Na AND Ca PICK-UP FROM HALL BATH IN INGOT FURNACES

David H. DeYoung

Molten Metal Processing Center,
Alcoa Technical Center,
Alcoa Center, PA 15069, USA

ABSTRACT

A series of bench-scale tests were conducted to explore the reaction of cryolite bath with molten Al-Mg alloys. The reaction was clearly demonstrated; both Na and Ca concentrations in the aluminum dramatically increased after Mg was added. Temperature had a major impact on the reaction. At 700°C (1292°F) the Na and Ca increases upon alloying were approximately 16 ppm, while at 900°C (1652°F) the increases were approximately 320 ppm.

The Na and Ca increases were dependent on the Mg concentration. The quantitative relationship between the trace element increases and the Mg concentration support the following reactions:

$$2\,(Na_3AlF_6) + 3\,\underline{Mg} = 6\,\underline{Na} + 2\,AlF_3 + 3\,MgF_2$$

$$CaF_2 + \underline{Mg} = \underline{Ca} + MgF_2$$
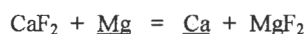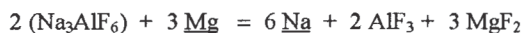
The reaction of Hall bath with Mg was also dependent on the quantity of bath added and the particle size of the bath. The reaction rates with -48 mesh bath were approximately twice the rates with +4 mesh bath. The trace element pick-ups increased non-linearly with the quantity of bath.

I. INTRODUCTION

Operational data from ingot plants that receive molten metal from a smelter shows that the Na and Ca concentrations in molten aluminum can increase upon alloying with Mg. This Na and Ca may need to be removed by furnace or in-line fluxing with a reactive gas such as chlorine, which has a number of negative consequences – Cl_2, HCl, and particulate emissions to the atmosphere, skim (with its environmental consequences), melt loss, and molten salt inclusions in the metal. To attempt to understand the Na and Ca pick-up occurring during alloying, a series of laboratory tests were conducted to explore the reaction of cryolite bath with Al-Mg alloys. Bath can enter ingot furnaces along with molten primary metal.

Several references in the literature suggest that cryolite can react with magnesium by a reaction such as

$$Na_3AlF_6 + 3\,\underline{Mg} = 3\,MgF_2 + 3\,\underline{Na} + \underline{Al} \qquad [1]$$
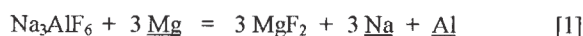
Guthrie et.al. (1) reported that the concentration of Na in a

0.1% Mg alloy in equilibrium with cryolite is 14 ppm at 727°C. Simensen (2) predicted that the Na content in an Al-5% Mg alloy saturated with cryolite at 700 °C is 0.23%.

The presence of bath in the melting furnace could also add Ca by the reaction:

$$CaF_2 + \underline{Mg} = \underline{Ca} + MgF_2 \qquad [2]$$
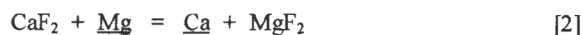
A thermodynamic calculation showed that for an Al-4.5% Mg alloy at 815 °C, the reaction should proceed until the Ca concentration in the alloy reaches 12 ppm. The details of this calculation will be given later in the paper.

This study was conducted to determine if, under conditions that simulate ingot plant operations, cryolite can add Na and Ca to molten aluminum and Al-Mg alloys by reactions such as those described above. The effects of temperature, quantity of bath added, particle size of bath added, and Mg concentration in the alloy on the Na and Ca pick-up were explored.
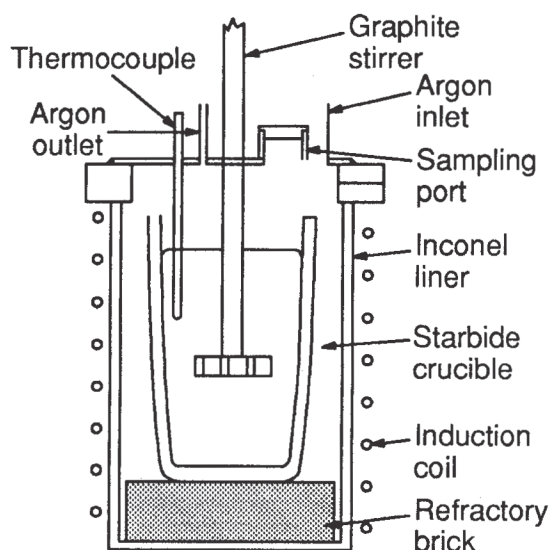

