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REMOVAL OF ALKALI METALS FROM ALUMINUM

by

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Abstract

The alkali metals Na, and to a lesser extent Li and Ca, are found as undesirable impurities in aluminum. These must be removed to extremely low levels for acceptable product quality. The traditional way to refine the metal is to flux with chlorine and an inert gas. This process is poorly understood, however, and excessive chlorine consumption and chloride emissions to the atmosphere may occur. This paper presents the results of an extensive experimental program conducted to characterize and optimize the process of fluxing with chlorine. One of the unique features of the program is the utilization of an on-line emissions monitor to control the fluxing process. A 25,000 pound melting furnace in the casting complex at the Reynolds Metals Company Corporate Research Center was used in these trials. The furnace is tilting with porous plugs in the bottom for fluxing. In-line gas fluxing was also done outside the furnace with an efficient spinning degasser. The experimental results obtained in this study, together with a theoretical analysis, have allowed Reynolds to construct a detailed model of the alkali metal removal process. This understanding allows one to significantly reduce chlorine consumption and chloride emissions during the metal refining process.

Introduction

It is a common practice to add chlorine to the inert gas used for furnace fluxing processes. Chlorine is required to remove reactive alkali elements. Sodium, and sometimes lithium, are introduced to the metal from the electrolyte. Sodium causes hot shortness in alloys which contain magnesium. Lithium creates an undesirable black film on foil products. Due to these unwanted properties, both elements must be reduced to very low levels.

On the other hand, Reynolds Metals Company desires to reduce chlorine consumption, and minimize chloride emissions to the atmosphere, as far as these goals may be attained without sacrificing metal quality. This paper summarizes the experimental results obtained in an extensive test program that was designed to provide the scientific and engineering knowledge required to meet both goals.

In the first part of this program, a detailed literature review and theoretical analysis was made of the removal of alkali metals. The result, reference [1], showed that additional experimental work was required, especially regarding fluxing in the furnace with either porous plugs or with lances. With an in-line treatment system (SNIF, ALPUR, HYCAST, etc.) the surface area of the bubbles is 3-4 times the area of the melt at the top of the reactor. For furnace treatment the situation is reversed: the melt surface is much larger than the bubble surface area. Because the reaction at the surface has not been well characterized to date, it is not possible to make a reasonable prediction of the results to be found during furnace fluxing.

In addition to providing information about the kinetics of some of the reaction mechanisms, these experiments were designed to evaluate the feasibility of using a real time, on-line monitoring system to measure the chlorine emissions produced. If this measurement can be translated into practice in the casthouse, it should be possible to control the chlorine fluxing process to minimize undesirable emissions.

Experimental Program

A 25,000 pound melting furnace in the casting complex at the Reynolds Metals Corporate Research Center was used in these trials. The furnace has porous plugs in the bottom for batch fluxing. Gas fluxing was also accomplished outside the furnace with a Hycast HI-45 degasser. The layout of the casting station and the locations where metal, gas, and LiMCA samples were taken are shown in Figure 1.

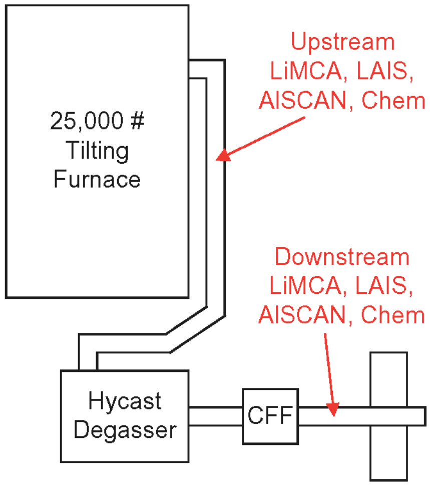

Figure 1. Casting Station

The most serious difficulty in studying alkali metal removal is that more than one reaction mechanism may operate simultaneously. This is why past studies are not very helpful. They were not able to separate out and measure the relative contributions of the different reactions. For this reason, an experimental program using four combinations of process treatments was planned. The four test conditions used are shown below in Figure 2. Each test was run twice, i.e. Test 1a and 1b.

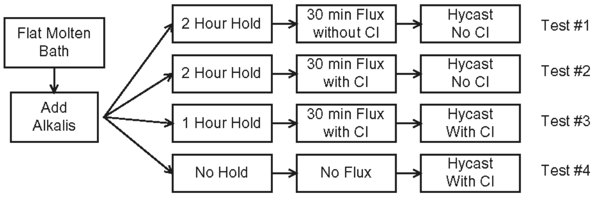

Figure 2. Test conditions employed in this study

The test procedure was to fill the furnace with 25,000 lb. of high alkali-containing sows and/or ingot slices, and to melt the charge overnight. Copper was added to the melt to bring the composition to about 1 wt. % Cu. The copper does not affect the reaction of alkali metals and aids in castability. No detectable amount of alkali metal (less than 1 ppm each of Na, Li, and Ca)[†] was found by the time the metal was molten and at casting temperature, so alkali additions were made to the furnace. Al-Li and Al-Ca master alloys and Na metal were plunged into the melt at an addition rate of 40 ppm Na, 30 ppm Li and 12 ppm Ca. The porous plugs were turned on briefly to stir the melt and mix the addition into the furnace. The gas flow through the plugs was turned off, metal samples were taken, and the refining procedures shown in Figure 2 were begun.

