

AIR EMISSIONS FROM ROTARY GAS AND ROTARY SALT INJECTION FURNACE FLUXING PROCESSES

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Abstract

To compare environmental emissions resulting from rotary gas injection to those from rotary salt flux injection, tests were carried out using commercially available injection equipment in a production holding furnace. Emission rates of particulate matter (PM), HCl, and Cl₂ were measured in stack gases. Data from this study was compared to data from prior measurements with conventional lance fluxing. Emissions from all fluxing processes were significantly less than the U.S. Secondary MACT standards. Emissions generally correlated with the chlorine utilization, the fraction of the chlorine or chloride feed that reacted with Na, Ca, and Li in the metal. For PM and HCl, the rotary gas process gave lower emissions than the rotary salt process. For Cl₂ emissions the reverse was true. The two processes were also found to give statistically equal rates of Na removal.

Introduction

Chlorine has long been used in ingot plants to refine molten aluminum. When chlorine or chlorine-inert gas mixtures are efficiently contacted with aluminum, the chlorine removes alkali and alkaline earth elements by forming chlorides of these elements. Chlorine also aids removal of inclusions by forming chloride salts that wet inclusions such as oxides and allowing gas bubbles to remove them by floatation, and it aids in separating dross from metal (i.e., it produces a “dry” skim). It can also help produce relatively small bubbles in an in-line degasser, aiding hydrogen removal. It does not assist in hydrogen removal by forming HCl.

Chlorine also has negative impacts on the ingot plant. It produces significant emissions of HCl, Cl₂, and particulate matter (PM). Chlorine requires special handling procedures, and in some countries its use necessitates a significant amount of training for all ingot employees. Its storage can have a small but finite risk to the plant and the surrounding communities.

Regulations around emissions of HCl, Cl₂ and PM have tightened in recent years and this has been a significant driving force for the aluminum industry to reduce its use of chlorine. The Secondary MACT standard (Maximum Achievable Control Technology) in the United States is one example of such increased regulation. According to this standard all secondary aluminum operations (includes ingot plants) must have emissions that are less than or equal to the lowest 12% in any equipment category when the law was enacted. This law was designed to drive the industry to use the best available control technology.

Although solid chloride salt fluxes have been used over the years, there has been a resurgence in their use because they can replace chlorine in some instances [1-5]. Addition methods range from the very simple addition of pre-weighed bags of flux or manual broadcasting of flux on the surface to the somewhat more complicated injection of fluxes into the molten metal using an inert carrier gas. The salt flux needs to meet the metallurgical requirement of removing alkali and alkaline earth elements at a rate comparable to chlorine gas so that cycle times are not increased, but the process also must have emissions low enough to meet environmental regulations.

From a chemical kinetics perspective, a large contact area between the salt flux and metal is required for fast trace element removal, and agitation and stirring of the metal containing flux promotes increased flux-metal contact area. Injection through a static lance was found not to have good reaction rates [6], while injection through a spinning rotor or propeller type device has been reported to give good reaction rates [4,7,8]. However, literature data on the emissions from salt fluxing by rotary injection is sparse. This paper reports on a study done to compare emissions of air pollutants from salt fluxing using a rotary injector to those that result from gas fluxing using a rotary injector.

Experimental

A commercially available rotary gas / flux injector designed for reverberatory furnace applications was used for these trials. With minor changes, the equipment could be switched from salt to gas injection. The work was conducted at Alcoa's Baie Comeau ingot plant using a 65 metric ton holding furnace. The charge consisted of essentially 100% molten primary metal that had not been pretreated by any other refining process. Alloy 5052 was chosen for the tests; one charge of P1020 was tested due to a change in the production schedule and is included in the paper because the emissions were quite different from the 5052 tests.

