trials
- The salt addition rate of 1kg/h within the salt lance and impeller fluxing trials equals an addition of chlorides within these trials more than double the addition rate of chlorine in the chlorine fluxing trials

Table 1:

Parameter	Lance Fluxing $Cl_2$	Lance Fluxing Salt	RGI Impeller Fluxing $Cl_2$ (large setup)	RGI Impeller Fluxing $Cl_2$ (small setup)	RFI Impeller Fluxing Salt
Rotor head diameter [inch]	--	--	7	6	7
Rotor shaft length [foot]	--	--	16	13	16
Rotor speed --[rpm]	--	--	210	400	250
Treatment period [min]	20	20	20	20	20
$N_2$ flow rate [l/min]	700	210	200	200	200
$N_2$ mass flow [kg/h]	49.1	14.7	14.0	14.0	14.0
$Cl_2$ flow rate [l/min]	76	--	76	76	--
$Cl_2$ mass flow [kg/h]	13.7	--	13.7	13.7	--
$Cl_2/N_2$	10.8 %	--	38 %	38 %	--
Salt mass flow [kg/h]	--	1.0	--	--	1.0
Salt type	--	PROMAG SI (MgCl-40%KCl)	--	--	REFINAL 352XR (MgCl-60-65%KCl; NaCl; CaF2)

In order to assess the metallurgical performance of the furnace fluxing operation the following monitoring procedures were applied within the trial campaigns:

1. **Alkaline removal kinetic of furnace fluxing**
  - The removal of the alkaline metals Na and Ca during the melt treatment was monitored by optical emission spectrometry (OES) of samples taken before, after and every 5 minutes during the treatment from the melt bath
  - The utilization of Cl<sub>2</sub> for alkaline removal through monitoring the concentration of Cl<sub>2</sub> in the off-gas of the holding furnace.
2. **Melt Quality at furnace exit**
  - The melt quality in terms of non-metallic inclusions was monitored by LiMCA and PoDFA technique
3. **Dross formation by furnace fluxing**
  - The dross amount generated during the fluxing process was monitored by weighing the dross from the 2<sup>nd</sup> skimming process (see Fig. 1)
  - The metal content in the dross from the 2<sup>nd</sup> skimming was analyzed by remelting it with salt at a certified laboratory

### Results and Discussion

The evaluation of the metallurgical performance of the furnace gas and salt fluxing treatment using impeller and lance will be discussed in terms of the applied process monitoring procedures:

- Alkaline removal kinetics
- Melt quality at furnace exit
- Dross formation by furnace fluxing

#### Alkaline removal kinetics

The main approach to study the alkaline removal kinetics of the applied melt treatment options was regular OES measurement of the concentration of Na, Ca and Mg in the melt during the treatment. Samples were taken every 5 minutes during the furnace treatment through the furnace door at a defined position within the furnace in all charges. Figure 2 shows an example of the Na concentration during an RGI impeller treatment with chlorine.

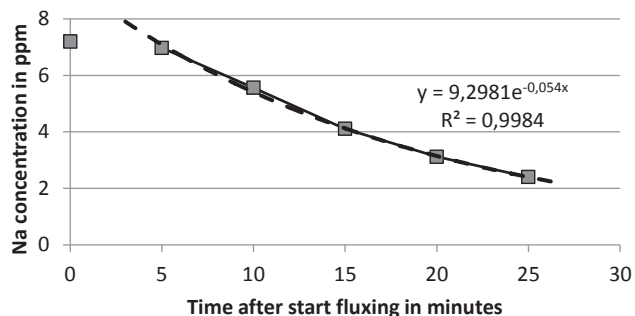


Figure 2: Na concentration over time in casting furnace during impeller chlorine fluxing of a 65t AlMg3 charge

The reaction of the chlorine with the Sodium in the melt is clearly visible by the constantly decreasing concentration. The removal rate was obviously lower within the starting period as a result of an initial inert gas purge before the actual chlorine addition to the fluxing gas. Due to the difficulty to differentiate between the fluxing period with and without chlorine after start of fluxing the initial five minutes period was neglected for further evaluation.