Figure 1 - Schematic diagram of apparatus used for bench-scale tests of cryolite bath - Mg reaction.

II. EXPERIMENTAL METHOD

The test procedure was to 1) melt smelter grade metal in a crucible containing bath, 2) alloy with Mg, and 3) periodically take metal samples. For each test, 27 lb. of aluminum was melted in a 9 in. OD x 7.5 in. ID x 14 in. high silicon carbide crucible (Starbide 509, American Refractories and Crucible Corporation). Depending on the test, up to 2.7 lb. of +4 mesh bath chunks were placed in the bottom of the crucible before the metal was added. The bath was obtained from an experimental Hall cell. The crucible containing this solid material was then heated by an AJAX induction furnace; the silicon carbide crucible was placed in a mild steel crucible which in turn was placed in a graphite crucible that served as a susceptor. A schematic drawing of the test unit is given in Figure 1. The reaction chamber in the induction furnace was gas-tight and during the experiments was purged with Ar at approximately 3.5 cm³/min. The primary purpose of the Ar was to minimize air-burning of the graphite susceptor and stirrer.

Once the desired temperature was achieved, stirring was begun at 100 rpm and an initial metal sample was taken by dipping metal out with a small steel cup and pouring into a scissor mold. For most tests, powdered bath (0.1 to 4.5 lb., -48 mesh) was added to the metal surface, and metal sampling continued for the next hour. Magnesium was added after 1 hour and metal sampling continued. Samples were analyzed by emission spectroscopy (quantometer) for Na, Ca, and Mg as well as the other usual elements.

III. RESULTS AND DISCUSSION

Results for the experiments are summarized in Table I. The Na and Ca concentrations at 60 minutes after the magnesium addition are given, as well as the maximum concentrations recorded during the test. The Na, Ca, and Mg concentrations obtained during one of the tests is plotted in Figure 2. This figure clearly shows that the Na and Ca concentrations increase after Mg is added and, therefore, demonstrate that Mg reacts with the bath present to add Na and Ca to the molten aluminum phase. Table I shows that the range of the trace element increase during the tests was large, varying from approximately 2 to 330 ppm depending on conditions.

Table I

Summary of Cryolite Bath-Mg Tests

Test No.	Date	T (°C)	Actual Temp.	Cryolite Bath Addition (lb.)		%Mg Addition	Trace Element Concentration (ppm)			
				+4 Mesh	-48 Mesh		After 60 min		Maximum	
							Na	Ca	Na	Ca
1	2/3	850	850-915	2.7	1.5	4.5	146	220	210	320
2	2/14	775	770-790	2.7	1.5	4.5	29	20	37	39
3	2/19	700	700-710	2.7	1.5	4.5	13	2	17	6
4	2/26	815		2.7	1.5	4.5	52	68	58	78
5	3/17	815	807-819	2.7	-	4.5	55	44	56	52
6	3/19	815	806-826	-	1.5	4.5	48	35	53	39
7	3/23	815	805-824	-	0.5	4.5	48	21	50	23
8	3/25	815	796-824	-	4.5	4.5	45	46	49	46
9	3/26	815	804-820	0.5	-	4.5	19	14	23	18
10	4/1	850	840-851	2.7	1.5	4.5	61	65	64	66
11	4/6	815	802-829	-	0.1	4.5	2	2	5	3
12	4/7	815	803-820	0.1	-	4.5	4	5	7	6
13	4/8	815	812-819	1.5	-	4.5	37	17	41	20
14	4/9	900	897-912	2.7	1.5	4.5	~190	~250	~330	~320
15	4/10	815	810-820	2.7	1.5	0.5	3	-	9	2
16	4/13	815	811-821	2.7	1.5	2	21	16	22	18
17	4/14	815	810-817	2.7	1.5	6.5	76	47	78	52