After the furnace was filled and alloyed, the metal was treated with either rotary gas injection or rotary flux injection for a nominal 30 minute time. Chemical samples were taken from the furnace every 3 minutes during the process to follow the Na, Li, and Ca concentrations. Samples were analyzed in the usual way by optical emission spectroscopy. Air emissions sampling was conducted during each flux cycle using methods comparable with the U.S. EPA Methods 1 through 5 (measurement of PM) and Method 26A (measurement of HCl and Cl₂). Gas samples were continuously drawn from the furnace stack and the emissions rates of particulate matter (PM), HCl, and Cl₂ were measured. The metal volume in each furnace charge was estimated using a level tool designed to measure the metal depth.

A 10% Cl₂ - 90% N₂ mixed gas at approximately 250 l/min (500 scfh) was used during gas fluxing. The rotor speed was approximately 350 rpm. During salt fluxing runs, N₂ was used as the carrier gas and the flowrate was 200 l/min (400 scfh). A pre-fused 60% MgCl₂ - 40% KCl salt was used. The quantity of salt used during a cycle was fixed at 25 kg, and the target feed rate was 1 kg/min. Rotor speed was approximately 250 to 300 rpm. A 40 cm diameter propeller type head was used on a 15 cm diameter shaft.

For a 30 minute flux cycle a total of 2.3 kg Cl₂ was injected into the furnace; the addition of 25 kg salt flux is equivalent to 11.2 kg of Cl₂. For gas fluxing the 2.3 kg Cl₂ added was close to the stoichiometric requirements for the Na, Ca, and Li in the furnace. For salt fluxing the 11.2 kg of Cl₂ equivalent was 3 to 11 times the stoichiometric requirement.

Results

Table 1 gives results of the trial. Four charges each were measured for gas and salt fluxing on alloy 5052, plus one additional charge of nominally pure aluminum (P1020) was measured. During one of the gas-fluxed charges, no chlorine was used to provide an emission baseline. Figure 1 shows typical decay curves for Na, Li, and Ca measured during each flux cycle. Samples were taken from the front of the furnace near one side, unless noted as "center". Center samples were taken from the front center to confirm adequate mixing in the furnace.

Sodium exhibited a continuous decay with time that could be fitted to either a linear or exponential curve. The initial Ca and Li concentrations were very low. Ca showed a slight decrease while Li did not change with time. The initial sodium concentrations ranged from 6 to 34 ppm. Initial concentrations for the other trace elements were much lower, ranging from 1 to 5 ppm for Ca and

from 0.2 to 2 ppm for Li. Very little Ca or Li was removed during the trials, so no attempt was made to analyze removal rates for these elements (Figure 1).

Table 1 Emission rates and 1st order Na removal rate constants during fluxing with rotary injected gas and rotary injected salt in a 65 metric ton reverberatory holding furnace

Test	Type	Alloy	Charge Weight (tonnes)	Emission Rates (kg/hr)			Na Removal Rate Constant		% Chlorine/Chloride Utilization
				Particulate Matter	HCl	Cl ₂	k _{Na} (min ⁻¹)	k _{Na} (cm ³ /s)	
1	Salt	5052	53	0.21	3.25	0.02	-0.0234	-8,820	2.7
2	Salt	5052	55	0.22	1.51	0.02	-0.0206	-7,960	4.7
3	Salt	5052	57	0.25	1.97	0.01	-0.0264	-10,630	9.8
4	Salt	5052	51	0.34	1.84	0.00	-0.0363	-13,090	16.3
5	Gas*	5052	54	0.03	0.00	0.00	-0.0016	-610	n.a.
6	Gas	5052	61	0.09	n.a.	0.37	-0.0220	-9,560	14.8
7	Gas	P1020A	65	0.69	0.51	0.54	-0.0267	-12,210	57.5
8	Gas	5052	51	0.15	0.10	0.27	-0.0192	-6,920	39.5
9	Gas	5052	57	0.17	0.18	0.22	-0.0227	-9,210	40.2