Gas samples were taken for analysis from the furnace stack during the holding and fluxing periods. An enclosure was also built to cover the Hycast unit so that fugitive emissions from this source could be collected and analyzed. These samples were analyzed for hydrogen chloride and other gases by an FTIR-CEM (Fourier Transform InfraRed-Continuous Emissions Monitor) supplied by Entropy, Inc.

Other important experimental conditions employed in these tests are described below, when presenting the results found.

Experimental Results

Furnace Holding and Fluxing

Metal samples were taken from the furnace at 15 minute intervals during the holding period, and every 10 minutes during the flux with porous plugs. An example of typical results obtained is shown in Figure 3. The concentration of the three alkali metals is plotted on a semi-logarithmic plot, because the theoretical relationship described in reference [1] for oxidation of alkali metals at the surface of the melt is given by:

$$\frac{\%_j}{\%_j^o} = \exp\frac{-k_s \rho A_s}{M} t \qquad (1)$$

where

$\%_j$ is the concentration of element j, with time

$\%_j^o$ is the beginning concentration of j, at zero time

k_s is the rate constant for the surface reaction (m/s)

ρ is the density of liquid aluminum (c. 2350 kg/m^3)

A_s is the surface area of the melt/air interface (m^2)

M is the mass of molten metal in the furnace (kg)

t is the holding or reaction time (sec)

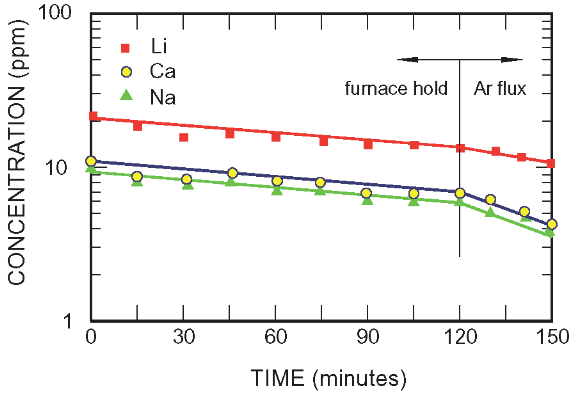

Figure 3. Alkali metal removal in the furnace (Test 1a)

Equation (1) has been used to calculate the empirical surface reaction rate constant, k_s. (The mass of metal is 11,350 kg, and A_s is equal to 12.6 m^2.) The results obtained for the six heats, which employed a furnace hold, are given below in Table 1.

The data is remarkably consistent, and all three elements are removed at the same rate. The rate constant for removal of Li, Ca and Na is equal to 0.24 x 10^{-4} m/sec.

[†] The Mg content in all heats was less than 20 ppm, the limit of detectability.

Table 1. Measured rate constants (k_s x 10^4 m/s) for alkali metal removal during furnace holds

Test	Li	Ca	Na
1a	0.24	0.24	0.27
1b	0.21	0.24	0.31
2a	0.29	0.24	0.25
2b	0.21	0.24	0.31
3a	0.26	0.30	0.16
3b	0.24	0.13	0.11
Average	0.24	0.24	0.23

Under the conditions employed in Test 1, a 30 minute flux (with argon only) was made using the porous plugs in the furnace. Because of the stirring produced by the gas flux, the rate of alkali metal removal was increased. The results are tabulated below.

Table 2. Rate constants (k_s x 10^4 m/s) for alkali metal removal during Ar flux in furnace

Test	Li	Ca	Na
1a	0.51	1.18	0.86
1b	0.61	0.71	1.08
Average	0.56	0.97	0.95

The interpretation of these results is more problematic. The rate constant increased, as expected, but in this case the removal rate of Li appears to be smaller than for Na or Ca. This is surprising, considering the results shown above in Table 1. There are only two tests, however, and the error associated with each test is significantly greater because the flux was only 30 minutes long and only three metal samples were taken. The level of uncertainty associated with the spectrochemical determination of metal composition is about 1 ppm, which also contributes to the error associated with the determination of the rate constant. This is especially true of the sodium and calcium concentrations, which by the end of these fluxes had dropped as low as 3 ppm.

In four heats, the furnace flux used an argon-5% chlorine gas mixture passing through the porous plugs. In this case alkali metal removal will occur by two separate reactions. The first reaction is oxidation by air at the surface of the melt. This reaction rate has already been determined above. The second reaction is by oxidation with chlorine at the bubble surface. Both reactions occur simultaneously. Consequently, the removal rate is given by the relation:

$$\frac{\%j}{\%_j^o} = \exp\frac{-k_t A_t \rho}{M} t \qquad (2)$$

where

$$k_t A_t = k_s A_s + k_b A_b \qquad (3)$$

and where

k_b is the rate constant for reaction at bubbles, and

A_b is the surface area of bubbles inside the melt

The measured values for k_tA_t are given below.

Table 3. Measured values of k_tA_t (m^3/s x 10^4) during flux with Ar-5% Cl gas in furnace

Test	Li	Ca	Na
2a	12.1	22.6	24.4
2b	15.3	14.9	24.4
3a	15.7	21.6	29.3
3b	12.5	16.8	21.6
Average	13.9	19.0	24.9

Once more, the removal rates for calcium and sodium are higher than for lithium. Table 4 gives a summary of the removal rates for the different furnace conditions. The rates given are based on the lithium data because it is the most consistent. In addition to the removal rate constants, the table includes the length of time that the model predicts it would take to halve the lithium concentration in the furnace.