The portion of Na and Ca that came directly from the Mg was insignificant. Two Mg samples were analyzed and found to contain 31 and 32 ppm Na and 20 and 8 ppm Ca, respectively. For a 4.5% addition the magnesium would add at most 1.5 ppm Na and 0.9 ppm Ca.

A. Shape of Concentration vs. Time Curves

Figures 2 through 5 show some representative concentration vs. time curves obtained from the tests. The trace element increase was influenced by all the variables explored -- temperature, bath quantity, bath particle size, and magnesium concentration. Before reporting these effects, trends regarding the shape of the concentration vs. time curves given in Figures 2 through 5 will be discussed. In some tests the Na and Ca concentrations increased sharply just after the Mg was added, then gradually decreased with time (Figures 2 and 3). In other tests the concentrations increased, then leveled off at steady-state values (Figure 4), and finally in other tests the Na and Ca concentrations continued to increase throughout the tests after the Mg was added (Figure 5).

These differences can be summarized as follows:

1. Na increased after Mg was added, then decreased through the remainder of the test if the temperature was high (>815°C), the quantity of bath was low, or if the Mg concentration was decreasing.
2. Na reached a steady state if the temperature was intermediate (775°C<T≤815°C), sufficient bath was present, and the Mg concentration was approximately constant.
3. Na continually increased throughout the test if the temperature was low (≤775°C).
4. Ca increased after Mg was added, then decreased if the temperature was high (>850°C) or if the Mg concentration was <2% and decreasing.
5. Ca continuously increased throughout the test if the temperature was ≤850°C and the Mg concentration was either >2% or was constant.

In most of the tests the Na concentration reached a steady-state level, whereas the Ca concentration did not reach a steady state. The shape of the concentration vs. time curves (initial
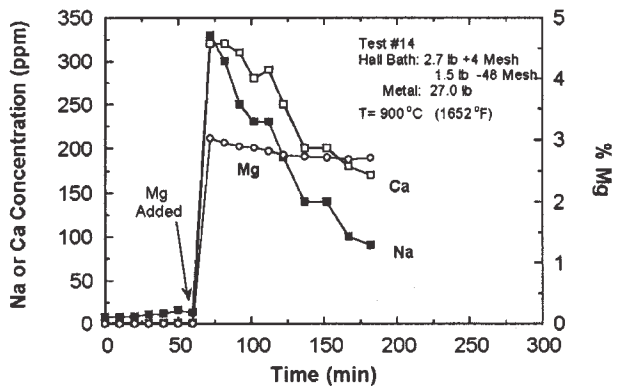

Figure 2 - Trace element increase in molten Al caused by alloying with Mg when cryolite bath was present. Nominal temperature was 900 °C.
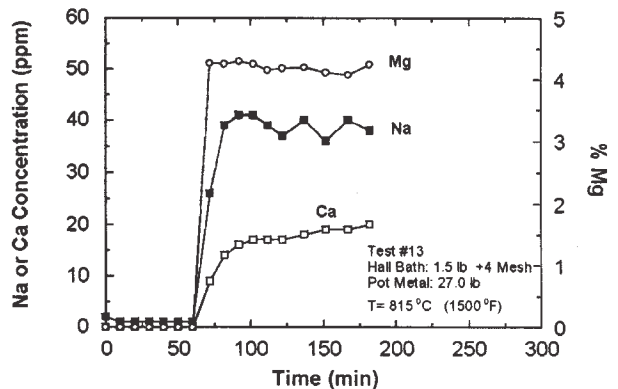