* No Cl₂

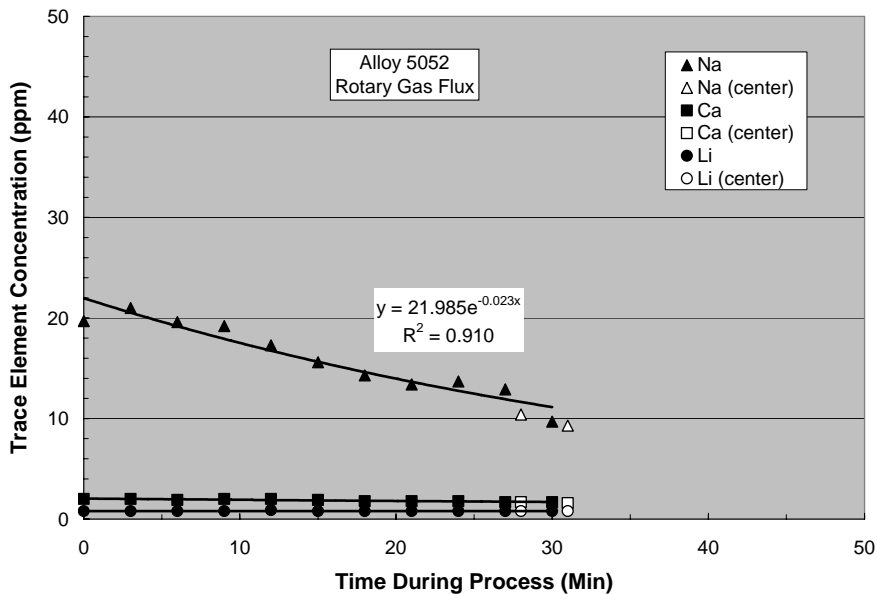


Figure 1 Decay of trace element concentrations during a typical treatment cycle with rotary injection of 90%N₂ – 10%Cl₂. Test No. 9.

Fluxing processes with rates controlled by mass transport of the trace element to the gas bubble or salt flux droplet generally follow first order kinetics and the rate is proportional to the concentration of trace element present at any time. First order kinetics are quite common in high temperature processes where the chemical reactions are fast as compared to diffusion-controlled mass transport. If the reaction rate is limited by transport of the chlorine reactant to the bubble surface, the kinetics would typically be zero order and the rate would be constant with time and directly proportional to the feed rate of the chlorine reactant [9].

For a first order process in a batch reactor, the rate decreases as the removal proceeds. The variation of concentration with time can be described by an exponential equation such as

$$[Na] = [Na^0] \exp[-(kA\rho/M)t] \quad (1)$$

where $[Na]$ is the concentration at any time, $[Na^0]$ is the initial concentration, k is the first order rate constant, A is the area available for reaction, M is the weight of metal present in the furnace, ρ is the metal density, and t is time. Since the area for reaction in a furnace fluxing process cannot be easily measured, it is combined with k and the product treated as one variable.

A linear fit would describe the data almost as well as an exponential fit. In this sense the data does not distinguish between zero and first order. However, inspection of all the rate curves in Figure 2 shows that the rate does depend on the concentration of Na. For example, the initial rate or slope is higher in charges with higher initial Na concentrations. For this reason, the rate will be analyzed according to a first order model for kinetics.

Rate constants given in Table 1 were calculated from the exponential coefficients for each curve in Figure 2 and Equation 1. Also given are the measured emission rates.

