

ALKALI REMOVAL AND REDUCED CHLORINE USE DURING FURNACE FLUXING

by

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Abstract

A series of furnace fluxing trials was performed at the Reynolds Casting Research Center as part of a DOE funded NICE³ project. The purpose of this work was to characterize the alkali removal efficiency of three different chlorine/inert gas fluxing methods; flux wands, porous plugs and a Pyrotek PHD-50 in-furnace spinning degasser. In addition to determining the relative alkali removal efficiencies of these three methods, the alkali decay curves have been used to develop a model describing the optimum chlorine addition rate during fluxing. This model has been verified for all three fluxing methods by measuring the excess hydrogen chloride in the furnace stack during fluxing using a FTIR (Fourier Transfer InfraRed) emissions monitor. This work has also shown that it is possible to use the FTIR to control the chlorine input rate to the furnace flux such that HCl emissions are minimized and alkali removal rates are maximized.

Introduction

The alkali elements typically found in aluminum are lithium, sodium and calcium. They are frequently brought into the casthouse with molten metal from the reduction cells. Sodium is introduced to the metal from the electrolyte used to reduce alumina. Lithium is sometimes added to the reduction cells in order to improve the electrical efficiency of the cell. Excessive amounts of lithium and sodium are known to cause surface quality issues in some products, and sodium is known to cause hot shortness in magnesium alloys. It is not unusual for certain alloys to have alkali requirements of less than 1 ppm.

In the past, the most common way to remove these alkali metals from aluminum melts was to flux them with either pure chlorine or chlorine/inert gas mixtures. In reduction facilities, these fluxes are often performed by inserting graphite tubes or steel wands into the furnace and sparging the metal with the flux gas. There are a number of other methods currently used to reduce or remove

the alkalis, including charcoal filtering, TAC[®], MgCl₂/KCl based solid salt furnace fluxes and in-line rotary degassers.

The first part of this project was completed and reported in reference [1]. This work showed the greater alkali-removal efficiency of an in-line spinning degasser over furnace fluxing with porous plugs. Following the completion of this work, there was great interest in finding the alkali removal efficiency of furnace fluxing with flux wands and of an in-furnace spinning flux unit. The in-furnace spinner theoretically would have high alkali removal rates due to greater mixing, finer bubbles, and better bubble dispersion. To this end, further trials were set-up where fluxing in the furnace was accomplished using flux tubes and using a Pyrotek PHD-50 furnace fluxing unit. The PHD-50 is a single rotor unit that can be positioned in the furnace in a variety of locations and angles, and set to run at various speeds and flux gas flowrates.

After finding the alkali removal rates for the different furnace fluxing methods, a mathematical model describing the optimum chlorine input for these methods can be developed with the chemistry data. This model can be verified by using an FTIR continuous emissions monitor to measure the real time hydrogen chloride emissions produced during these fluxes. In addition to verifying the chlorine addition rate model, trials were set-up to show that the FTIR could be used to control the chlorine input to the flux such that HCl emissions were minimized while the maximum alkali removal rate was achieved.

Experimental Procedure

A 25,000 pound melting furnace in the casting complex at the former Reynolds Metals Corporate Research Center was used in these trials. This tilting furnace has four porous plugs in the bottom for fluxing with argon or argon/chlorine mixtures. The fluxing system uses mass flow controllers, and the flowrates of the process gases can be changed in-situ while the system is

fluxing. For most fluxes, the flux gas flow rates were 2.19 SCFM of argon and 0.11 SCFM of chlorine for a 5% Cl₂ mixture. For these trials, two steel flux wands were set-up to allow wand fluxing in the furnace. During wand fluxing, the furnace door was left open about ten inches and the wands were run through the opening. For fluxing with the PHD-50, the furnace door was left open about four feet so the rotor would fit through the door. A curtain was used across the opening to reduce the heat loss from the furnace during the flux period. The PHD-50 rotor consisted of a 72" long 5" diameter graphite shaft with a 12" pitched five blade head on the end, a design that is similar to an in-line spinning degasser. The rotor was inserted into the melt at a 25° angle from the floor. For these tests, the rotor speed was set to 275 RPM, which is slower than recommended. This speed was determined by visually inspecting the surface of the melt during operation and trying to minimize the roostertail and splashing that the rotor kicked up, while getting the best mixing/bubble dispersion.

