

FINAL REPORT

Project Title: Molten Metal Treatment by Salt Fluxing with Low Environmental Emissions

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Executive Summary

Background: Primary and secondary molten aluminum processing and refining involve fluxing metal with either pure chlorine gas or chlorine and inert gas mixture. The stack emissions caused by this gas injection include dust particles, hydrogen chloride, chlorine, and aluminum chloride gases. Recently, Secondary Aluminum Maximum Achievable Control Technology (MACT) under the Clean Air Act (finalized in March 2000) has set very tough new limits on particulate matter (PM) and total hydrogen chloride emissions from the furnaces. Additionally, chlorine gas is highly toxic and its handling, storage and use pose risks to employees and the local community. This project is motivated by the desire to reduce or eliminate chlorine use entirely from furnace aluminum treatment, and reduce emission of associated pollutants during use of chlorine as a fluxing agent. The proposed investigation has the objective of eliminating or reducing the use of chlorine gas fluxing by solid chloride salts while minimizing the energy consumption by (1) optimizing fluxing process thereby reducing processing time, and (2) improving metal quality thereby reducing scrap and rework. This project is aimed at reducing the energy needs of the US aluminum industry by 150 billion BTU/year by the year 2008, when the new technology is expected to be fully implemented, reduction of chlorine fluxing usage by approximately 1 million lbs per year, reduction of carbon dioxide (greenhouse gas) by an estimated 1.24 lb per ton of aluminum produced per year, reduction of industry-wide (domestic) carbon dioxide by approximately 18.6 million lb per year by the year 2008, elimination of bag-house and wet scrubber technology for emission control and reduction of its maintenance costs.

Project Objective: The proposed project, between the Ohio State University and Alcoa, is to investigate, understand, and minimize the emissions resulting from solid chloride flux addition to molten metal for alkali impurity and non-metallic inclusion removal. In this three-year program, it is proposed to study the salt metal interactions and monitor the emissions at laboratory scale at OSU and verify the findings on commercial scale at Alcoa. The information obtained in these experiments will be used for developing mathematical models, which will help in optimizing the process.

Conclusions - From this research, the following conclusions can be drawn.

- (1) Interactions between molten aluminum alloys and slats containing magnesium and potassium chloride salts were studied.
- (2) Harmful chloride gas injection which causes emission of harmful HCl gas formation, discharge of unused chloride gas, and particulate matter into the environment can be replaced by Chloride salt injection.
- (3) HCl gas formation and emission depended and was found to be directly related to the amount of MgCl_2 in the salt. The salt ALC-2 having composition with least amount of MgCl_2 (25 %) and balance KCl showed the lowest emissions in all tested conditions. Fusal (40% MgCl_2) showed the second lowest emissions and emitted less HCl than the blended form of the same composition 40 % MgCl_2 and balance KCl which is ALC-1.
- (4) The fused form of ALC-3 salt (60 % MgCl_2) called Zendox with composition of 60% MgCl_2 and balance KCl, showed higher emissions. ALC-3 salt had less emission than Zendox but more than the ALC-1 and ALC-2 salts.
- (5) It was found that increasing the atmospheric water content in the furnace increased the HCl emissions. When furnace was switched off, the water content decreased and the HCl emissions also went down.
- (6) Increasing the content of alloying elements in aluminum alloy increased the emissions but was it uncertain if this response was due to one particular element such as Mg or a combination of many elements. The elements that were present in 7xxx alloy were Fe, Cu, Mg, and Zn.
- (7) Mixing generated more emissions but mixing was necessary for impurity removal as well. The lowest emissions were found with conditions when the burner was off and the melt was not stirred.
- (8) 1100 alloy which is commercially pure metal, had less emissions than the 7xxx alloy.
- (9) Most of the Ca and Li impurities can be removed in less than 10 minutes.

Recommendations – This project has conclusively found that the salts containing MgCl_2 (25 to 60%) and balance KCl can be successfully used to remove alkaline impurity from aluminum alloy melt economically, with less environmental gas and particulate emissions, and will save energy.

Most of the experimental work was done in lab scale furnace containing up to 50 lbs. of aluminum alloy. Pilot plant experiment at an aluminum plant will be useful to extrapolate the laboratory results to actual plant operation.

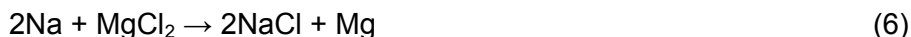
Final Report

Introduction -

Alkaline impurities are picked up in the primary and secondary aluminum from the Hall-Heroult electrolytic cell. The impurities cause defects in many of the aluminum alloys and therefore must be removed. Traditionally the removal of alkaline impurities has been done by injecting Chlorine gas into the melt. The following reactions result by chlorine gas fluxing.



The impurities (Na, Li, and Ca) react with chlorine and form chlorides. At the same time, Al forms AlCl_3 (g) which later reacts with moisture and produces HCl gas. Thus excess unreacted chlorine and HCl gases are emitted into the atmosphere. The exhaust gases also carry undesirable particulate matter with it. These gases were recognized by the DOE as harmful. The Clean Air Act of 2000 was implemented in order to reduce the particulate matter and HCl gas emissions. The use of salt fluxing as an alternative to chlorine gas has been considered as a cleaner alternative to remove the impurities. The injection of salts while removes impurities, has other advantages. Salt injection has no excess chlorine emission problem, less HCl gas is emitted, and as a consequence less particulate matter is generated and emitted in the atmosphere. The injected salts are generally mixture of MgCl_2 and KCl. Following reactions take place as salt interacts with the metal.





Following are some other advantages of salt fluxing compared to the chlorine gas injection. The salts can be added at any time; faster impurity removal rates may be obtained; requires less holding time; handling and storage are easy compared with chlorine gas; and there is no need for stack emission scrubbers for unreacted chlorine gas. The projected energy savings through salt fluxing are through the reductions in the amount of chlorine gas needed to remove the impurities and through reduced holding times. Current holding processes use natural gas burners where 6 million BTU/hr is used to hold 100,000 lb furnace at 1350°F. Assuming a conservative estimate of 33% reduction in holding time salt fluxing will save 5 min or 150 billion BTUs per year for the entire domestic industry. The reduction of natural gas use will reduce 18.6 million pounds of CO₂ emissions from the entire Aluminum industry. Also, 1 million lb of chlorine gas will be saved per year.