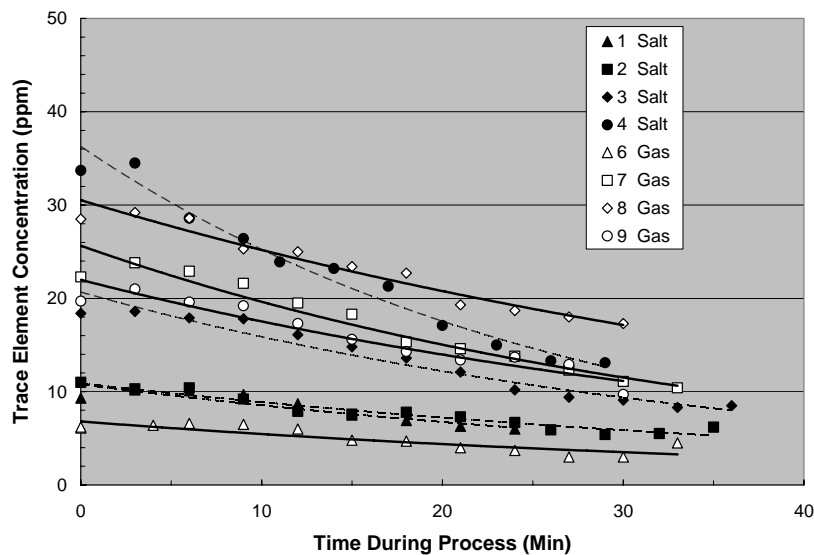


Figure 2 Na removal during rotary injection fluxing with mixed chlorine gas and solid chloride salt flux

Discussion

Emissions

The mean values for emission rates are compared in Figure 3. In addition to the results obtained with the rotary salt and gas injection treatment, results from previous work using conventional 12 mm ID lances are included. A statistical analysis of the emissions data was performed using JMP software (SAS Institute, Cary, NC, USA). The emission rates of PM, HCl, and Cl₂ are compared in Figures 4, 5, and 6.

The graphical presentation in Figure 4 requires some explanation. Each point represents the result of one test, the diamond for each condition indicates the mean value by the line across its center and the 95% confidence level by its height. The horizontal lines near the top and bottom of each diamond indicate the 95% confidence intervals for comparisons between the groups – if these lines overlap for the two groups, then the means are not significantly different at 95% confidence. The widths of the diamonds are proportional to the number of samples in each group.

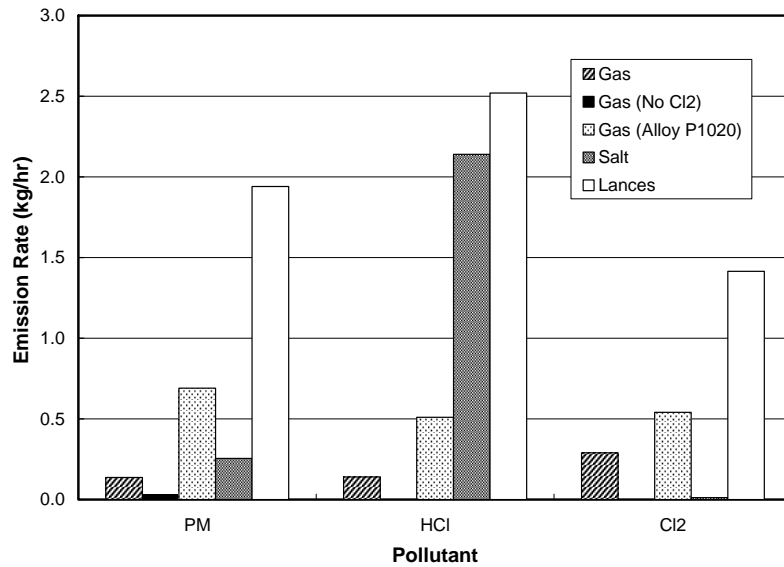


Figure 3 Average emission rates for rotary gas injection, rotary salt injection, and conventional lance fluxing. Alloy was 5052 unless otherwise noted.

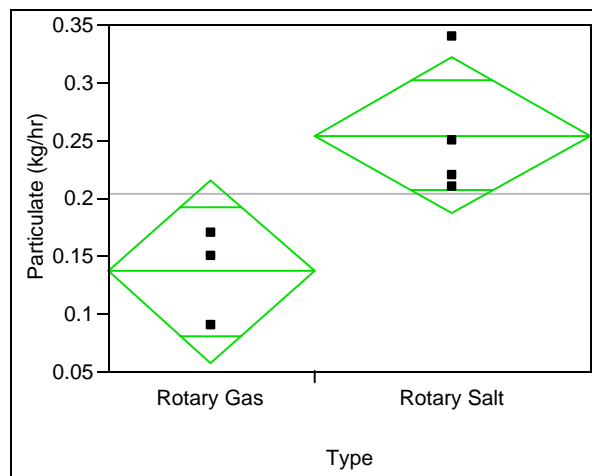


Figure 4 Statistical comparison of results for particulate matter (PM) emissions from rotary injection processes