Table 4. Lithium removal rates for the three furnace conditions

	Hold	Ar Flux	Ar/Cl Flux
k_s (m/s x 10^4)	0.24	0.56	-
k_tA_t (m^3/s x 10^4)	3.02	7.05	13.9
ρk_tA_t (kg/s)	0.71	1.66	3.27
Time to halve Li (min)	185	79	40

The FTIR analyzer was used to measure the concentration of HCl in the stack gas of the furnace during these four tests. During this time the door to the furnace was left partially open during the entire 30 minute flux period to take metal samples. The damper to the furnace was opened, and the furnace controls were set so that the burner would not come on during the flux. In this way, the gas flow through the stack was maintained nearly constant, and it was possible to obtain a reliable measurement of gas flowrate and the emission rate of HCl. A typical result of these measurements is shown in Figure 4.

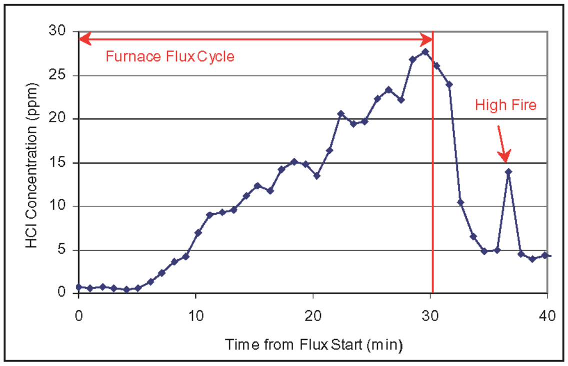

Figure 4. HCl Concentration in the Furnace Stack During Ar-Cl Furnace Flux (Test 3a)

The HCl concentration starts out at a low value and gradually increases to about 30 ppm at the end of the 30 minute flux period. The spike in HCl concentration, which occurs when the burner comes on, is presumably caused by desorption of chloride on furnace walls and at the melt surface when hot combustion gases fill the furnace

In Line Treatment

The alkali metal removal was also measured in the Hycast degassing station. This is a three-chambered unit with rotors in the first two chambers. When chlorine was used, the Ar-Cl gas mixture was employed only in the first stage. The second stage used only argon as a flux gas.

For this case the removal of each alkali metal is governed by the equation:

$$C_j^e = \frac{C_j^o}{1+\dfrac{60k_t\rho A_t}{\dot{M}}} \qquad (4)$$

where

C_j^o is the original or entering concentration

C_j^e is the exiting concentration

The factor of 60 arises because the metal flow rate, $\dot{M}$, is in kg/min, and the mass transfer coefficient, k_t, is in m/sec. The factor k_tA_t is defined by Equation (3). For the analysis of experimental data, it is convenient to rearrange Equation (4) so that:

$$\frac{C_j^o}{C_j^e} = 1 + \frac{60k_t\rho A_t}{\dot{M}} \qquad (5)$$

In all tests the casting rate was the same, and $\dot{M}$ was equal to 95 kg/min or 210 lb/min.

In test conditions 1 and 2 the metal going through the Hycast unit was degassed without chlorine. This represents the base line case, where alkali metal removal occurs only at the surface of the melt by oxidation. In this case $k_tA_t = k_sA_s$. The alkali metal removals observed without chlorine fluxing are shown below in Table 5. The calculated removal ratios shown are averaged values taken from a number of samples. During the approximately 2 hour cast, metal samples were taken before and after the Hycast unit every 10 minutes. The resulting pairs of samples are more than sufficient to give an accurate measure of the removal ratio for each element. For the heats shown below, an argon-only flux was used in the Hycast. All alkali metal concentrations are in given in ppm.

Table 5. Removal of alkali metals in Hycast

	Average C^o			Average C^e			Average C^o/C^e		
Test	Li	Ca	Na	Li	Ca	Na	Li	Ca	Na
1a	6.3	2.1	2.3	3	<1	<1	2.1	>2.1	>2.1
2a	4.3	1.8	1	2	<1	<1	2.1	>1.8	>1
1b	7.5	3	1.8	3.8	<1	<1	2.0	>3	>1.8
2b	5.8	1.8	1	2.8	<1	<1	2.1	>1.8	>1

In test conditions 1 and 2 a two hour furnace hold and a 30 minute furnace flux were employed so the concentration of alkali metal elements entering the Hycast degasser were fairly low. In the case of Ca and Na, the concentrations were sufficiently small so that the concentration after degassing was less than the limit of detectability in our spectrochemical analysis. Thus, a reliable numerical value is obtained only in the case of Li, which was present in the highest quantities. For this element, C^o/C^e is equal to 2.1, which means that $60k_s\rho A_s$ is equal to 104.5 kg/min, or k_sA_s is 7.4×10^{-4} m^3/sec.

This value of kA represents the 'baseline' value, and describes the removal rate of alkali metal by oxidation at the metal surface in the launder, Hycast unit, and filter box. When chlorine is used in the Hycast, the reaction rate should increase, because there will also be a reaction with chlorine in the bubbles. The analysis of the data in this case is complicated by a number of factors, however, and it is useful to examine in detail the results found in a typical heat.

In Table 6 the results of chemical analysis before and after the Hycast unit are presented. (See Figure 1 for sample locations.)