Experimental Set-up and Variables -

A schematic of the experimental set-up is shown in Fig. 1, and a picture of the experimental set-up is given in Fig. 2. Tests were conducted using a gas fire furnace provided by Alcoa. Other tools needed for the experiments were a skimming tool, spoon, melt sample maker, and stirring paddle. These tools were periodically sandblasted and then coated with boron nitride to prevent oxidation of the tools and prevent any contamination of the melt with iron. The crucible used had a height of about 15 inches and inner diameter of approximately 11 inches. The stirring paddle's dimensions were 3 x 4 x 0.5 inches, and it was made of 304 stainless steel.

Aluminum alloys were melted in a 50 lb crucible and a custom made exhaust hood was placed over the melt. A thermocouple was placed in the melt to monitor and maintain the melt temperature at a set point in a range between 1200 °F and 1400 °F. Various salts were then added to the melt, and the gas emissions were monitored, analyzed, and recorded by an FTIR continuous emissions monitoring system.

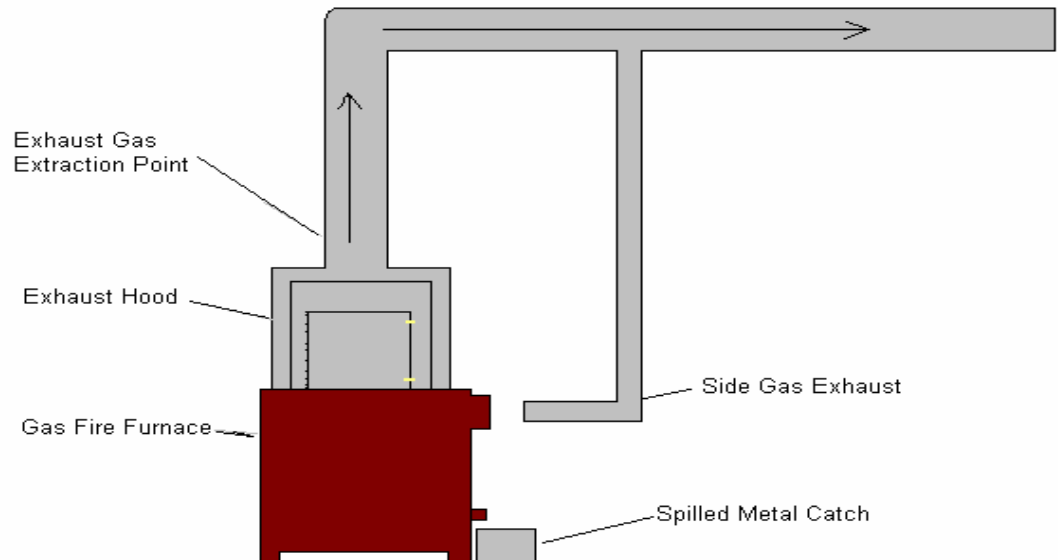


Figure 1: Schematic of experimental setup



Figure 2: Picture of the experimental set-up.

Experimental variables in the study were as follows:

Metal - commercially pure (AA1100) or other alloys such as AA7050,

Salt composition,

Melt stirring,

Change of water content caused by furnace operation i.e. furnace on or off, and Ca and Li impurities of varying starting concentration.

Metal – Commercially pure aluminum (AA1100) contained 0.05-0.20 %Cu, 0.1% Zn, and 0.095 % Zn+Fe. Composition of AA7050 alloy was 0.12% Si, 0.15%Fe, 2.0-2.6 % Cu, 0.1 %Mn, 1.9-2.6 %Mg, 0.04 %Cr, 5.7-6.7 %Zn, and 0.06 %Ti. Other two alloys that were planned for future experiments if project continued might be AA5182 and AA6061.

Salt Composition - Five different salts were used during testing: ALC-1, ALC-2, ALC-3, Zendox, and Fusal. The difference among the three ALC salts is their composition. All of the salts are a combination of MgCl_2 and KCl in varying amounts. Please note that ALC-2 has the lowest (25 %) MgCl_2 content. The fusal and zendox salts are prefused forms of ALC-1 and ALC-3 respectively. Table 1 shows the composition of the salts used.

Table 1: Salt composition and type used for experiments

Salt	% MgCl_2	% KCl	Type
ALC-1	40	60	Blended
Fusal	40	60	Fused
ALC-2	25	75	Blended
ALC-3	60	40	Blended
Zendox	60	40	Fused

Another salt was considered that had iron impurities that were picked up during mining. It was found that no distinguishable difference in emissions could be observed, and they were not used further. Figure 3 shows a picture of the three salts that were used in the tests. The ALC

salts were bright white flakes, and the presence of iron particles adds rust colored flakes. The Zendox and Fusal prefused salts are dull white pellets.

Melt Sirring – A stirrer was installed on top of the furnace which stirred the melt in some experiments. Results were more consistent if melt was stirred during the run.

Moisture Content – The moisture content changed with the intensity of the gas fired furnace. During the period when the furnace was in heating mode at high intensity, the water content in the flame was higher, and this resulted in higher emissions of HCl gas. To maintain a constant temperature at any set point, the furnace intermittently switched on and off the heating mode. In some experiments, furnace was turned off after a set temperature was attained. The results with experiments, when furnace was off, were more consistent and reproducible.

Impurity Addition – Some experiments were conducted after adding impurity to the melt. Various amounts of Ca and Li impurities were added to the melt in some experiments and the emitted HCl in the exhaust gases were monitored. Samples were picked up with time and the rate of impurity removal was analysed.