Figure 4 - Trace element increase in molten Al caused by alloying with Mg when cryolite bath was present. Nominal temperature was 815 °C.
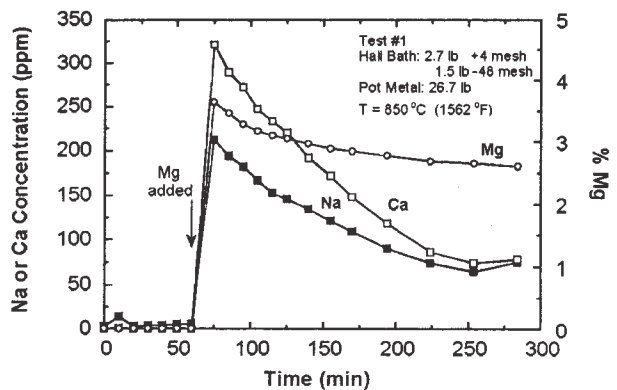

Figure 3 - Trace element increase in molten Al caused by alloying with Mg when cryolite bath was present. Nominal temperature was 850 °C.
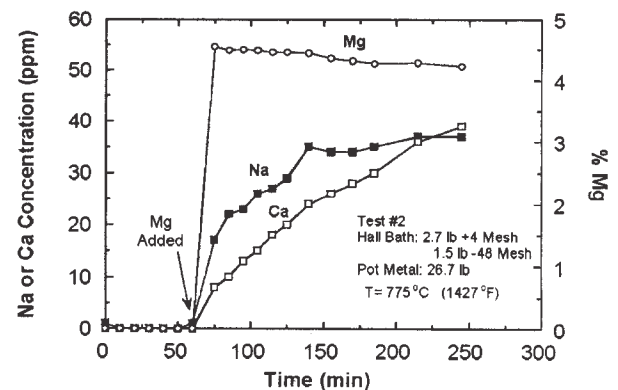

Figure 5 - Trace element increase in molten Al caused by alloying with Mg when cryolite bath was present. Nominal temperature was 775 °C.

slopes) indicated that the reaction to produce Na was much faster than the reaction to produce Ca.

A reasonable explanation for the shapes of these curves is that two competing processes were occurring -- Na and Ca were being added to the metal phase by reaction of the Mg with NaF and CaF$_2$ contained in the bath, and Na and Ca were continuously being removed from the metal phase by vaporization and oxidation. The relative rates of these two processes then determined the shape of the concentration vs. time curve.

For Na, the shape of the curves lead to the following conclusions:

1. At T < 775°C, both the Hall bath-Mg reaction and the vaporization/oxidation are slow so that equilibrium is not reached.
2. At 775°C < T≤815°C, the Hall bath-Mg reaction rate is sufficiently greater than the rate of vaporization/oxidation so that equilibrium is reached.
3. At T > 815°C, the Hall bath-Mg reaction is slower than the vaporization/oxidation reaction, so equilibrium is not reached.

For Ca, the shape of the curves lead to similar conclusions, except the temperatures defining the regimes are different:

1. At T < 850°C, both processes are slow and equilibrium is not reached.
2. At T = 850°C, steady state is reached.
3. At T > 850°C, the Hall bath-Mg reaction is slower than the oxidation reaction, so equilibrium is not reached.