Figure 1 shows an outline for the eleven tests performed. Tests #1 through #4 were done in 1999 and reported in [1]. The main purpose of these tests was to compare the alkali removal efficiencies of porous plug batch and in-line fluxing. Various combinations of porous plug and in-line fluxing were tested. An ingot was cast for each of these tests and each was repeated. The Baseline Test was a repeat of the Test #3 condition, except with the flux extended out to 60 minutes so more data could be gathered.

Tests #6, #7, #9, and #10 were run in order to determine the alkali removal efficiencies of the various methods. Tests #5, #6, and #8 were run to demonstrate the possibility of controlling the chlorine input to the furnace using the FTIR such that HCl emissions are minimized and alkali removal is maximized. Each of these tests was repeated once or twice. Ingots were cast for one run of Test #7 and one run of Test #8 in order to monitor the metal cleanliness at the furnace exit and compare it to the data collected from the porous plug fluxes.

In order to track the alkali removal of the different flux methods, the melt was dosed with sodium, lithium and calcium before each test. For all the trials, the furnace was charged with a 1% copper alloy. Once the metal was molten, alkalis were added at a target of 40 ppm of Na, 30 ppm Li and 12 ppm Ca. After adding the alkalis, the melt was stirred thoroughly and skimmed. At this point, the hold period commenced for each test.

The alkali removal rate for each of the different processes was tracked by taking chemistry samples during the hold and flux times. During the hold periods, samples were taken at least every 20 minutes. During the flux periods, samples were taken at least every 10 minutes. These samples were analyzed for lithium, sodium, calcium and magnesium. Ransley samples were also taken during the flux periods in order to characterize the hydrogen removal during the flux. In addition to the chemistry and hydrogen samples, the HCl emissions in the furnace stack were measured with the FTIR during all of the flux periods.

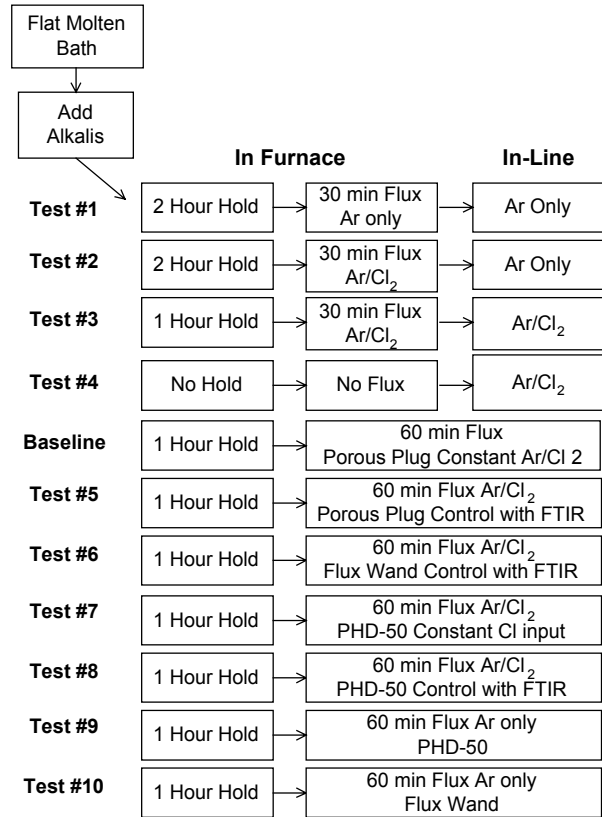


Figure 1. Test conditions employed in this study

Based on visual inspection, the PHD-50 generated smaller flux gas bubbles than the porous plugs or flux wands. It also appeared to produce greater turbulence and mixing in the furnace. Judging by the size of the flames produced when the bubbles broke the surface of the melt, the higher the percent of chlorine added to the flux gas the finer the bubbles were. When chlorine was used, the amount of dross generated by the PHD-50 operation and its dry texture was similar to that generated by the other fluxing methods. When only argon was used in the PHD-50, the dross was very wet, and a thick ring of sludge formed around the turbulence zone generated by the rotor.