Figure 3: MgCl₂ - KCl salts in blended and fused forms

Experimental Procedure

As stated above, 50 lbs of metal was melted in the gas fired crucible. Typically, it took about 3 hours to melt and bring it to about 1400 °F. Any skim floating on the melt surface was removed. The salts tested were weighed to 90 g (± 0.3 g) then wrapped with two layers of aluminum foil. The FTIR was controlled by Calcmeter software package and was calibrated before starting the experiments every day of testing by flowing 100% nitrogen gas for about 60 seconds with the calibration module of Calcmeter running. After the calibration was complete, fiberglass wadding was packed into the stainless steel cylinder at the end of the FTIR's umbilical hose to prevent any particulate matter from entering the FTIR. Once the melt was in the correct temperature range, the FTIR umbilical cord was inserted to the exhaust hood for gas extraction and then the data collection from Calcmeter was started. The exhaust hood door was opened and then the salt being tested was placed on the surface of the melt. All exhaust gases were analyzed and recorded through the FTIR gas analyzer. During the set of experiments with melt stirring, the melt was stirred and mixed by the mixing paddle. Furnace burner was on or off in different experiments.

After each test was complete, the burner was again turned on, if it was off during the experiment, and melt was heated until the melt temperature reached the testing temperature range. After the melt temperature reached the desired value, the dross layer was again removed using the skimming tool, and then the next experiment started. Thus several runs were made using the same melt in the crucible. Periodically, this melt was taken out of the crucible and new metal ingot was charged in the crucible for melting.

Results and Discussion

Table 2 lists the number of experiments and the variables for each experiment for AA7xxx alloy. These are total experiments performed in the last year using this alloy. The experimentation started with fresh AA7050 alloy. Experiments listed in Table 2 are for alloy AA7xxx. The reason for listing them as an alloy 7xxx, is that each set of experiments started with alloy 7050 but as experiments went on, the Mg content decreased. Thus the alloy was no more 7050 and so it is referred to as alloy 7xxx. The results also indicated that Mg content in an alloy had a

great influence on the amount of HCl emission. So it was decided to perform controlled experiments starting with alloy 1100 which is commercially pure aluminum. Table 3 lists experiments and their conditions for this alloy. It was planned that after these experiments, the Mg content will be gradually increased, and experiments were planned to be made with 0.1, 1.0, 2.0, 4.0, and 6.0% addition to 1100 alloy. These experiments would be able to quantify the effect of Mg in alloy on the HCl emissions. Unfortunately, the FTIR started having a lot of noise after the initial 1100 experiments listed in Table 3. Some selective experimental results are given here.

Table 2: Experimental conditions and number of expts for AA7xxx alloy

Temp, °F	Stirring	Furnace Heating	ALC-1	ALC-2	ALC-3	Zendox	Fusal	Impurity
1400	No	On	13	15	5	7	4	None
1400	No	On	4	9				20 ppm Ca
1400	Yes	On	4	5				None
1350 - 1390	Yes	Off	8	10	7			None

Table 3: Experimental conditions and number of expts for AA1100 alloy

Temp, °F	Stirring	Furnace Heating	ALC-1	ALC-2	ALC-3	Zendox	Fusal	Impurity
1350 - 1390	Yes	Off	8	8	6	4	4	None

Figures 4 and 5 show water and HCl gas contents during typical experiments. As the natural gas furnace's thermocouple reduced the furnace output to regulate the set point temperature, the atmospheric water (combustion byproduct) content was lowered and resulted in subsequently reducing the amount of HCl emissions. Then as the burner

returned to full output, the atmospheric water content increased, which increased the HCl emissions, as can be clearly seen in Figs. 4 and 5. The initial drop in water content in Fig. 5 occurred sooner than in Fig. 4 and resulted in the first peak in HCl emissions (with similar conditions except for the time into the test of thermocouple regulation) to be half the time than that of Fig. 4. The HCl peak values also decreased to a smaller value. These figures clearly show that the presence of water vapor has a pronounced influence on HCl formation and emission.

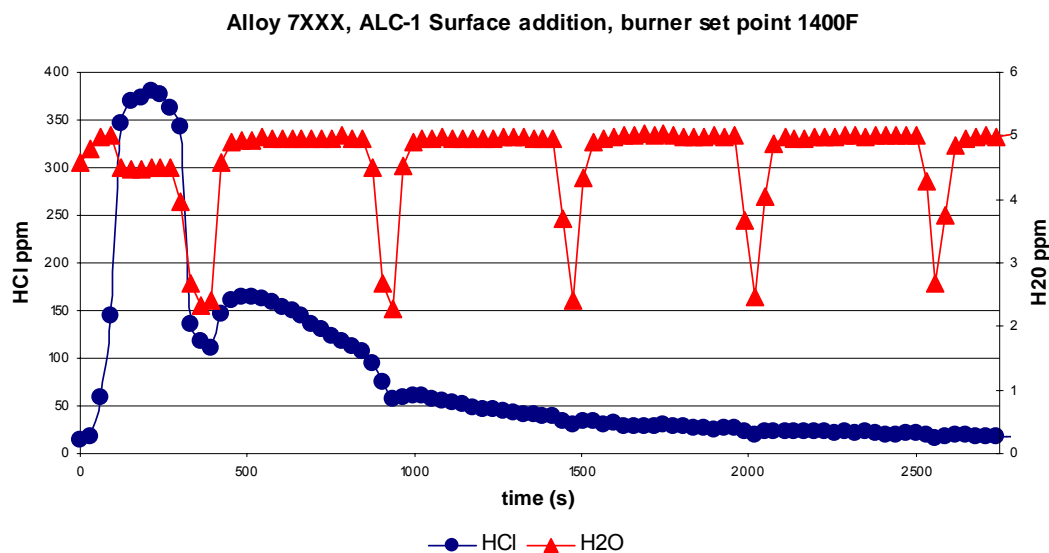


Figure 4: H₂O content drops as burner reduces output for temperature regulation and shows H₂O content variation and its dependence on HCl emissions.