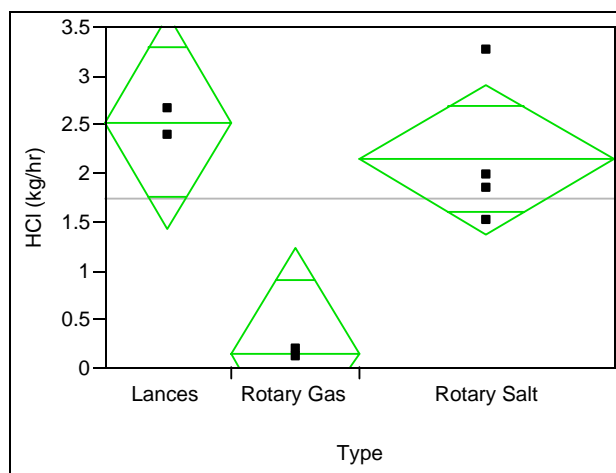


Figure 5 Statistical comparison of results for hydrogen chloride (HCl) emissions from three fluxing methods

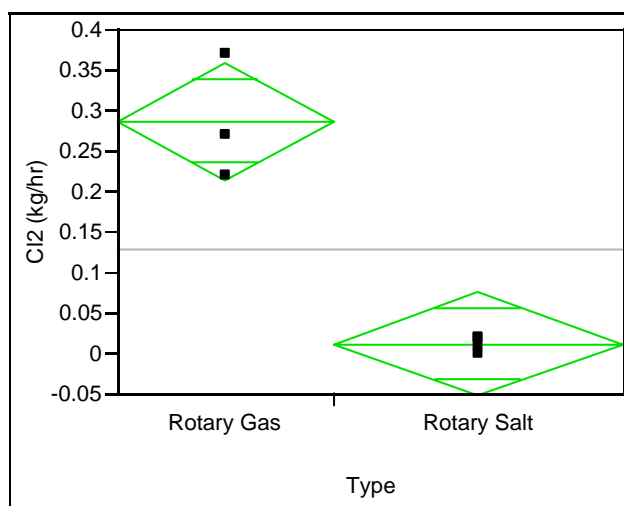


Figure 6 Statistical comparison of results for chlorine emissions from rotary injection processes

The difference in the mean values for PM emissions resulting from injected salt and chlorine mixed gas was statistically significant (Figure 4). Gas fluxing gave lower PM emissions than injected salt. The data from conventional lance fluxing was not included in the analysis summarized by Figure 4 because values were significantly higher and the much greater variance in the data from this past work had the effect of masking the statistical significance between injected salt and gas fluxing in the present study. The PM emissions from both rotary injection processes were much lower than emissions from tube fluxing (Figure 3).

It is hypothesized that PM emissions can arise from two sources. One possible source is metal droplets that form as gas bubbles break the metal surface. As these droplets are carried away into the flue, they will solidify and can oxidize. The second possible source is the hydrolysis of chlorides (gas or liquids) that either vaporize or are ejected as liquids as gas bubbles break the surface [10]. One example would be the hydrolysis of MgCl_2 ,



In this case, the MgO would be carried away in the flue gas and become part of the particulate matter. Since there is much more splashing and surface turbulence with conventional lance fluxing, more PM would arise from the first mechanism. Since lance fluxing is less efficient than the rotary injection, a large excess of chlorine is used leading to the formation of excess MgCl_2 during fluxing. This would give more PM formed by the second mechanism. Both hypotheses for the formation of PM suggest that the inefficient lance fluxing leads to more PM. The difference in PM between rotary salt injection and rotary gas injection will be covered later in the paper.