Alkali Decay and Optimum Chlorine Model

As described in reference [2] the decay of alkali metals in molten aluminum during a batch operation is given by the following exponential decay equation:

$$C_j(t) = C_j^0 \exp \frac{-\rho_{Al}(k_t A_t)_j}{M} t \quad (1)$$

where:

- $C_j(t)$ is the concentration of alkali element j, over time
- C_j^0 is the concentration of alkali element j at time zero
- ρ_{Al} is the density of liquid aluminum (2350 kg/m³)
- $(k_t A_t)_j$ is a rate constant and area for alkali element j defined below (m³/min)
- M is the mass of molten metal in the furnace (11350 kg)
- t is the holding or reaction time (min)

The rate constant $k_t A_t$ used in Equation (1) is composed of two parts. The first part is associated with the surface reaction or oxidation of the alkalis. It accounts for the decay of the alkali elements while the furnace is holding or being stirred without the use of a reactive agent. The second part is associated with the reaction between the chlorine and the alkali at the metal/flux bubble interface. The relation defining the rate constant is:

$$k_t A_t = k_s A_s + k_b A_b \quad (2)$$

where:

- k_s is the rate constant for the metal / air surface reaction
- A_s is the metal-air interface surface area (12.6 m²)
- k_b is the rate constant for the Cl / metal reaction
- A_b is the total bubble surface area (m²)

There are empirical relations in the literature for finding these removal rate constants based on the average flux bubble size, gas flow rates and stirring intensity. By tracking the alkali metal consumption during the different flux processes, values for $k_s A_s$ and $k_t A_t$ can be found directly using Equation (1) for a given furnace and fluxing process via experimentation.

Once a fluxing operation has been characterized in a given furnace, the alkali decay rate during the flux can be predicted for each of the elements. Knowing this decay rate, and knowing the chlorine reaction rate constant $k_b A_b$, the optimum chlorine addition rate can then be found:

$$Cl_{opt}(t) = \rho_{Al} \frac{MW_{Cl_2}}{\rho_{Cl_2}} \sum \frac{a_j}{MW_j} (k_b A_b)_j C_j(t) \quad (3)$$

where:

- $Cl_{opt}(t)$ is the optimum amount of chlorine at time t (liter/min)
- MW_j is the molecular weight of element j
- ρ_j is the density of element j
- a_j is the stoichiometric constant (1 for Ca, Mg, 1/2 for Na, Li)
- $C_j(t)$ is the concentration of element j at time t

In this case, the optimum amount of chlorine means achieving the maximum alkali removal rate while producing the smallest amount of hydrogen chloride emission. For any fluxing process involving chlorine, the chlorine input to the system needs to be as close to the optimum as possible. At values greater than the optimum, an excessive amount of chlorine is going into the system and hydrogen chloride and particulate emissions will go up the furnace stack. At values less than the optimum, there will be little or no emission, but the maximum alkali removal rate will not be achieved. This deficiency leads to longer cycle times, as the furnace must be fluxed longer to achieve the required chemistry.

There are some caveats to using this model to control the chlorine flow in both a furnace flux or in-line degasser. First, the optimum chlorine addition rate will drop over the course of the flux period. As the alkalis are consumed, less chlorine is needed to react with the remaining alkalis. It is difficult to have the required level of control over the chlorine input rate to exactly follow the optimum curve. Second, the optimum chlorine addition rate is going to be dependent on the starting alkali levels. Since each new furnace load has a different level of initial alkalis, a different optimum curve will exist. This uncertainty could be overcome by using a

‘worst case’ alkali scenario, but care must be taken to avoid excess HCl emissions. Third, if there is significant bath carryover from the potroom, this will, to some extent, invalidate the decay rate constants. This invalidation is because bath in the furnace provides a source of sodium to the melt. Even after it is fluxed out, the sodium can come back up over time, especially when magnesium is added with bath present. If the sodium model decay rate is not correct, then the optimum chlorine addition relation will not be correct. Finally, the presence of magnesium at levels greater than about 200 ppm can greatly affect the removal rates of the alkalis and invalidate the optimum chlorine relation given above. Because of this, it is convenient to flux out as much of the alkali metals as possible in the furnace prior to adding magnesium.