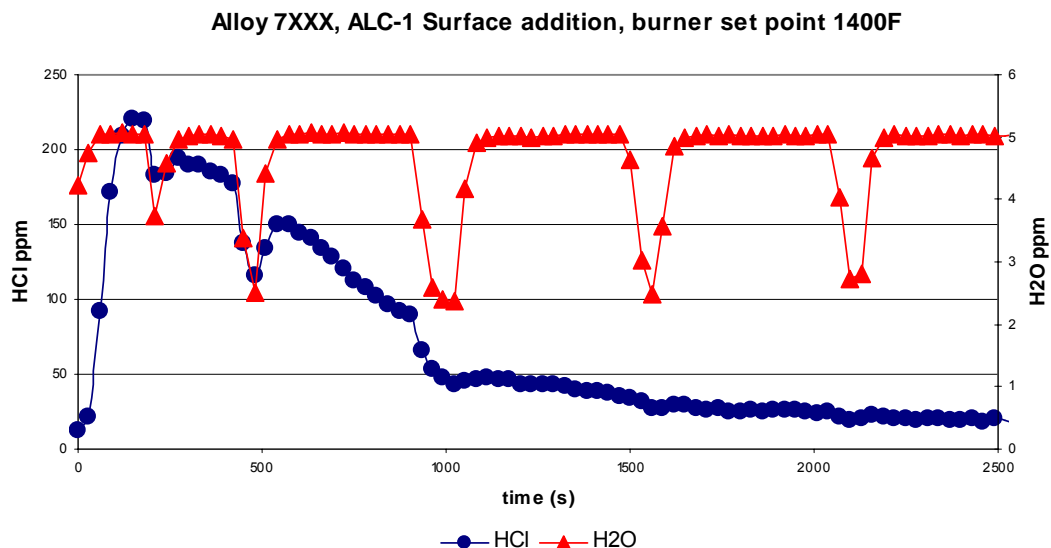


Figure 5: H₂O content drops as burner reduces output for temperature regulation and shows H₂O content variation and its dependence on HCl emissions.

Figure 6 shows seven consecutive experiments with 7xxx alloy and Zendox salt. The figure illustrates that the amount of HCl emission is different for different experiments for the same salt bath as Mg content is reduced with each experiment. Since the furnace switches off intermittently, it causes the drop in HCl emission. The melt was not stirred in these experiments. Figure 7 shows HCl emission in consecutive experiments with 7xxx alloy and ALC-1 salt when furnace was off and melt was stirred.

Zendox, 7XXX, burner on, surface additions

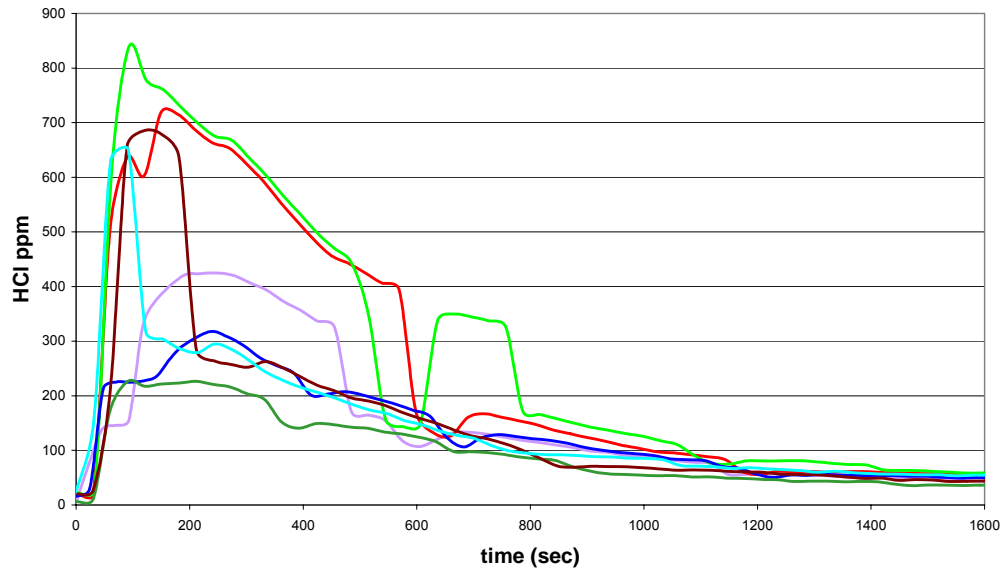


Figure 6: HCl emission with furnace on, no melt stirring, in 7 consecutive experiments with 7xxx alloy and Zendox salt.

ALC-1, 7XXX, mixing, burner off

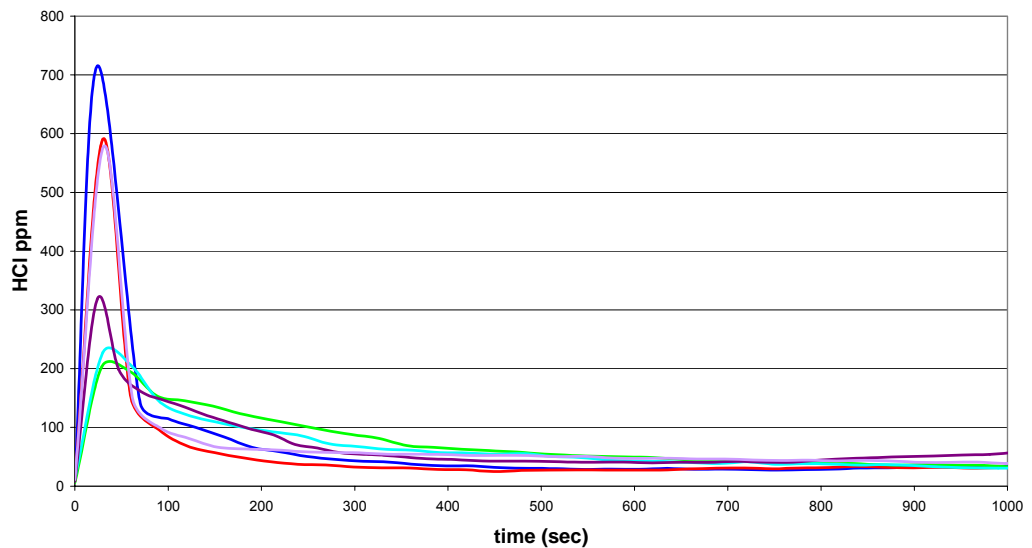


Figure 7: HCl emission with furnace off, with melt stirring, in consecutive experiments with 7xxx alloy and ALC-1 salt.

Figure 7 shows that still there are variations from experiment to experiment as Mg content gradually decreases but even then the results show a lot less variation. Similar results with 1100 metal and ALC-2 salt are shown in Fig. 8. It is clear that the amount of HCl emission are lot less in this set of experiments, and the variation is also least. Please note that the scale of HCl ppm is different in Figs 7 and 8. In Fig. 7 the peak HCl goes to 700 ppm whereas in Fig. 8 the peak HCl concentration is only 90.