B. Temperature Effect

To analyze the effects of the independent variables, the maximum trace element concentrations obtained were used as the dependent variables. Concentrations obtained at a specific time after the Mg addition (e.g., 60 minutes) could also be used as the dependent variables, but identical conclusions would be obtained.
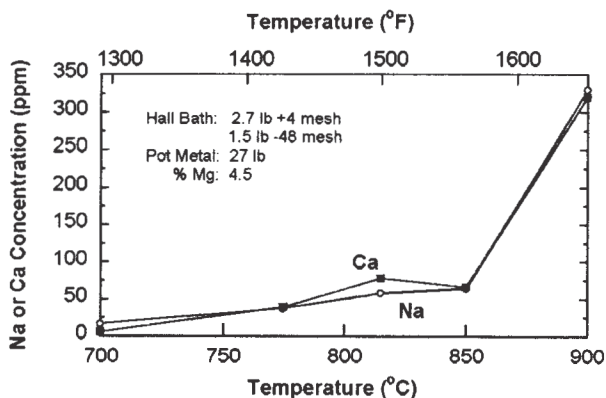
The effect of temperature on the reaction is shown in Figure 6 -- the Na and Ca concentrations increase with increasing temperature. The effect is nonlinear and increases dramatically at temperatures higher than 850°C (1562°F). At any given temperature, the Na and Ca concentrations are approximately equal.

At 1300 °F the trace element pick-up was on the order of 20 ppm or less, a level that could be removed by in-line metal treatment units. At 1400°F and higher the magnitude of the increase is 40 ppm or greater and would probably require furnace fluxing for removal. It should be noted that although the bulk temperature during alloying may be near 1400°F, in reverberatory furnaces the surface temperatures could at times be as much as 200°F to 300°F hotter (3).

C. Effect of Magnesium

The influence of the Mg concentration on the Na and Ca concentrations in the metal is shown in Figure 7. The data plotted were taken from tests run at conditions under which a steady-state or close to a steady-state was achieved. All data obtained during the "steady-state" from each run were included in these plots. There was a good linear correlation for Na, while the correlation for Ca was not as good. Part of the reason for the poorer correlation is that the Ca-reaction was slower than the Na reaction and a steady state (and therefore equilibrium) was not normally reached. Judging from the Ca data in Figure 7, equilibrium may have been reached at low concentrations of Mg (<2%), but not at the higher concentrations (>4%).

D. Comparison with Theory

The variations of Na and Ca with Mg can be compared to theoretical predictions. One possible reaction to produce Na is Reaction 1,
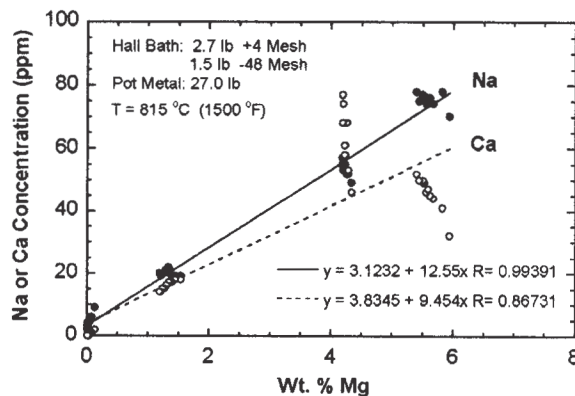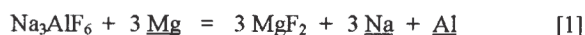
$$Na_3AlF_6 + 3\,\underline{Mg} = 3\,MgF_2 + 3\,\underline{Na} + \underline{Al} \qquad [1]$$

Figure 6 - *Effect of temperature on the maximum trace element pick-up caused by Mg additions to molten Al with cryolite bath present. Values reported here are maximum values recorded during the 3 to 5 hour tests.*

Figure 7 - *Effect of Mg concentration on the Na and Ca pick-up in molten Al caused by Mg additions with cryolite bath present.*

Another possible reaction to produce Na in the metal could be:

$$2\,(Na_3AlF_6) + 3\,\underline{Mg} = 6\,\underline{Na} + 2\,AlF_3 + 3\,MgF_2 \qquad [3]$$

where the underlines indicate the elements that are dissolved in the molten aluminum phase. The equilibrium constant for Reaction 3 is:

$$K = \frac{a_{Na}^{\,6}\;a_{AlF_3}^{\,2}\;a_{MgF_2}^{\,3}}{a_{Mg}^{\,3}\;a_{Na_3AlF_6}^{\,2}} \qquad [4]$$