Table 6. Removal of alkali metals in Hycast
(Test 4b, with Cl in Hycast)

Time	C^o-upstream			C^e-downstream			C^o/C^e		
(min)	Li	Ca	Na	Li	Ca	Na	Li	Ca	Na
10	19	9	7	7	2	<1	2.7	4.5	>7
20	18	8	7	7	2	<1	2.6	4.0	>6
30	17	8	6	7	1	<1	2.4	8.0	>6
40	16	8	6	3	<1	<1	5.3	>8	>6
50	16	8	6	4	<1	<1	4.0	>8	>4
60	15	7	5	2	<1	<1	7.5	>7	>5
70	14	7	5	2	<1	<1	7.0	>7	>5
80	14	7	5	2	<1	<1	7.0	>7	>5
90	13	6	4	2	<1	<1	6.5	>6	>4
100	11	5	4	1	<1	<1	11	>5	>4

The removal ratio for Li starts out at a low value and then increases during the cast. The same happens for Ca, although to a lesser extent. This information is puzzling when considered by itself, but there are two other important facts that point to what is happening. The first is seen in the above table. Although the removal ratio changes, the amount of each element removed is nearly constant. In the case of Li, 10-13 ppm has been removed throughout the entire cast. The second clue is given by the results of the FTIR analysis of gas collected from the Hycast unit during this cast. The results obtained are shown below in Figure 5. The chlorine flowrate was initially 0.04 CFM (1.13 liters/min), but this gave no significant HCl emission, and the flow was increased to 0.06 CFM (1.70 l/min) 23 minutes into the cast. This higher chlorine flux also did not give significant emissions, and the flow was increased to 0.09 CFM (2.55 l/min) 45 minutes into the cast. This chlorine flow rate gave a significant level of HCl emission. The fume began to collect in the cast house, and, towards the end of the cast, it was decided to cut back the Cl flow to 0.06 CFM. The HCl emissions dropped accordingly.

The results in Figure 5 show clearly that, for the first 45 minutes of the cast, 100% of the chlorine going into the Hycast was consumed. This means that the removal ratio of alkali metals during this time is limited not by the kinetics of the reaction (which is governed by diffusion of alkali metals to the bubbles) but by the delivery rate of chlorine. Consequently, it is not possible to obtain any meaningful kinetic data during this period.

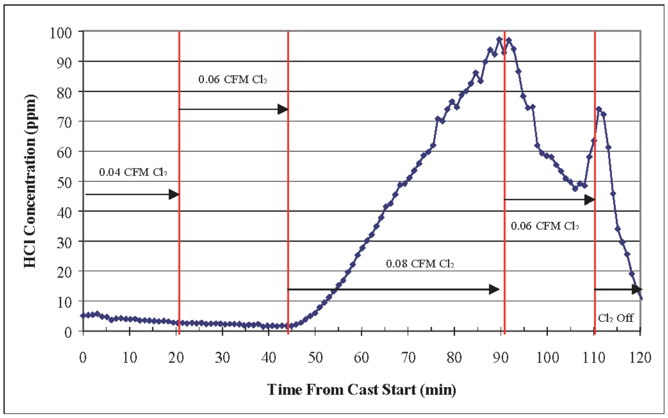

Figure 5. HCl Concentration in Off Gas from Hycast During Ar-Cl Flux (Test 4b)

The casting rate employed in this study is fairly low, and so the average metal residence time in the first stage of the Hycast unit is about five minutes. Twice this value, or a time of 10 minutes, would be required to reach a new process steady state once a process change is made. This is effectively the time required to sweep all of the old metal out of the well mixed Hycast chamber. Thus, the first sample in this heat, which would yield meaningful kinetic data, would be the 60 minute sample. At this time, and at all subsequent times during the cast, there is excess chlorine in the purge gas, and so the reaction rate is limited by kinetic factors.

During this time period the removal ratio for Li averaged 7.44. The levels of Na and Ca are smaller than Li, so for these elements the final, exiting concentration (C^e) was < 1 ppm. Thus, we can only say that the removal ratios for Ca and Na are greater than, or equal to, about 7 and 5, respectively.

In Test 4a similar results were obtained. However, meaningful kinetic data could be collected only for the last metal sample taken at the end of the cast. In this case the removal ratios observed were 6.5 for Li, ≥ 7 for Ca and ≥ 2 for Na. Averaging the removal ratios for Test 4a and 4b, a removal rate, k_sA_s of 40.4 x 10^{-4} m^3/sec can be calculated. Note that this removal rate is based on the assumption that an excessive amount of chlorine was being used in the Hycast.

In Tests 3a and 3b, a furnace hold and flux were employed, and the concentrations of alkali metal reaching the Hycast were lower. In these heats the metal leaving the Hycast had less than 1 ppm each of Li, Na, and Ca. So it is not possible to calculate a meaningful numerical value of the removal ratios.

Metal Cleanliness and Hydrogen Levels

Metal cleanliness was measured during all of the experiments run using two LiMCA units, which collected at the furnace exit and downstream of the in-line filtration. Inclusion levels upstream were extremely low, with N_{20} values less than 1.0 K/kg for all of the casts monitored. Levels downstream were erratic and were heavily influenced by microbubble carryover from the Hycast degasser, rendering them unusable. A statistical analysis was performed to determine the effects of the furnace flux on the inclusion levels measured at the furnace exit, and the results are shown below in Table 7.