ALC-2, 1100, mixing, no burner

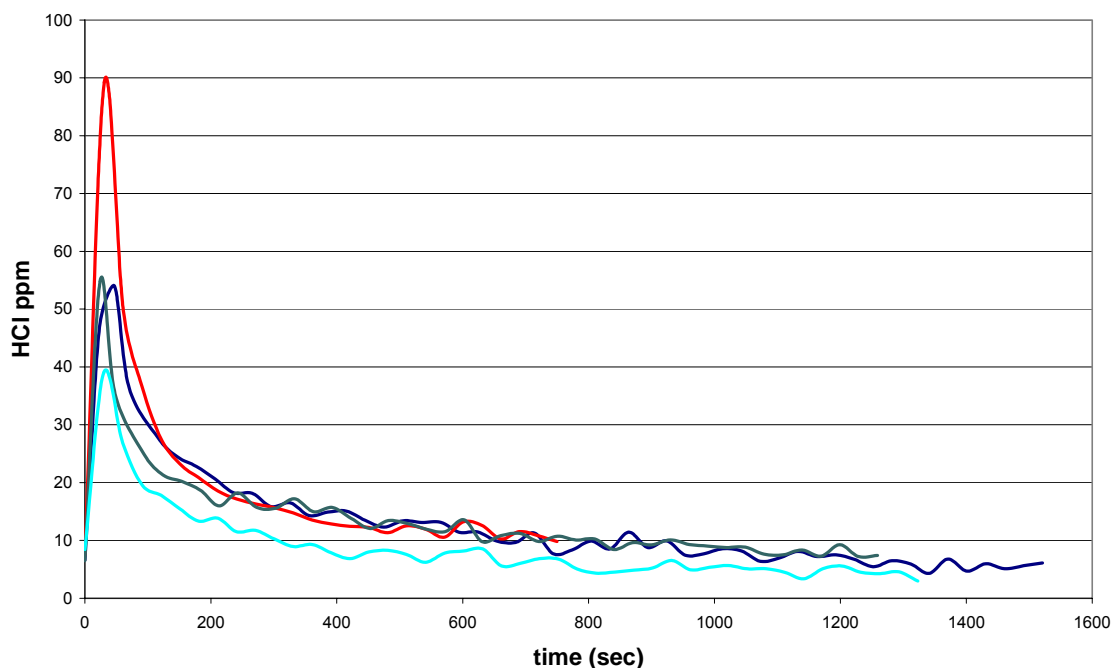


Figure 8: HCl emission with furnace off, with melt stirring, in consecutive experiments with 1100 alloy and ALC-2 salt.

Figure 9 shows a comparison of three experimental conditions and their effect on HCl emissions. The combination of mixing with the burner off (green curve with lowest peak) clearly has the lowest emissions but the mixing with the burner on (at higher moisture content) shown by red curve with the highest peak has the highest HCl emissions. This is the worst condition from the emissions point of view. The intermediate, blue curve is for no mixing and burner was on.