Taking the logarithm of both sides of the equation and rearranging gives:

$$6\log a_{Na} = 3\log a_{Mg} + \log K$$
$$- \log \frac{a_{AlF_3}^{\,2}a_{MgF_2}^{\,3}}{a_{Na_3AlF_6}^{\,2}} \qquad [5]$$

Since $a_i = f_i\,(wt.\%\,i)$, the equation becomes:

$$\log(wt\%Na) = \frac{1}{2}\log(wt\%Mg) + \frac{1}{2}\log\frac{f_{Mg}}{f_{Na}}$$
$$+ \log K - \log\frac{a_{AlF_3}^{\,2}a_{MgF_2}^{\,3}}{a_{Na_3AlF_6}^{\,2}} \qquad [6]$$

Assuming the ratio of the activity coefficients f_{Mg}/f_{Na} is approximately constant over the concentration range explored and the ratio

$$\frac{a_{AlF_3}^{\,2}a_{MgF_2}^{\,3}}{a_{Na_3AlF_6}^{\,2}}$$

is approximately constant, then the log(wt.% Na) should vary linearly with log(wt.% Mg) with a slope of 1/2. Figure 8 shows the data plotted in log-log coordinates. A least-squares line through the Na data has a slope of 0.54, very close to the theoretically predicted slope for Reaction 3. This agreement provides evidence that Reaction 3 is the reaction responsible for the Na increase in the metal. The theoretical slope for Reaction 1 would be 1, which does not agree with the data.

A possible mechanism for the calcium pick-up is:

$$CaF_2 + \underline{Mg} = \underline{Ca} + MgF_2 \qquad [2]$$
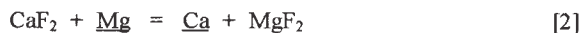
A corresponding analysis to the sodium case gives the following equation:

$$\log(wt\%Ca) = \log(wt\%Mg) + \log\frac{f_{Mg}}{f_{Ca}}$$
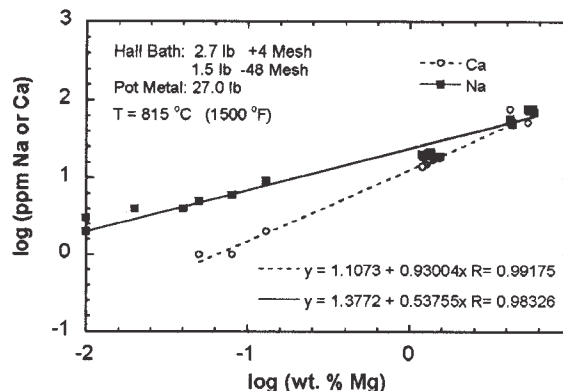$$+ \log K - \log\frac{a_{MgF_2}}{a_{CaF_2}} \qquad [7]$$

Figure 8 - Log-log correlation between trace element and Mg concentrations resulting from Mg additions to molten aluminum with cryolite bath present.

This equation predicts a log (wt.% Ca) vs. log (wt.%. Mg) curve will have a slope of 1. Figure 8 shows the slope of the line for the Ca data is 0.93. (In this plot only the Ca data considered closest to the equilibrium was used for the two tests at concentrations greater than 4% Mg.) The agreement between 0.93 and the theoretical slope of 1 provides support for Reaction 2 being responsible for the Ca pick-up.

The standard free energy change ($\Delta G°$) for Reaction 1 at 815 °C is -92.0 kJ/mole; for Reaction 3 the standard free energy change is +165.6 kJ/mole (4). The activity coefficient for Mg (γ_{Mg}) at 750 °C was reported to be 0.79 (5), and the activity coefficient for Na at 727 °C was reported to be 293 (6). Using a regular solution assumption to extrapolate these values to 815 °C

$$RT_1\ln\gamma_{Na}\big|_{T_1} = RT_2\ln\gamma_{Na}\big|_{T_2} \qquad [8]$$

gives activity coefficients for Mg and Na of 0.80 and 185, respectively. For a 4.5 wt.% Mg alloy ($a_{Mg} = 0.039$) the equilibrium Na concentrations at 815 °C from Reactions 1 and 3 are calculated to be 0.53% and 43 ppm, respectively. The "equilibrium" Na concentration in a 4.5% Mg alloy at 815 °C measured in this study is shown in Figure 7 to be approximately 59 ppm. This is additional evidence that Reaction 3 is responsible for the Na pick-up.