HCl emissions from fluxing with injected gas were statistically lower than from injected salt by a factor of 15, and injected salt was not different from conventional tube fluxing (Figure 5). This suggests that with rotary salt injection, a significant amount of MgCl_2 becomes airborne and hydrolyzes by Reaction 2. Since MgCl_2 was added as a pre-fused MgCl_2 -KCl material, the activity of MgCl_2 is lowered by virtue of its solution with KCl and hence its vapor pressure is lowered. This suggests injecting salt flux should produce less HCl than injected chlorine, not more. However, looking at it in a different way, perhaps injecting gas produces MgCl_2 that is in solution with the reaction product NaCl, and is of a finer droplet size that is more likely to stay in suspension in the metal. The injected salt process gives coarser salt droplets that float to the surface and have a greater tendency to become airborne by surface turbulence or by vaporization.

The Cl_2 emissions resulting from injected salt was very low, and much less than the Cl_2 emissions from rotary injected gas. The mean values for the two processes were significantly different (Figure 6). As in the case with PM emissions, the data for tube fluxing were not included in the analysis summarized in Figure 6 because the large values for conventional fluxing and the large variance would otherwise mask the statistical difference between the rotary injection processes. Figure 3 shows the large difference between conventional lance fluxing and the other processes.

The explanation for this relative order is straight forward. Lance fluxing uses the most gas and therefore the most chlorine and is least efficient. A portion of the Cl_2 is unreacted and ends up in the stack gases. Rotary gas injection uses less gas, is more efficient, and hence relatively less chlorine goes un-reacted. Rotary salt injection uses no Cl_2 gas and hence any chlorine present in stack gases is formed by a reaction such as



for which the thermodynamics ($\Delta G^\circ = +114.7$ kcal/mole at 750°C) drives the reaction strongly to the left leaving little Cl_2 formed at equilibrium. For example, at 750°C and an activity of Mg in the alloy of 0.01, the equilibrium partial pressure of Cl_2 for the above reaction is 3×10^{-23} atm.

Figure 7 shows that chlorine utilization with the rotary gas injection process is significantly greater than with the rotary salt injection process. The chlorine/chloride utilization is defined as the fraction of Cl_2 or MgCl_2 injected into the metal that actually reacts to form NaCl, CaCl_2 , or LiCl. This value was calculated from the process feed rates, the initial and final Na, Ca, Li concentrations in the metal, and the measured weight of metal in the furnace. The utilization increases with increasing initial alkali/alkaline earth element concentrations, which is consistent with first order reaction kinetics. Increasing the concentration of reactant in the metal phase will increase the reaction rate, and increasing the reaction rate will increase the fraction of chlorine or chloride that reacts during the gas or molten salt droplet residence in the metal. Another way to put it, the same number of moles of Cl_2 or MgCl_2 chasing more moles of reactants will yield higher reaction rates and higher utilization values.

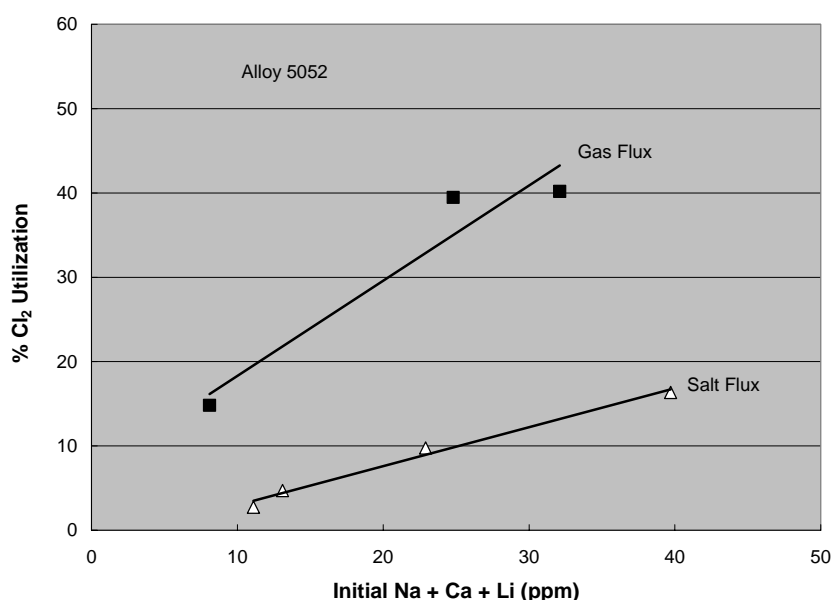


Figure 7 Chlorine/chloride utilization for rotary injection processes

This large difference in chlorine/chloride utilization can explain differences in the emissions of PM and HCl. Chlorine that does not react with Na, Ca, Li will either 1) react to form MgCl_2 which can form HCl and PM by Reaction 2, 2) react to form AlCl_3 which will form HCl and PM by an analogous reaction,