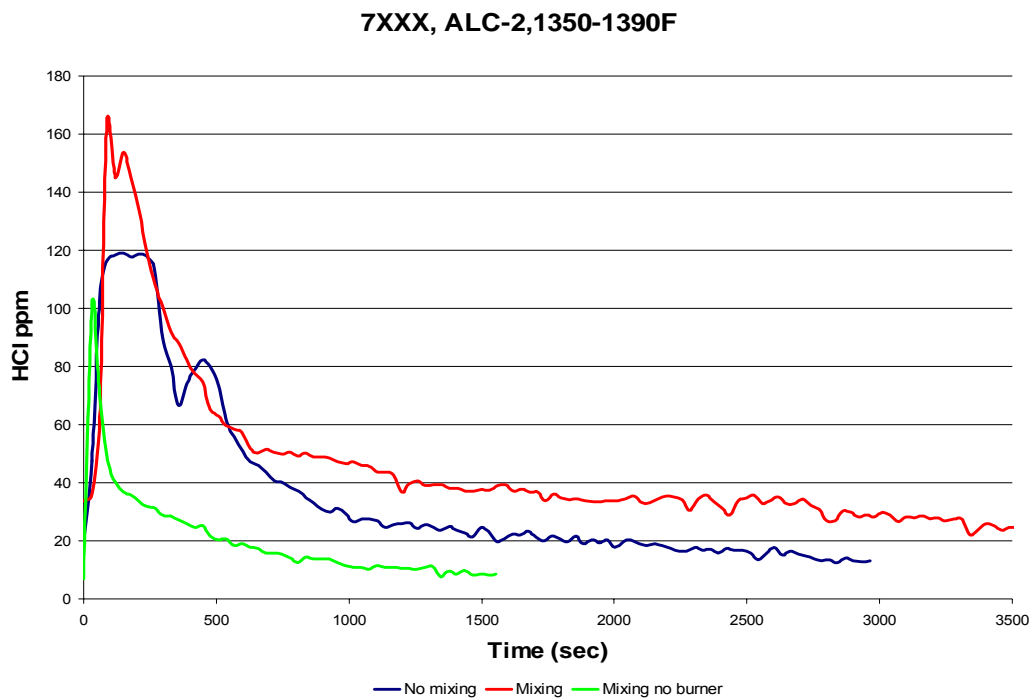


Figure 9: Combinations of the variables mixing and no burner

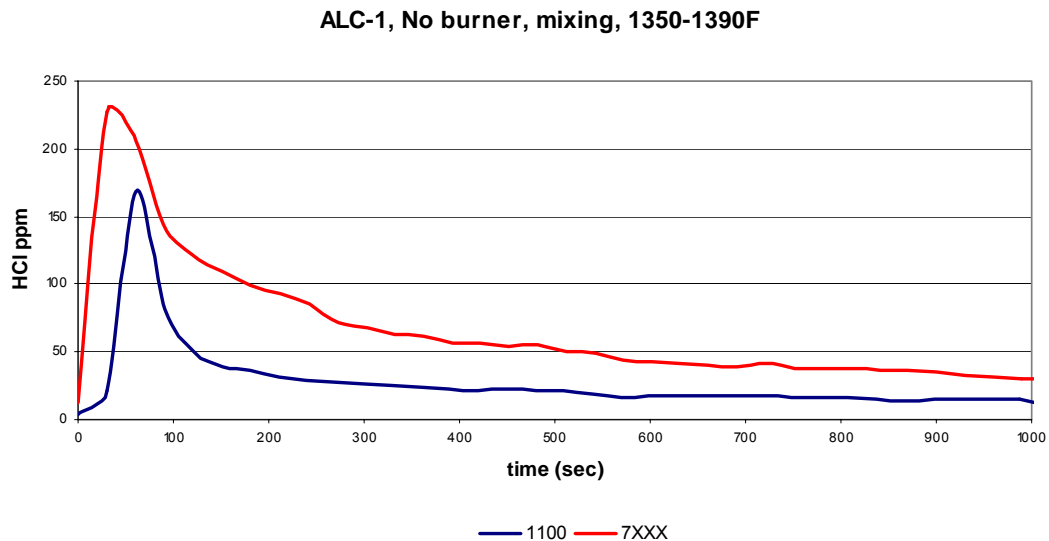


Figure 10: Comparison of HCl emissions in alloy 7XXX against alloy 1100 with ALC-1 salt.

The investigation of the metal's composition dependence upon total emissions shows that the more alloyed the melt the higher the emissions will be. The 7XXX alloy was shown to have higher emissions than the 1100 alloy under the conditions being mixing of the melt, without the burner, and with all salts tested. Figure 10 shows this conclusion with salt ALC-1 and figure 11 shows this with salt ALC-2. These figures also show that the emissions are higher with ALC-1 than with ALC-2. ALC-1 has more $MgCl_2$ compared to ALC-2 salt.

ALC-2, No burner, mixing, 1350-1390F

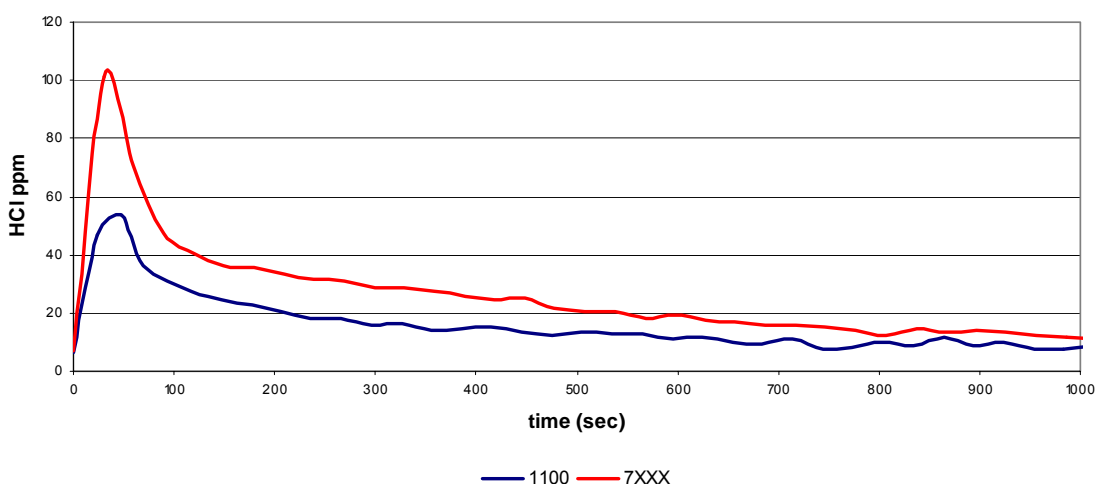


Figure 11: Comparison of HCl emissions in alloy 7XXX against alloy 1100 with ALC-2 salt.

Table 3 lists quantities obtained by the integration of emission data (average of 5 tests or more) through 800s by Remion middle sum method. These are simply the area under the curve and would be directly proportional to the HCl emission for a given system. The results show that alloy 1100 had lower emissions than alloy 7XXX for all salts. ALC-2 is seen to have the lowest emissions of all salts. Table 3 and Fig. 12 also show that Fusal, which is the fused salt of ALC-1's composition, emitted less HCl gas than ALC-1. On the other hand, Table 4 shows that Zendox, which is prefused salt of ALC-3 composition, had more emissions than ALC-3 salt and was highest of all salts.

Table 4: Integration of emissions through 800 seconds (units are ppm*seconds).

Alloy	ALC-1	Fusal	ALC-2	ALC-3	Zendox
AA7xxx	61300		26400	68700	
AA1100	27500	15000	12500	23600	35800

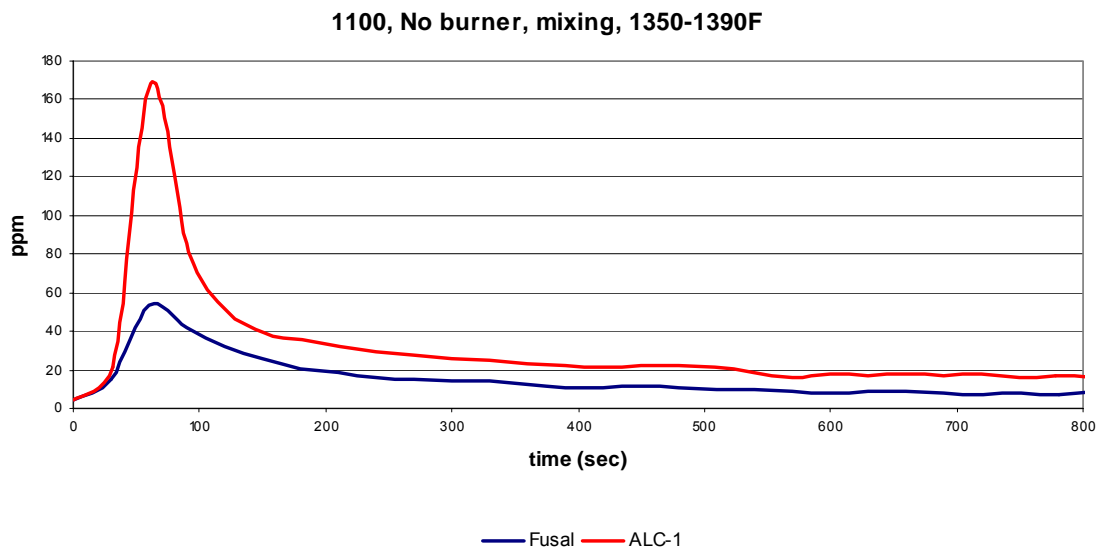


Figure 12: Comparison of HCl emissions with ALC-1 and Fusal in 1100 metal.