The removal of alkaline metals by chlorine and reactive salts can generally be described by a 1<sup>st</sup> order chemical reaction according to the following equation [2]:

$$c(t) = c_0 \cdot e^{-k \cdot t} \quad (1)$$

with the time  $t$  dependent and initial concentration  $c(t)$  and  $c_0$  and the removal rate constant  $k$ .

Under the assumption, that the alkaline removal kinetics in all monitored charges can be described by a first order chemical reaction the charges can be compared by the rate removal constant  $k$  only. This can be determined by an exponential fit to the concentration-time-curve as shown in figure 2 (removal rate constant here: 0.054). The figures 3 and 4 show the removal rate constants  $k$  for Sodium and Calcium in the monitored AlMg3 charges grouped according to the applied furnace fluxing procedure (see table 1 for processing parameter).

Constantly low Sodium removal rates were recorded for the salt lance fluxing process with an average removal rate constant of 0.013 min<sup>-1</sup>. The identical addition rate of salt using the RFI impeller resulted in significantly higher removal rates in all charges. The simple standard furnace lance fluxing treatment (0.035 min<sup>-1</sup>) with a 10% Cl<sub>2</sub>/N<sub>2</sub>-mix was comparable with the salt impeller treatment and impeller treatment with chlorine using the “large” setup of head and shaft (0.038 min<sup>-1</sup>). The best performance was achieved by the chlorine impeller treatment using the “small” setup (0.055 min<sup>-1</sup>). The highest Calcium removal rates were also achieved with this setup after identification of optimized process parameter in the first trials (figure 4).

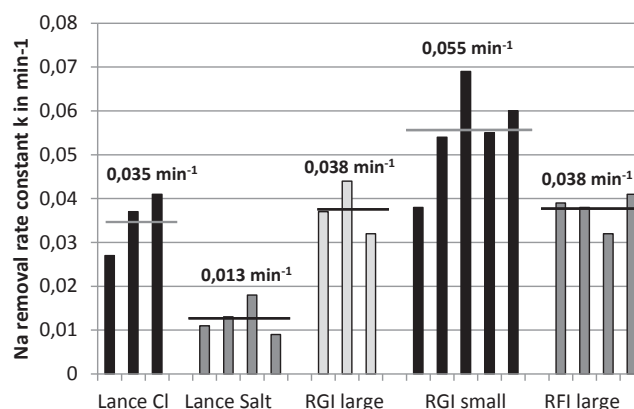


Figure 3: Na removal rate constant  $k$  of 1<sup>st</sup> order kinetic for different casting furnace fluxing procedures in AlMg3 charges

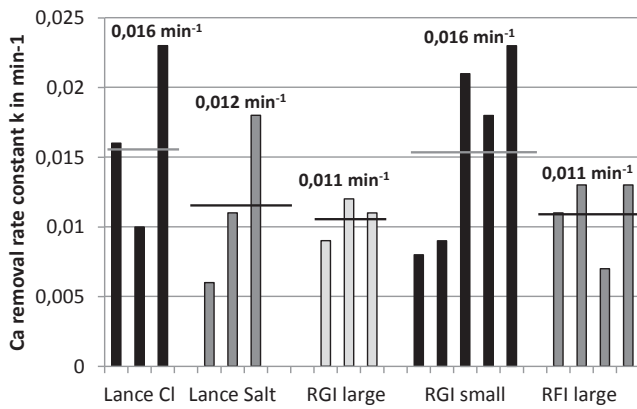


Figure 4: Ca removal rate constant  $k$  of 1<sup>st</sup> order kinetic for different casting furnace fluxing procedures in AlMg3 charges

Overall the results indicate an improved metallurgical performance using chlorine compared to salt fluxing, impeller treatment compared to lance fluxing and a significant influence of the operational parameter on the metallurgical performance of the RGI impeller treatment. The improved performance of the impeller treatment might be explained by the improved melt stirring and reduced bubble size compared to the lance treatment, which was especially beneficial for the chemically more complex salt fluxing process. The different performance of the two chosen RGI setups might be also explained by the melt mixing and bubble formation associated with the higher radial velocity of the rotor head and indicated the necessity to optimize the operational parameters for the individual furnace situation.