or 3) escape as free Cl₂ which can partially hydrolyze to produce HCl. MgCl₂ from the salt flux that does not react with Na, Ca, or Li will primarily end up on the metal surface (with dross) where it can hydrolyze (or vaporize and hydrolyze) by Reaction 2 to form PM and HCl. Less reaction with Na, Ca, Li in the metal makes more chlorine/chloride available to form pollutants. Since the utilization of the salt flux is much less than with chlorine, it stands to reason that the salt flux will produce more pollutants.

It should be noted that not all of the unreacted chlorine or chloride reacts to form HCl. Equilibrium calculations using the FACT Sage thermodynamic program shows that a portion but not all Cl₂ will react with H₂O in combustion gases.

Figure 3 shows that the PM, HCl, and Cl₂ emissions with rotary gas injection of P1020 were significantly higher than for gas injection in alloy 5052. This information supports the hypothesis that PM and HCl emissions are caused to a large extent by hydrolysis of chlorides. Since P1020 has no Mg, much of the injected chlorine will react with Al to form AlCl₃. Since AlCl₃ has a sublimation point of 178°C, any produced by reaction of molten aluminum will be emitted as a gas and will form PM and HCl by Reaction 4. Related to this, the Cl₂ emissions are higher in P1020 because there is no Mg and therefore a smaller fraction of the injected chlorine reacts and remains in the metal or dross.

It is of interest to compare these emissions results to the U.S. Secondary MACT requirements. Figure 8 gives the results in units of kg emissions per metric ton of metal treated, along with the Secondary MACT limits. These figures show that all emissions for all three treatment processes were well below the limits for PM and HCl, which are both 0.2 kg/tonne (0.4 lb/ton). Despite this, the reduction in PM using rotary injection technology could aid plants utilizing the averaging provisions of the SMACT rule. That is, in some instances compliance can be attained by averaging higher emitting furnaces and in-line degassing units with lower emitting units. Also, although there is no SMACT limit for Cl₂, there are local emission limits for Cl₂ (and HCl and PM) throughout the world.

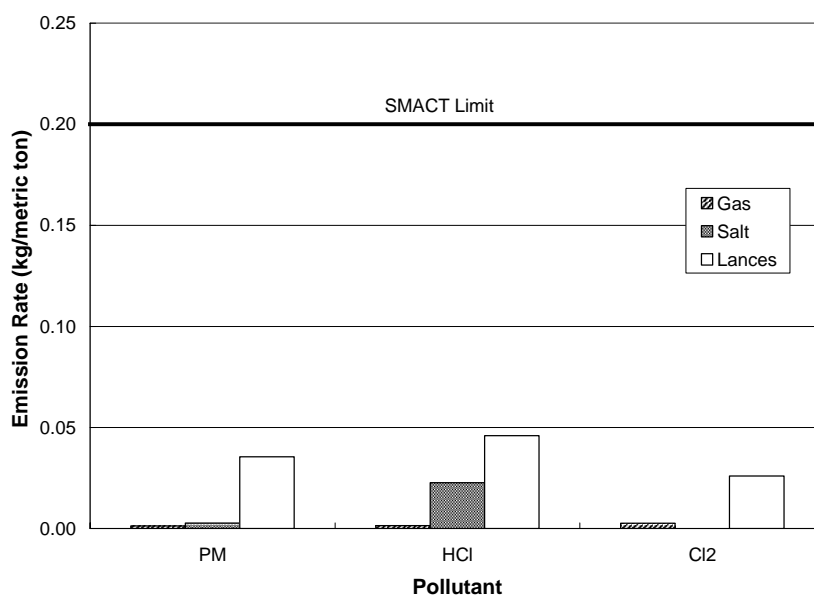


Figure 8 Average emission rates given on a basis of quantity of emissions per metric ton of metal treated