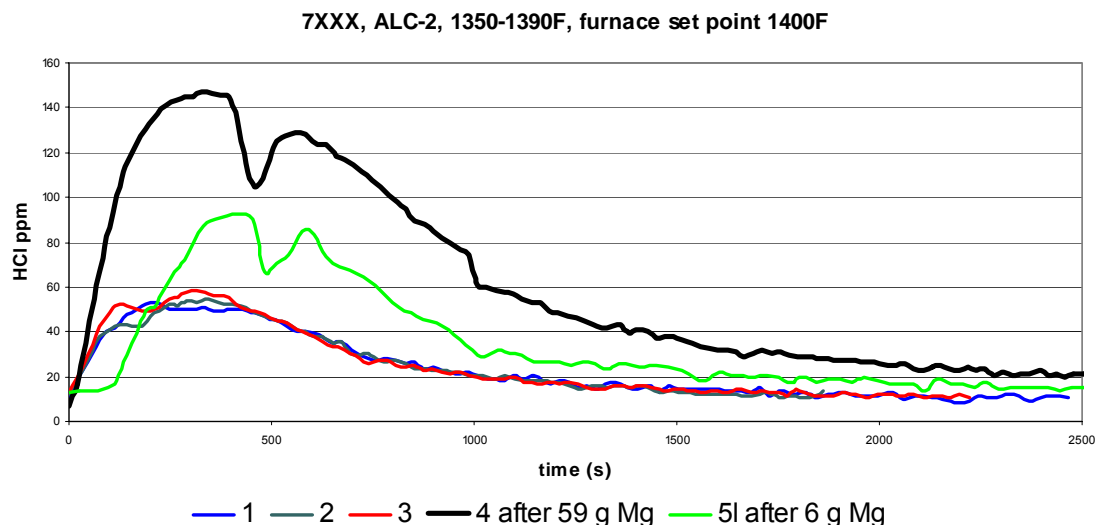


Figure 13: HCl emissions with 7xxx alloy and ALC-2 salt; 3 runs after repeated experiments have lower emission but black and green are cases after addition of unused 7xxx alloy.

As tests were run the surface dross was removed and along with it some of the melt was also removed. This slowly decreased the amount of the melt and periodically more of each fresh alloy was added to maintain the melt at approximately 50 lb metal. Figure 13 shows three curves (1, 2, and 3) with lower emissions. These were obtained after repeated experiments with the same melt bath of 7xxx alloy. The green and black curves with higher emissions were the first test runs after additional alloy 7XXX was added to the melt. These tests were run with the burner on so inflection by atmospheric water content is seen. The higher water and Mg content had the combined effect of increasing the HCl emissions.

Impurity Removal / Mathematical Model:

A known quantity of impurity (Ca or Li) was added to the melt and initial sample was taken. Samples were then taken with time. These samples were analyzed at Alcoa Technical Center for the impurity content. The rate of impurity removal was calculated by the following rate equation model.

$$\% j / \% j_0 = \exp [-k_s \rho A_s t / M]$$

% j= conc with time

k_s = rate constant (m/s)

% j_0 = beginning conc

ρ = density (2300kg/m³)

A_s = surface area(m²)

M = mass (kg)

Figures 14 through 17 show the rate of impurity (Ca or Li) removal data. It can be seen that most of the impurity is removed in less than 10 minutes.

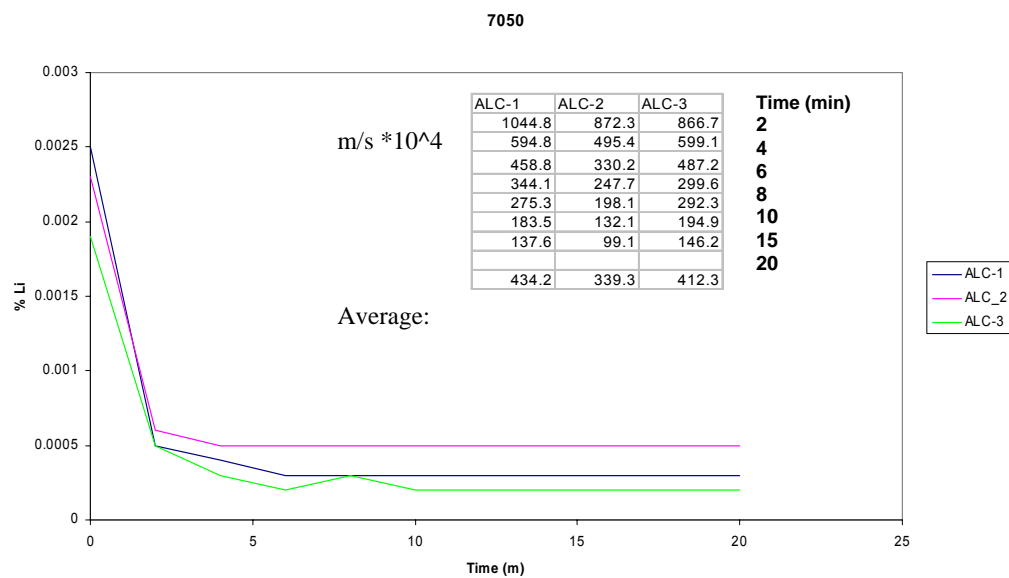


Figure 14: Rate of Li removal in AA7050 with time with three salts (ALC-1, ALC-2, and ALC-3)