Figure 5 compares the Sodium removal kinetics monitored within this project with literature data for 5000 series charges. The monitored Sodium reduction rates for the RFI salt impeller treatment of the reported study agree with the literature data, while improved performance was monitored in all chlorine fluxing processes. Especially for the RGI impeller treatment higher performance was evident in the current study, which might be related to the higher chlorine concentration in the fluxing gas and a high utilization of the available chlorine to reduce Sodium. However, in previous studies no influence of the chlorine concentration in the Sodium removal was monitored [12].

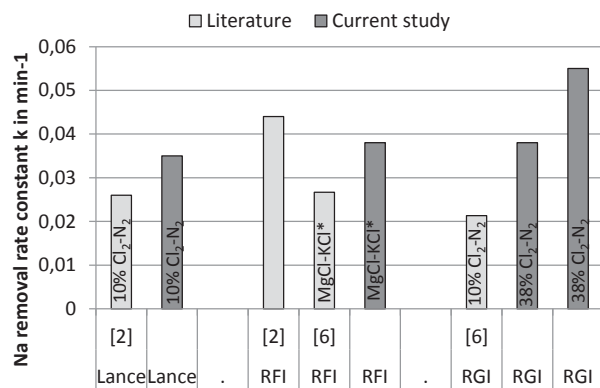


Figure 5: Na removal rate constants for 5000 series fluxing trials in literature (Béland et.al. [2]; DeYoung/Lavesque [6]) and current study (\* addition rate 1 kg/min)

An elevated concentration of chlorine in the treatment gas due to limited utilization of the chlorine gas increases the risk of negative environmental effects. DeYoung and Lavasque [6] studied the environmental aspects of furnace fluxing processes and stated that chlorine impeller fluxing had less emission regarding particulate matter and hydrochloric acid, higher emission of molecular chlorine than salt impeller fluxing. The emission of molecular chlorine was in both cases significantly less than during lance chlorine fluxing.

In order to study the utilization of the fluxing agent and the environmental aspect of chlorine fluxing the emission of molecular chlorine was monitored during fluxing (figure 6). Similar Cl<sub>2</sub> concentration in the process off-gas was monitored for the RGI treatment with both setups, but about 40% less than during lance chlorine fluxing in this study and 60% less than reported by DeYoung and Lavasque [6] for a similar setup. The lower chlorine emission despite the higher chlorine concentration in the fluxing gas combined with improved Sodium removal rates indicated a high utilization of the reactive gas in the reported trials. As expected even lower emission of chlorine was monitored for RFI salt fluxing as salt is more prone to produce particulate matter and hydrochloric acid.

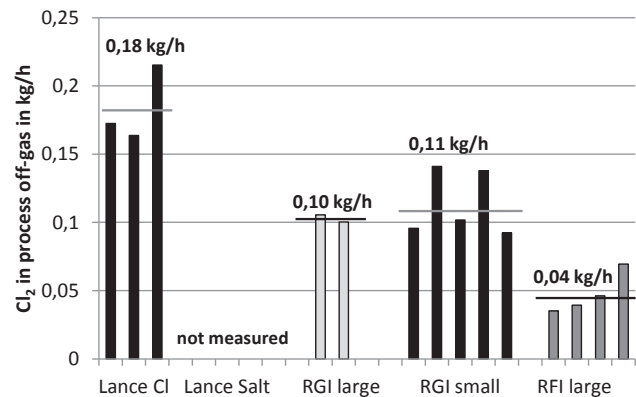


Figure 6: Concentration of molecular chlorine in process off-gas during casting furnace fluxing

#### Melt quality at furnace exit

The melt quality at the casting furnace exit was monitored to describe the efficiency of the applied furnace fluxing procedures to remove undissolved non-metallic inclusions. The inclusion concentration was monitored continuously using LiMCA technology and spot-wise by PoDFA samples within the steady-state casting period. Figures 7 and 8 show the average LiMCA N20 and PoDFA value grouped according to the applied furnace treatment technique. The LiMCA N20 value reports particles in the size range of 20µm to 300µm. In both cases the results were normalized to the average concentration in charges monitored prior to the trial campaigns with standard lance chlorine melt treatment.