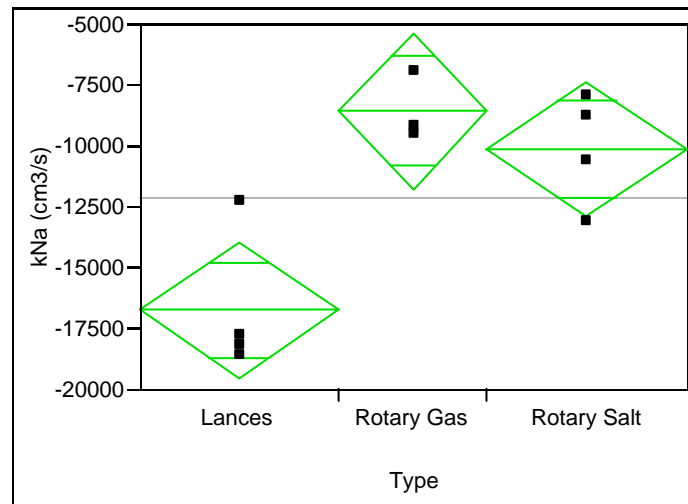


Figure 9 Statistical comparison of results for Na removal rate constants from three fluxing methods

Na Removal Kinetics

Inspection of the general shapes of the curves in Figure 2 shows that salt flux removes Na as fast as the mixed chlorine gas does. Figure 9 gives results of a statistical analysis of the removal rate constants. Also included in this analysis is data obtained from past work with conventional graphite lances. The rates constants are negative because Equation 1 defines a removal process as having a negative rate constant. So more negative values indicate faster Na removal.

Figure 9 shows that the removal rate constant for fluxing with injected salt is not statistically different than fluxing with injected chlorine mixed gas, at the 95% confidence level. It also shows that conventional tube fluxing was significantly better than either of the two processes. Since both salt and gas fluxing rate constants are not statistically different, either process can be described by the average rate constant of all of the data,

$$[\text{Na}] = [\text{Na}^0] \exp[(-9460\rho/M)t] \quad (5)$$

Although fluxing with tubes or lances is considered to be an inefficient process, the results shown here indicate that it removed Na faster. The multiplicity of tubes and the greater total gas flowrate overcome the inherently more efficient rotary injection processes.

Conclusions

1. The emissions of particulate matter (PM) and HCl for both the rotary gas injection and rotary salt injection furnace treatment processes were well below the U.S. Secondary MACT limits of 0.2 kg/tonne. (There is no limit for Cl₂.)
2. The rate of PM emissions for the rotary gas process was lower than the rate for the rotary salt process, and both were much lower than rates from conventional lance fluxing.
3. The rate of HCl emissions from rotary gas injection was lower than from rotary salt injection; the rate from rotary salt injection was statistically equal to the rate from lance fluxing.
4. The rate of Cl₂ emissions from rotary gas injection was significantly greater than from rotary salt injection. Cl₂ emissions from both processes were significantly less than from conventional lance fluxing.

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5. The chlorine / chloride utilization for rotary salt injection was less than for rotary gas injection. This difference explains the higher PM and HCl emission rates for the rotary salt process.
6. Both the rotary gas and salt injection processes gave statistically equivalent rates of Na removal. Rates of Na removal with both processes were lower than with conventional lance fluxing. This is due to the multiplicity of lances used and the far greater total quantity of gas used in lance treatment. Considering the fraction of chlorine or chloride actually reacting with Na, lance treatment is much less efficient than either of the rotary injection processes.

Acknowledgements

The contributions of C. R. Myers in collecting data are greatly appreciated. The careful review of the manuscript by D. C. Chesonis and K. Kitzman is acknowledged.

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