Table 7. Analysis of Upstream Inclusion Levels

Experiment	Avg. N_{20} (K/kg)	Homogeneous Groups (N_{20})	Start Li (ppm)
Test 2	0.15	*	6
Test 3	0.20	*	6
Test 1	0.35	*	8.5
Test 4	0.80	*	18.5

This table shows that Tests 2 and 3 had upstream inclusion levels that were statistically no different at a 95% level of confidence, while Test 1 had more inclusions, and Test 4 had even more still. Tests 2 and 3 used a argon/chlorine flux, Test 1 used an argon only flux, and Test 4 had no flux at all. This would indicate that the fluxing in the furnace with argon reduces the inclusions coming out of the furnace, and using argon and chlorine reduces them even more. Taking a closer look at the data shows another likely cause. The tests that had no flux and chlorine-free fluxes also tended to have slightly higher levels of alkalis coming out of the furnace. Table 6 shows the average lithium levels at the start of the cast for the four tests. There is a very clear, direct correlation between the lithium levels and the inclusion measurements. In all cases, the inclusion levels seen were very low.

The dross skim weights from both the furnace and the Hycast were recorded, and there was found to be no correlation between the skim weights and the use of chlorine as a furnace flux. The dross was drier, however, when chlorine was used.

Hydrogen levels were also measured using an AlSCAN. A statistical analysis of these measurements showed that there was no correlation between the upstream hydrogen levels and the furnace fluxing conditions. It also showed no difference between the downstream hydrogen levels or the overall removal efficiency of the Hycast degasser when it was run with chlorine or without chlorine. Therefore, chlorine usage in this furnace or in-line degasser had no effect on hydrogen levels.

Discussion of Results

This experimental program allows us to construct, for the first time, a detailed model for the various aspects of alkali metal removal in molten aluminum. The three most important parts of the process are:

1. Oxidation of alkalis at the surface
2. Reaction with chlorine gas at surface of bubbles, and
3. Predicting chlorine emissions during gas fluxing.

Each of these is considered separately below.

Oxidation at the Surface

In reference [1] it was suggested that the oxidation rate at the surface would increase with the stirring in the melt, according to the relationship:

$$k_s \propto (\varepsilon)^{1/4} \qquad (6)$$

where

ε is the specific stirring intensity in the melt (watts/m^3)

In order to determine the validity of Equation (6), it is necessary to calculate ε for the conditions employed in this study. This theoretical analysis was conducted as part of this study. The necessary equations are derived in reference [2]. For porous plugs in the furnace, the stirring intensity is given by:

$$\varepsilon \cong \rho^2 gGH / M \qquad (7)$$

where

g is the gravitational constant (9.8 m/sec^2)
G is the total gas flow rate (1.06 x 10^{-3} m^3/sec)†
H is the metal height above the porous plugs (0.51 m)

As noted above, the mass, M, of metal in the furnace is equal to 11,350 kg. The specific stirring intensity, ε, during the furnace flux is calculated to be 2.6 watts/m^3.

The stirring in the Hycast unit has been studied in detail by researchers in Norway [3]. The results are reviewed in reference [2] and example calculations are given. For the rotation speed employed in these trials, 750 rpm, the stirring intensity in the Hycast unit is 3500 watts/m^3.

The stirring intensity during the furnace hold, with no gas flowing through the porous plugs, is not easily determined, but it would presumably be a small fraction of the stirring produced by the porous plugs.

One task remains. The mass transfer coefficient for the surface reaction in the Hycast unit must be calculated. Above it was found that the total k_sA_s is equal to 7.4 x 10^{-4} m^3/sec. This includes the reaction above the Hycast rotors, where the surface area is about 1 m^2, as well as in the launders, filter box, and the settling basin of the Hycast unit. In the latter areas, the total surface area is about 2 m^2. In the latter case, where there is little stirring and the surface of the melt is relatively quiescent, the mass transfer coefficient will be near the value of 0.24 x 10^{-4} m^3/sec found during the furnace hold. Thus, we obtain the mass transfer coefficients tabulated below.

Table 8. Mass transfer coefficients for surface oxidation

Condition	k_s x 10^4 (m/sec)			Stirring Intensity (watts/m^3)
	Li	Ca	Na	
Hold	0.24	0.23	0.24	---
Flux (Ar)	0.56	0.97	0.95	2.6
Hycast (Ar)	6.9	≥6.5	≥4.5	3500

All three elements exhibit the same removal rate during the furnace hold and about the same value during the Hycast trials. It would therefore be reasonable to average the results of all three elements during the furnace flux with argon. When we do this, k_s is equal to 0.83 x 10^{-4} m/sec. The results are plotted in Figure 6. The straight line drawn to connect the points is given by the equation:

$$k_s = 0.63 \cdot 10^{-4} (\varepsilon)^{0.29} \qquad (8)$$

Considering the experimental error, the exponent in Equation (8) is essentially the same as the value of 1/4 in Equation (6).

If Equation (8) is valid to very low levels of stirring, the stirring intensity during the furnace hold would be about 0.04 watts/m^3. This value has been assumed in the plot shown in Figure 6.