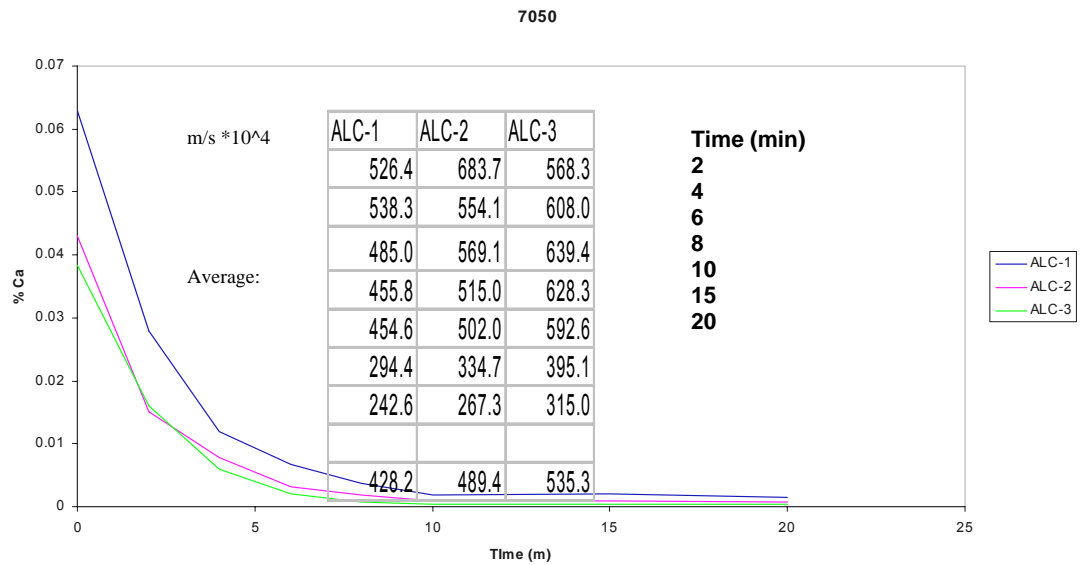


Figure 15: Rate of Ca removal in AA7050 with time with three salts (ALC1, ALC2, and ALC3)

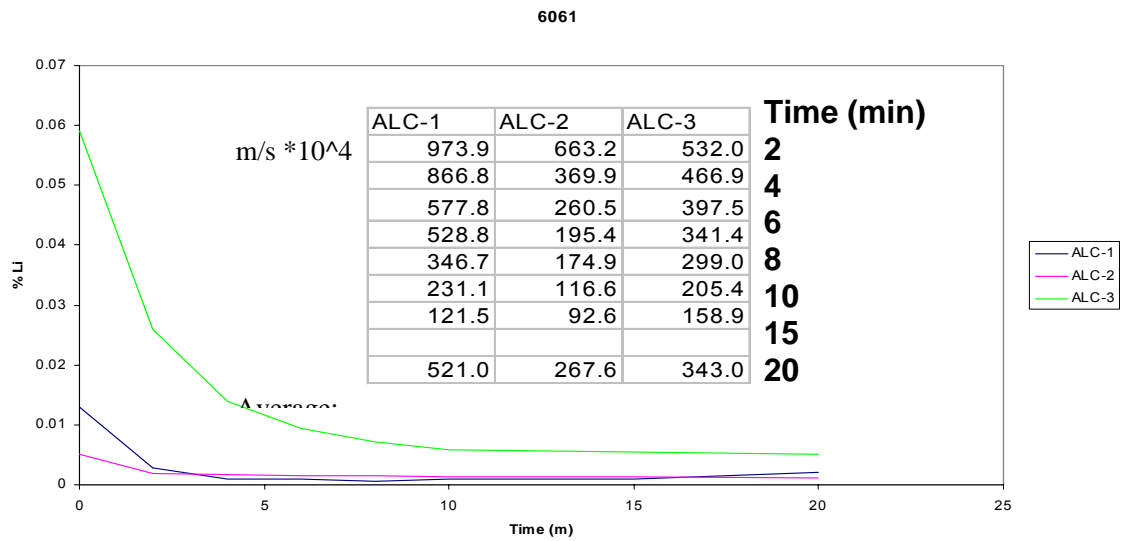


Figure 16: Rate of Li removal in AA6061 with time with three salts (ALC-1, ALC-2, and ALC-3)

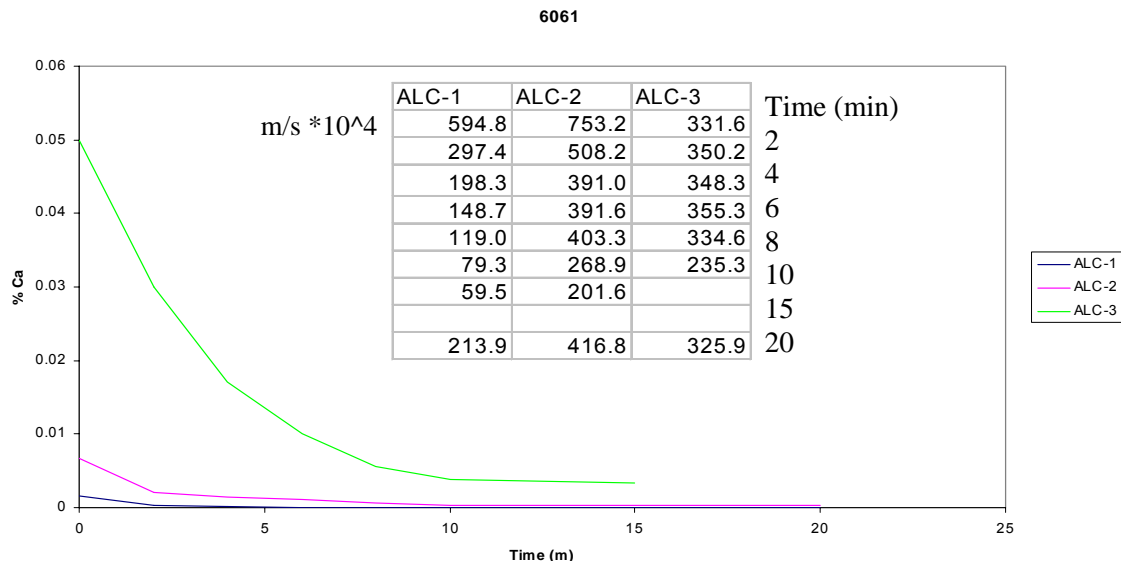


Figure 17: Rate of Ca removal in AA6061 with time with three salts (ALC1, ALC2, and ALC3)

Conclusions -

From this research, the following conclusions can be drawn.

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