Experimental Results

Alkali Removal

Tables I, II and III give the average removal rate constants determined by tracking the alkali decay rates for the different furnace processes, calculated by curve fitting the chemistry data to Equation (1). The tables give the average $k_t A_t$ for each of the alkali elements in units of m³/hr. They also give the estimated time required to half the concentration of each of the alkalis during the given process. For fluxes that used chlorine, these removal rates were calculated using the alkali values collected during time periods where an excessive amount of chlorine was being used. They therefore represent the maximum efficiencies possible for the given fluxing method. It is assumed that when less than the optimum chlorine is input, the removal rate will fall somewhere in between the argon/chlorine values and the argon only values.

Table I Average $k_t A_t$ (m³/hr) for Furnace Hold Periods

	Furnace Hold		
	Li	Na	Ca
Avg. $k_t A_t$ (m ³ /hr)	0.89	0.88	0.72
Half-Life (min)	210	211	259

Table II Average $k_t A_t$ (m³/hr) for Ar Only Fluxes

	Li	Na	Ca
	Flux Wands (Ar only)		
Avg. $k_t A_t$ (m ³ /hr)	1.86	2.25	2.86
Half-Life (min)	100	83	65
Porous Plugs (Ar only)			
Avg. $k_t A_t$ (m ³ /hr)	2.70	3.80	5.11
Half-Life (min)	69	49	36
PHD-50 (Ar only)			
Avg. $k_t A_t$ (m ³ /hr)	1.14	2.43	2.31
Half-Life (min)	163	77	81

As expected, the hold period had the slowest removal rate. During the hold, all three alkalis were removed at a similar rate, taking over three hours to halve their concentration. The argon fluxes removed alkalis faster, halving their concentration in the neighborhood of an hour. This reduction is due purely to the increased stirring generated by the flux bubbles which exposes fresh metal and the alkalis it contains to the atmosphere in the furnace. It is interesting to note that for the no chlorine flux, the calcium and sodium are removed quicker than the lithium, with calcium being removed the quickest with wands or porous plugs,

and sodium with the PHD-50. Also, the PHD-50, despite the large amount of stirring, had lower overall removal rates than the other two fluxing methods when only argon was used.

This changed dramatically when chlorine was added to the flux gas. Table III shows that the PHD-50 had the fastest removal rates, with the sodium level being halved in only six minutes. The calcium and lithium removal rates were also fastest with the PHD-50. The porous plugs were next, and the flux wands were the least efficient.

Table III Average $k_t A_t$ (m^3/hr) for Ar/Cl Fluxes

	Li	Na	Ca
Flux Wands (Ar/Cl)			
Avg. $k_t A_t$ (m^3/hr)	2.48	6.64	4.09
Half-Life (min)	75	28	45
Porous Plugs (Ar/Cl)			
Avg. $k_t A_t$ (m^3/hr)	5.16	11.49	6.47
Half-Life (min)	36	16	29
PHD-50 (Ar/Cl)			
Avg. $k_t A_t$ (m^3/hr)	7.28	31.27	14.80
Half-Life (min)	26	6	13

Figure 2 shows a plot of the measured alkali decay during one of the trials (Test #8A) along with the model curves described by the average removal rates given above. The decay model fits the data very well. In order to develop the optimum chlorine addition rate, the total chlorine removal rate constant needs to be separated into its two parts as shown in Equation [2]. The value of $k_b A_b$ can be calculated for each of the alkali elements by taking the $k_t A_t$ found for the argon/chlorine flux and subtracting away the $k_s A_s$ found from the argon only flux. In the argon only flux, the reduction in alkalis is wholly due to the surface reaction and $k_t A_t$ equals $k_s A_s$.