A large variation of the melt quality at the furnace exit was monitored by PoDFA for charges with standard lance chlorine fluxing, which indicated that other process conditions, like settling period, alloying practice or furnace cleanliness status had significant influence on the particle concentration. This large variation was also evident in the trial charges with alternative

furnace fluxing procedures, which makes a sound evaluation of the removal efficiency based on the exiting data difficult. A long-term study would be necessary for a sound evaluation of the influence of the furnace treatment options on the particle flotation characteristics.

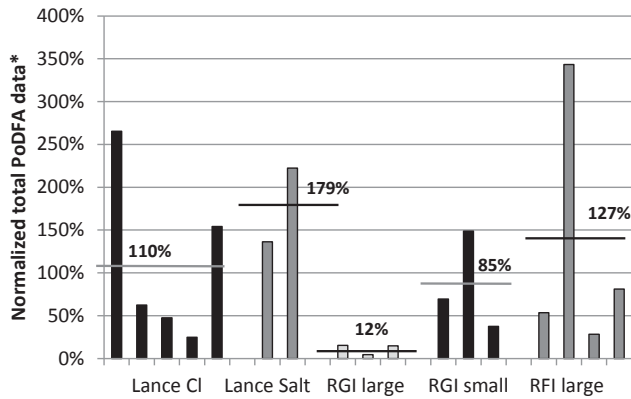


Figure 7: Normalized PoDFA data at furnace exit in trial charges for five furnace fluxing procedures (\* normalization based on average PoDFA concentration in charges prior to trial campaigns)

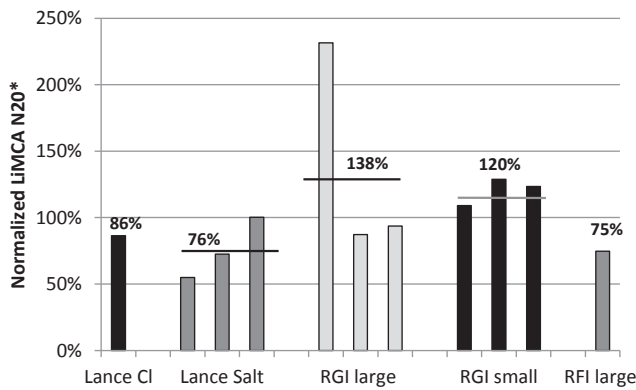


Figure 8: LiMCA N20 data at furnace exit in trial charges for five furnace fluxing procedures (\* normalization based on average LiMCA counts in charges prior to trial campaigns)

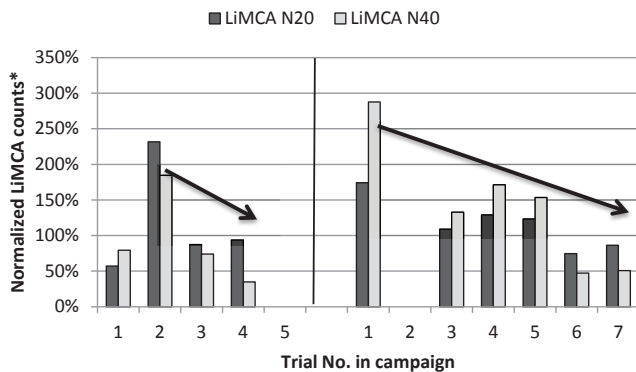


Figure 9: Normalized LiMCA N20 and N40 counts in sequence of charge in trials campaign (\* normalization based on average LiMCA counts in charges prior to trial campaigns)