The standard free energy change ($\Delta G°$) for Reaction 2 at 815 °C is +108.5 kJ/mole. The activity coefficient for Ca was estimated using literature data and a regular solution extrapolation for temperature. Jacob et. al. (7) report the activity coefficient for Ca (γ_{Ca}) as 0.0059 at $X_{Ca} = 0.1$ and at 1100 °C (relative to pure liquid Ca and Al as standard states). Using a regular solution assumption the activity coefficient for Ca at 815 °C (1500 °F) was estimated to be 0.0015. Using this value and an activity coefficient for Mg of 0.80 and assuming the activity of CaF$_2$ in cryolite bath is 0.05 (bath containing approximately 0.05 mole fraction CaF$_2$), the equilibrium concentration of Ca in an Al - 4.5 wt.% alloy at 815 °C is calculated to be 12 ppm. This is the same order of magnitude as the measured value of approximately 40 ppm shown in Figure 7. A modest change in
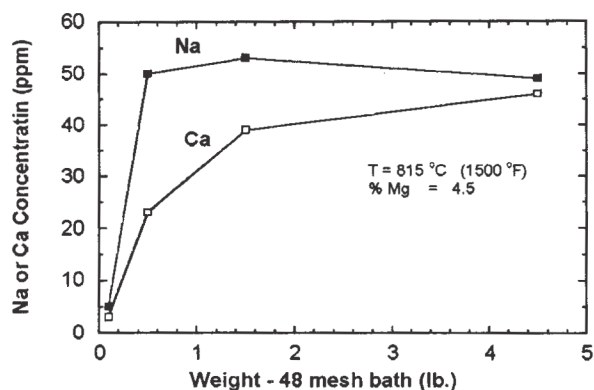
Figure 9 - Effect of the quantity of -48 mesh bath on the trace element pick-up caused by Mg additions to molten aluminum.
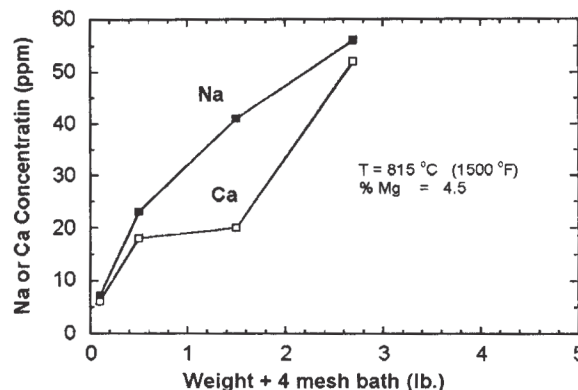

Figure 10 - Effect of the quantity of +4 mesh bath on the trace element pick-up caused by Mg additions to molten aluminum.

the activity coefficient for Ca or the activity of CaF_2 would easily account for the discrepancy.

E. Effects of Bath Quantity and Particle Size

Figure 9 shows the trace element pick-up as a function of the amount of -48 mesh bath added to the system. The Na pick-up increases quickly then reaches a plateau, whereas the Ca pick-up continued to increase over the range tested though the slope of this curve decreased with increasing bath weight.