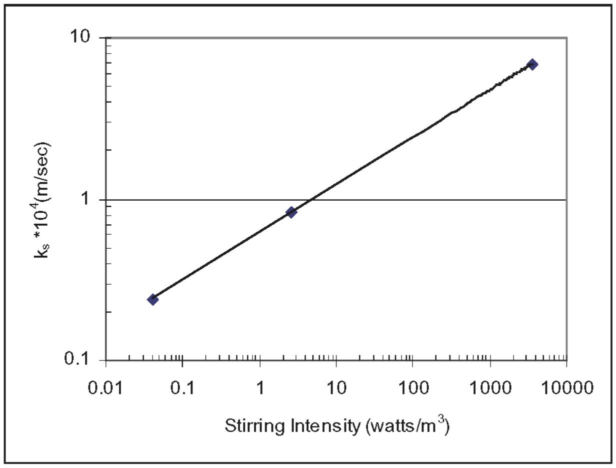

Figure 6. Rate constant for surface oxidation, k_s, as a function of stirring intensity

There have been a number of earlier studies [4-12] of the oxidation rate of alkali metals in aluminum, but only the experiments of Krüger and Patak [6] are sufficiently detailed to allow us to calculate rate constants for the surface oxidation reaction. Two experimental conditions were studied in a 14 kg (30 lb.) melt. In the first, the melt was allowed to stand at two temperatures (730 and 800 °C) without any stirring. In the second, a paddle vane rotor was placed into liquid aluminum and rotated at 600 rpm. The temperature in this trial was 800°C. Rate constants calculated from their results are shown below:

rate constant, k_s	experimental conditions
1.28 x 10^{-4}	730 °C, no stirring
1.98 x 10^{-4}	800 °C, no stirring
12.6 x 10^{-4}	800 °C, stirring
(8.1 x 10^{-4})	730 °C, stirring (est.)

If temperature affects the values of rate constant in the stirred melt, in the same proportion as in the unstirred melts, then the rate constant with stirring at the lower temperature would be 8.1 x 10^{-4}. (This is an estimate and is given above in parentheses.) This value is very close to what was found in the Hycast unit during this study. The value for the unstirred melt at 730°C is about 5 times what was observed during the furnace hold in this work. Of course, the furnace used in this study contains 800 times the amount of metal. Also, Krüger and Patak's experiments were conducted in an induction melting furnace, whose field would have caused some stirring. Thus, a significant difference in the results of the two studies in the 'no stirring' condition is not unexpected.

A final comment is needed. There is a significant body of evidence in the foundry literature to suggest that Ca and Sr are much slower to oxidize than Na. All three elements have been used as modifiers in Al-Si casting alloys, and the modifying effect of Na 'fades' much faster than either Ca or Sr. In our experiments, however, Ca, Li and Na all had (within experimental error) the same rate constant for oxidation. The reason for the apparent disparity may be seen in a study reported by Langerweger [12]. He added 6 ppm Li to an Al-10%Si-0.09%Sr melt and found the oxidation rate of Sr increased by a factor of

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† This flow is equal to 2.5 SCFM or 63.7 l/min.

four times. Thus, when Li and Na are present in significant quantities, it would seem they promote the rapid formation of a heavy, porous oxide film into which dissolved Sr and Ca readily migrate. When Na and Li are not present, however, the oxidation rate of Ca (and by analogy, Sr) would be significantly slower.

Reaction with chlorine in bubbles

When fluxing with an Ar-5%Cl flux in the furnace, the total kA observed for alkali metal removal, k_tA_t, is presented in Table 3. If the results obtained for each of the three elements (Li, Na and Ca) in all heats are averaged then k_tA_t is equal to 19.3 x 10^{-4} m/sec. If one subtracts from this value the average kA observed for the surface reaction (see Table 2; k_sA_s = 0.83 x 10^{-4} m/sec x 12.6 m^2 = 10.4x 10^{-4} m^3/sec), then one finds the kA for the reaction of alkali metals with chlorine in the bubbles:

$$k_bA_b = (19.3 - 10.4) \times 10^{-4}\ m^3/sec = 8.9 \times 10^{-4}\ m^3/sec$$

It is not absolutely necessary for the analysis that follows, but it is instructive to break up this kA into its individual components. In reference [1] it was shown that the rate constant is a weak function of bubble size. That is,

$$k_b \cong 0.00083\left(\frac{d^o}{d_b}\right)^{1/4} \qquad (9)$$

where

d^o is equal to 0.01 m
d_b is the average diameter of bubbles (m), and
k_b is the rate constant for the reaction with bubbles (m/sec)

It can also be shown that the total area of bubbles in the furnace, which are produced by the porous plugs, is equal to:

$$A_b = \frac{G}{d_b/6}\cdot\frac{H}{U} = \frac{G}{d_b/6}\cdot\frac{H}{\sqrt{gd_b/2}} = \frac{GH}{0.369d_b^{1.5}} \qquad (10)$$

where

U is the steady state rise velocity of the bubbles (m/sec)

Using these two equations, the average bubble size is 11 mm and A_b is equal to 1.12 m^2 (G = 1.06 x 10^{-3} m^3/sec, and H = 0.51 m).

The term $k_b\rho A_b$ for the furnace flux with chlorine is numerically equal to 2.1 kg/sec. The units (kg/sec) give an indication of the importance of this term. It indicates the relative velocity, or speed, at which the metal can deliver alkali metals to the surface of bubbles. Consequently, this term may be used to determine the maximum rate at which chlorine can be delivered to the melt, and consumed by reaction with dissolved alkali metals, without producing chloride emissions.