One of the furnace processing parameters influencing the particle concentration might be explained by the LiMCA data. The average LiMCA counts in charges with high Sodium removal, like the RGI charges with small setup of head and shaft, showed increased particle concentration at furnace exit, especially compared to lance fluxing. In figure 9 the LiMCA N20 (20-300 $\mu$ m) and LiMCA N40 (40-300 $\mu$ m) values of all RGI gas fluxing and RFI salt fluxing trials are shown in the sequence of the trials. Charges without data were not monitored using LiMCA. An overall decreasing particle concentration was monitored over the sequence of the two casting campaigns, starting from a level above general cast house standard. Such behavior might be explained by a wash-out and cleaning effect of particles from the furnace walls by the possibly more efficient impeller treatment. Here an extensive long-term monitoring would be also favorable to really judge the equipment capabilities in this respect.

#### Dross formation by furnace fluxing

The treatment of the melt within the casting furnace prior to the start of the cast produced additional dross due to surface distortion and particle flotation and is therefore an important factor for the cast house cost position. In order to understand the dross formation by the furnace fluxing treatment the furnace was skimmed shortly before and after a defined period after the furnace treatment period. The dross from the second skimming process was weighted and separately stored from the standard cast house dross for further evaluation.

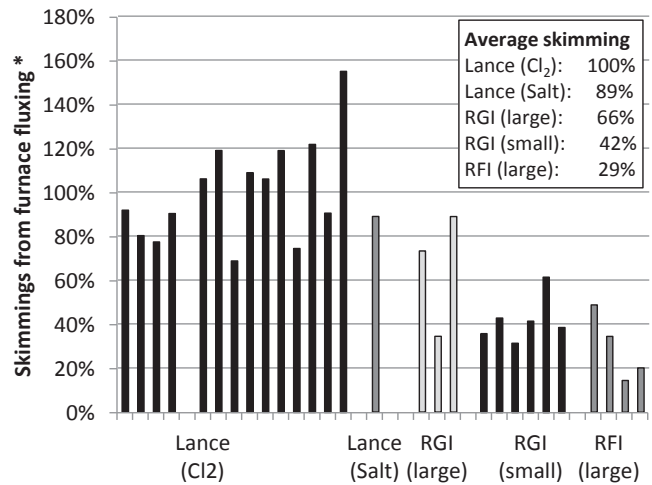


Figure 10: Skimming weights from furnace fluxing operation (\*normalized to skimming weights from lance chlorine fluxing)

Figure 10 shows the dross weight of the second skimming process for the trial campaigns compared to average dross weights for standard lance fluxing evaluated prior to the start of the fluxing trials period. The average dross weight by the fluxing process using lance with chlorine agreed well with the reference monitored prior to the trials, but showed some variation with a standard deviation of 25%. Only one charge of the salt lance fluxing procedure was monitored during the trials, but the dross amount in this charge was within the standard variation of the chlorine lance fluxing charges. Contrary to the lance fluxing the majority to the impeller treatment showed much lower dross weight outside the standard deviation of the chlorine fluxing process. The benefit of the impeller treatment regarding the dross



formation by the furnace fluxing step was in the range of 50-70% for charges with optimized impeller process parameter.

It is generally assumed, that a reduction in the dross amount by the furnace treatment is an effect of an improved separation of entrained liquid Aluminium from the dross resulting in drier dross [12]. The metal content of the dross from the furnace treatment in the monitored charges was therefore analyzed in a certified institute by re-melting with salt. The results of this evaluation confirmed the visual impression of the skimmed dross as the metal content was identical to standard operation. The reduction in the amount of dross produced was therefore a real effect of reduced melt surface turbulence by the impeller treatment and a real benefit for the cast house.

### Summary and Conclusions

The metallurgical performance of lance and impeller furnace melt treatment using chlorine-nitrogen gas or salt as fluxing agent was evaluated in production at the Hydro Aluminium Rolled Products cast house Hamburg in terms of furnace cycle time, dross generation and environmental aspects.