Figure 10 gives a similar set of curves for +4 mesh bath. In this case neither element reaches a plateau. These curves show that the bath particle size as well as quantity affects the extent of the Hall bath-Mg reactions. At lower quantities, the reactions proceed to a greater extent with the smaller particle size, while at higher quantities, the reactions proceed to approximately the same extent. Since a mass balance indicates that only a very small fraction of the bath added actually reacts (0.1 lb. bath would add 1075 ppm Na to 27 lb. of aluminum), the data suggests the reaction rate is limited by the surface area of the bath available for reaction. With -48 mesh bath, 0.5 lb. of bath is required to provide enough surface area for the Na reaction to proceed to equilibrium, while it appears that 4.5 lb. of bath is required to provide enough surface area for the slower Ca reaction to proceed to equilibrium. With +4 mesh bath, it appears that 2.5 lb. of bath is required for reactions to proceed to equilibrium.

The shape of the curves in Figure 10 has an important implication for the Na reaction -- reducing the quantity of bath will not necessarily reduce the Na pick-up. If the reaction follows the same type of curve in a commercial furnace, it is important to know where on the curve today's plant operations fall. The plateau begins at 0.5 lb. bath; this translates to 1850 lb. in 100,000 lb. metal.

The reaction rates occurring just after the Mg addition were obtained by measuring the initial slopes of the concentration vs. time curves. Figure 11 shows the variation of the rates of the Na and Ca reactions with the quantity of bath added to the system. It is clear that the reaction rate is faster with the
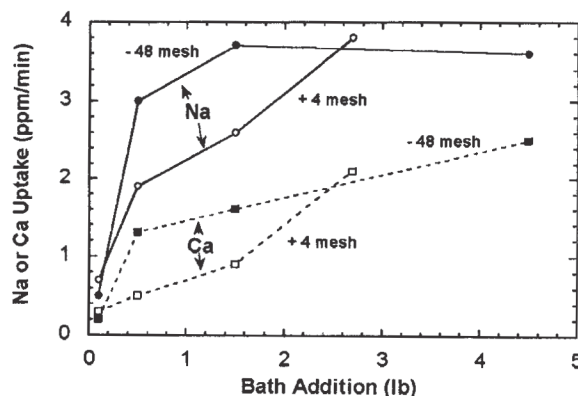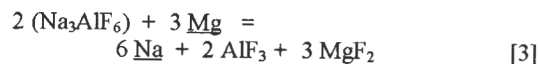

Figure 11 - Rates of Na and Ca pick-up resulting from reaction of cryolite bath with Mg in an Al-4.5%Mg alloy. Bath added was either -48 mesh or +4 mesh size. Temperature was 815 °C (1500 °F).

smaller particle size, and that the rate increases with the quantity of bath. These dependencies support the hypothesis that the reaction rate is limited by the available surface area of the bath particles.

IV. CONCLUSIONS

1. The bench-scale tests showed that the addition of Mg to aluminum in the presence of bath caused the Na and Ca concentrations in the metal to dramatically increase.

2. The data support the reactions:

$$2 (Na_3AlF_6) + 3 \underline{Mg} = 6 \underline{Na} + 2 AlF_3 + 3 MgF_2 \qquad [3]$$

and

$$CaF_2 + \underline{Mg} = \underline{Ca} + MgF_2 \qquad [2]$$

as being the reactions responsible for the Na and Ca pick-up.

3. The Na and Ca levels obtained in the tests were the result of two competing processes -- the addition by the above reactions and the removal by vaporization/oxidation. The reaction to add Na is approximately twice as fast as the reaction to add Ca.

4. The reactions were found to be strongly dependent on temperature. At 700°C (1292°F) the Na and Ca pick-up were approximately 16 ppm, while at 900°C (1652°F) the increases were approximately 320 ppm.

5. The reactions were both dependent on the Mg concentration. The variation of Na and Ca with the Mg concentrations gave quantitative evidence for the above reactions.

6. The reactions were influenced by both the quantity and particle size of bath added. The variation of the trace element increase with bath quantity was nonlinear, and in the case of Na, the pick-up reached a limiting value.

7. The reaction rates with -48 mesh bath were 50% to 100% greater than the reaction rates with +4 mesh bath.

V. ACKNOWLEDGMENTS

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