For the Hycast unit, when fluxing with Ar only, we found that k_sA_s was equal to 7.4 x 10^{-4} m^3/sec, or $k_s\rho A_s$ = 1.7 kg/sec. When fluxing with Ar-Cl gas mixtures, with chlorine concentrations in excess of what could react with dissolved alkali metals, the removal ratio was found to be 7. From Equation (5) we calculate that $k_t\rho A_t$ is equal to 9.5 kg/sec. It follows that $k_b\rho A_b$ equals 9.5-1.7 or 7.8 kg/sec, and that k_bA_b equals 33.2 x 10^{-4} m^3/sec. Using Equations (9) and (10) above, and noting that G = 0.4 x 10^{-3} m^3/sec, and $H \cong$ 0.5 m, we find that the average bubble diameter is 3.2 mm and the total bubble area is 3.0 m^2.

It is useful and instructive to compare the operating characteristics of the two gas fluxing operations used in this study. These are summarized below.

Table 9. Comparison of gas fluxing operations

Process Item	Porous Plugs	Hycast
gas flow (l/min)	64	24
d_b (mm)	11	3.2
A_b (m^2)	1.12	3.0
$k_b\rho A_b$ (kg/sec)	2.1	7.8

The important role of bubble size is evident from this comparison. With the Hycast unit one has 3.7 times the refining capacity (in kg/sec) with only 38% of the gas consumed. It may also be noted that the operating characteristics shown above are within 10% of what may be calculated theoretically for the Hycast unit, from relations given in Reference [3].

Chlorine Emissions

As noted above, the term $k_b\rho A_b$ gives us an indication of how fast the metal system can deliver alkali metals to chlorine-containing bubbles. It therefore follows, from a simple mass balance given in Reference [1], that the maximum chlorine gas delivery rate, is given by:

$$V_{Cl}^{\max} = \frac{k_b\rho A_b \cdot 22400 \cdot 60}{100}\sum\frac{a_j}{m_j}\%j \qquad (11)$$

or

$$V_{Cl}^{\max} = 1.344 \cdot k_b\rho A_b \cdot \sum\frac{a_j}{m_j}ppm_j \qquad (12)$$

where

$V_{Cl}^{\max}$ is the maximum chlorine gas flow (liters/min)
a_j is a stochiometric constant (equal to 1 for Ca, 1/2 for Na and Li)
m_j is the molecular weight of element j
ppm_j is the concentration of j in parts per million

The rate constants found in this study and Equation (12) have been used to calculate the chloride emissions produced during Test 3a. Equation (12) was used to calculate the maximum chlorine gas flow that will be consumed to produce alkali metal salts. Note that $V_{Cl}^{\max}$ depends on the concentration of the alkali metals present. If the actual chlorine gas flow used is greater than $V_{Cl}^{\max}$, then the excess chlorine is assumed to be emitted as HCl. The concentration in the off gas is then calculated from the total gas flow up the furnace stack (measured to be 3300 CFH or 1.56 m^3/min). The results of this calculation are given below. The agreement with the measured gas composition, shown in Figure 4, is remarkably good. This confirms the validity of our kinetic models, and the use of Equation (12).

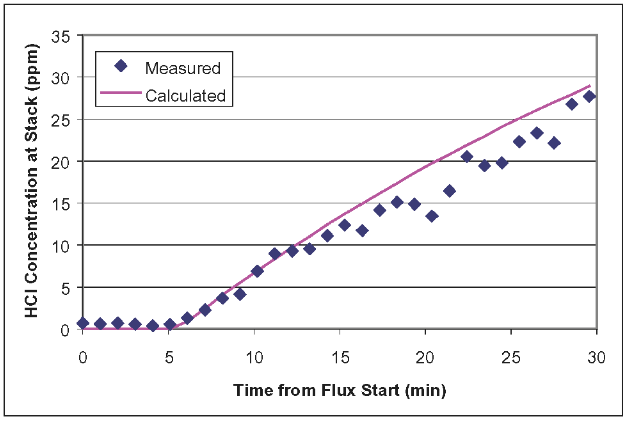

Figure 7. Calculated chloride emissions for Test 3a

In this heat, as well as in the other three tests using an Ar-Cl flux in the furnace, the chloride emissions were observed to increase with time. This is because the levels of Li, Na, and Ca decrease during the flux, and $V_{Cl}^{\max}$ will also drop.

Therefore, for best results, the chlorine concentration in the flux gas should decrease with time, in proportion to the removal of alkali metals in the melt. This would be true for all batch fluxing processes. If an on line gas measurement system were available, it would be possible to determine when HCl emissions start to increase, and the decrease in chlorine gas flow could be set to begin at that time.

For fluxing in the Hycast unit, the situation is somewhat different. In this case the process is continuous, and the maximum chlorine gas flow rate would not usually change dramatically with time. (There was a drop in alkali metal contents of 20-40%, however, as alkalis continued to oxidize in the furnace during the course of the two hour cast.) Equation (12) can be used to predict the maximum chlorine gas flow, if ppm_j is used to represent the **exiting** metal composition. It may be more convenient to use the following expression, however:

$$V_{Cl}^{\max} = 1.344 \cdot k_b \rho A_b \cdot \frac{1}{1+60k_b \rho A_b / \dot{M}} \cdot \sum \frac{a_j}{m_j} ppm_j^o \qquad (13)$$

where

ppm_j^o is the concentration of j entering the Hycast unit

The term $1+60k_b \rho A_b / \dot{M}$ in the denominator is equal to the removal ratio given in Equation (5).

Measurements of HCl evolution from the Hycast were made in four Tests: 3a and 3b, and 4a and 4b. The results for Test 4b are given above in Figure 5.