The evaluation might be summarized in following points:

- The removal of alkaline metals from the melt by furnace gas and salt fluxing can be described by a first order chemical reaction
- Higher Sodium removal kinetics was achieved in charges using chlorine-nitrogen-mix compared to charges using reactive salts and by using an impeller treatment compared to lance fluxing. The highest Sodium and Calcium removal rates were therefore achieved by a furnace chlorine impeller treatment, while the reaction kinetic was additionally influenced by the equipment setup and operational parameters
- The use of an impeller treatment with chlorine resulted in 40% less emission of molecular chlorine compared to lance fluxing most likely due to an increased utilization of the chlorine for alkaline removal
- The introduction of the impeller melt treatment seemed to change the furnace condition by a particle wash-out effect from the furnace lining. This resulted in an higher concentration of non-metallic inclusions at the furnace exit within the first charge and a continuously decreasing concentration level in the subsequent charges.
- The furnace melt treatment with an impeller resulted in more than 50% less dross generation in the fluxing step compared to standard lance fluxing with chlorine gas

It might be concluded from this evaluation:

- The removal kinetics for alkaline metals was largely influenced by process gas bubble formation and the melt stirring capabilities of the melt treatment technique. The bubble size setting the terminational velocity of the bubbles and the reactive surface area. High utilization of the reactive gas or salt and short diffusion distances enhanced the chemical process. The impeller treatment shows significantly improved performance compared to lance fluxing
- The condition of casting furnaces regarding collection and release of non-metallic inclusions is a complex process, which seem to be influenced by the furnace treatment

- The dross formation during the furnace melt treatment was determined by the disruption of the melt surface with significant improved operational performance of impeller treatment vs. lance treatment
- A key factor to reach optimum metallurgical performance of a furnace treatment taking cycle time, dross formation and environmental aspects into account is an adequate adjustment of the furnace treatment setup and the processing parameter to the actual furnace conditions

### Acknowledgements

Finally we would like to thank our colleagues at the cast houses and at the research centre Bonn for their support and discussion.

### References

- [1] C. Celik, D. Doutre, "Theoretical and Experimental Investigation of Furnace Chlorine Fluxing", *Light Metals 1989*, 793-800
- [2] G. Béland, C. Dupuis, J.P. Martin, "Improving Fluxing of Aluminium Alloys", *Light Metals 1995*, 1189-1195
- [3] E. Williams, R. McCathy, S. Levy, G. Sigworth, "Removal of Alkali Metals from Aluminium", *Light Metals 2000*, 785-793
- [4] E. Williams, "Alkali Removal and Reduced Chlorine Use During Furnace Fluxing", *Light Metals 2001*, 1053-1060
- [5] G. Béland, C. Dupuis, G. Riverin, R. Desmeules, L. Rose, "Rotary Flux Injection: Chlorine-Free Technique for Furnace Preparation", *Light Metals 1998*, 843-847
- [6] D. DeYoung, R. Lavesque, "Air Emissions from Rotary Gas and Rotary Salt Injection Furnace Fluxing Processes", *Aluminium Cast House Conference*, 2005, 7-16
- [7] R.A. Frank, P.J. Flisakowski "In-Furnace Refining Using Pyrotek's HD-2000 and FIF-50 Rotary Injection Systems", *Light Metals 2004*, 779-787
- [8] P. LeBrun, A. Mathis "Improved Molten Metal Quality at the Outlet of the Furnace Through the IRMA Treatment", *Light Metals 2004*, 789-792
- [9] M.B. Taylor, "Which Method to Choose for Alkaline Reduction", *7<sup>th</sup> Aluminium Cast House Conference*, 2001, 139-150
- [10] R. Bridi, M. Smith, "Improvements in Casthouse Processing Using In-Furnace Refining Systems", *8<sup>th</sup> Aluminium Cast House Conference*, 2003, 1-14
- [11] J. Coutenay, "A New Fused Magnesium Chlorine Containing Refining Flux Based on a Ternary System", *Light Metals 2012*, 1063-1068
- [12] D.C. Chesonis, E.M. Williams, D.H. DeYoung "Meeting Environmental Challenges in the Casthouse", *Light Metals 2009*, 653-657