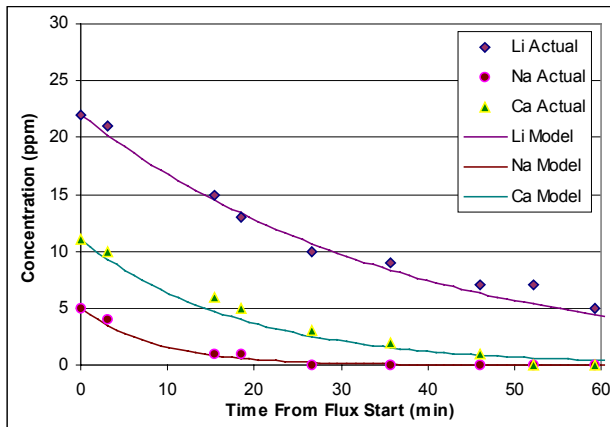


Figure 2: Alkali decay and model from Test #8A (PHD-50 Ar/Cl)

Table IV shows the different parts of the reaction rate constants for the alkali elements. The higher number indicates a faster removal rate. This table shows that the chlorine reaction with sodium is much stronger than with the other alkalis for all three processes. This difference is expected, since NaCl is more stable than the other alkali chloride salts at furnace temperatures. It is also interesting to note that CaO is the most stable oxide at furnace temperatures, and the calcium removal rate is the greatest

of the surface reaction rates for the flux wand and porous plug fluxes.

Table IV Reaction rate constants for Ar/Cl based fluxes

		Total =	Surface +	Chlorine
		$k_t A_t =$	$k_s A_s +$	$k_b A_b$
		(m^3/hr)	(m^3/hr)	(m^3/hr)
Flux Wands	Li	2.48	1.86	0.62
	Na	6.64	2.25	4.39
	Ca	4.09	2.86	1.23
Porous Plugs	Li	5.16	2.70	2.46
	Na	11.49	3.80	7.69
	Ca	6.47	5.11	1.36
PHD-50	Li	7.28	1.14	6.14
	Na	31.27	2.43	28.84
	Ca	14.80	2.31	12.49

Optimum Chlorine Addition

With the decay rates and chlorine reaction rate constants available, the optimum chlorine addition rate can be calculated using Equation [3]. Figure 3 shows the calculated optimum chlorine input over 40 minutes of fluxing with porous plugs for the Baseline A Test. This curve was generated using only the starting alkali levels and the rate removal constants. Also plotted is the actual chlorine input rate used for this test, 0.11 SCFM.

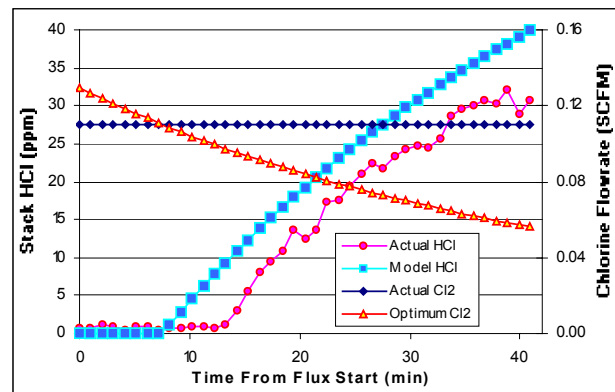


Figure 3: Actual and optimum chlorine input and emission during the Baseline A test (Porous Plugs with Ar/Cl)

For the first eight minutes of the flux period, not enough chlorine is being used to reach the maximum removal efficiency of the system. This indicates that all of the chlorine going into the system is consumed before it reached the surface of the melt, and there should be no HCl emissions. As the alkalis are steadily consumed the optimum level of chlorine needed drops below the actual input level. At this point, an excessive amount of chlorine is being used and unreacted chlorine escapes from the melt surface. This escape will result in a HCl emission in the furnace stack. The predicted HCl emission can be calculated by subtracting the optimum curve from the actual curve. Figure 4 also shows the predicted and actual HCl emissions, as measured with the FTIR. The two curves show good agreement, although the model HCl starts rising a few minutes earlier than the actual. Similar models can be built for the fluxes with wands or the PHD-50.