Unfortunately, the interpretation of this particular plot is complicated by two factors. The first is the long response time in the gas collection system. In order to conduct these trials in a timely fashion, a large enclosure was constructed to cover the entire Hycast assembly. This enclosure had to be high enough to cover the rotor assembly at its maximum height, and so had a volume of 4100 ft^3 (116 m^3). It took about 25-30 minutes to reach a steady state value for the HCl composition in the collected off gas. The second complicating factor is the change of metal composition with time. At 45 minutes into the cast the metal upstream from the Hycast in Test 4b had 16 ppm Li, 8 ppm Ca, and 6 ppm Na. Using Equation (13), we find that the maximum chlorine flow to be 0.093 CFM (2.63 l/min). The last upstream metal sample of the cast had 11 ppm Li, 5 ppm Ca, and 4 ppm Na, which corresponds to a maximum Cl flow rate of 0.063 CFM (1.78 l/min). So, the results for this test make sense only in a qualitative way.

In the other three tests the change in metal composition during the cast was less, and the interpretation of the results is easier. Consider the off gas composition of the duplicate heat, 4a, given in Figure 8. Picking the probable 'steady state' values of HCl content as occurring at a time 25 minutes after the change in gas flow rate, we can construct the plot shown in Figure 9. From this Figure it appears that the maximum chlorine flow rate is about 0.05 CFM (1.41 l/min). From the metal composition at the end of the drop (13 ppm Li, 7 ppm Ca, and 1 ppm Na) we calculate a value of 0.071 CFM (2.0 l/min). These results, and those from heats 3a and 3b, are tabulated below. The agreement is good, although the calculated values (using Equation (13)) are consistently higher than the observed values. This is likely due to the fact that chlorine that stayed in the chamber, or escaped through openings at the top.

Table 9. Maximum Chlorine Gas Flow Rates in Hycast Unit

Test	Calculated	Measured
3a	0.021 CFM	0.017 CFM
3b	0.029 CFM	0.014 CFM
4b	0.071 CFM	0.050 CFM

In any future tests it would be worthwhile to redesign and reconstruct the Hycast cover so that it could be used as an in-situ off gas collection hood. In this way the response time would be quicker, perhaps a minute or two, and a major source of error would thereby be removed.

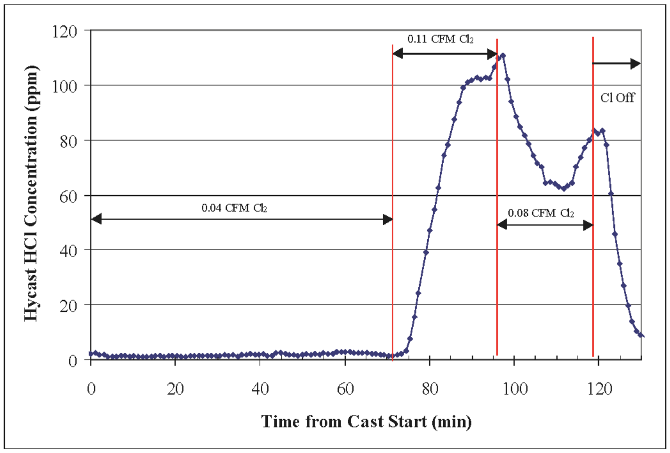

Figure 8. HCl emissions from Hycast (Test 4a)

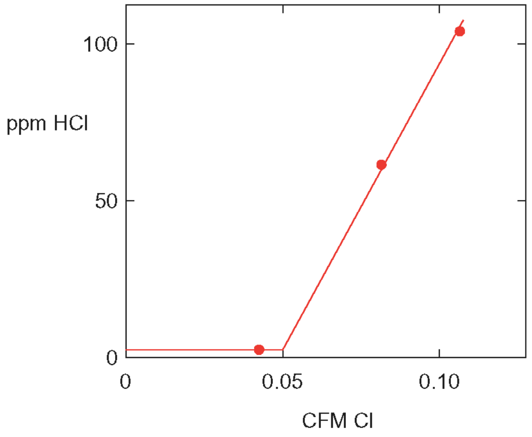

Figure 9. HCl emissions versus Cl flow rate (Test 4a)

Conclusions

A model of alkali removal based on fluxing processing practices has been verified. Rate removal constants for this model have been developed for a variety of alkali reduction methods, including furnace holding, fluxing with argon or an argon/chlorine mixture, and in-line fluxing with a Hycast degasser. Based on these models and on the experiments, it has been shown that, from a chlorine usage standpoint, a rotary degasser is a more efficient way to lower alkali levels.

In order to reduce the emissions from a chlorine based furnace fluxing system, the level of chlorine mixed in the flux gas should be reduced as the flux progresses and the alkalis are consumed. In the rotary degasser, an optimum system would be one where the chlorine levels would start to drop only when excess HCl emissions were present. This is a viable solution if some means of gathering real-time HCl measurements are possible. If permanent HCl detection is not possible, then chlorine practices could be developed based on incoming alkali levels, metal flowrate and a known degasser removal constant. This constant could be found by doing work similar to that done in this project.

The FTIR unit used in this testing provided an excellent way to gather real-time information on the HCl levels produced by fluxing processes. At the furnace, when stack gas velocities could be held constant and were well known, accurate emissions data was collected with the instrument. Results from the Hycast were less useful, primarily due to slow response times caused by the large size of the exhaust collection chamber.

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