# CALCULATED ALUMINUM OXIDATION RATES DURING ROTARY FURNACE MELTING THROUGH FLUE GAS ANALYSIS

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#### Abstract

Continuous flue gas composition measurements (CO, CO2, O2, H2) were made for three rotary aluminum melt furnace heats, with air/oxy/gas combustion. In many cases, during rotary furnace aluminum melting, furnace atmosphere conditions become increasingly reducing (higher CO and H2, lower CO2) as the heat progresses. This suggests that aluminum is being oxidized.

For these three heats, the measured flue gas CO, CO2 and H2 compositions were utilized, with C, H and O balance equations, to calculate instantaneous aluminum oxidation rates throughout the heat.

For medium gauge clean scrap (clean crushed wheels), calculated aluminum oxidation rate is zero. For dross, calculated total aluminum oxidation loss is 0.5%, based on aluminum tap weight, for both 50% O2 combustion and 90% O2 combustion. Instantaneous aluminum oxidation rates are highest at the end of the heat, corresponding to higher temperatures.

# Introduction

Flue gas analysis, consisting of measuring CO, CO2, O2 and H2 concentrations in flue gases, can be utilized to improve combustion system performance. For example, with an empty furnace, or under non-reactive furnace load conditions, measurement of flue gas concentrations can allow one to calibrate and/or confirm the combustion control system settings to achieve the desired combustion atmosphere (oxidizing, reducing or neutral). Flue gas analysis can also allow one to calculate furnace infiltration air flow rate, and adjust the flue damper or furnace pressure control system to minimize infiltration air. Flue gas analysis can also help to diagnose and correct problems with combustion control equipment. Examples of the application of flue gas analysis to achieve these goals, under empty furnace or non-reactive load conditions, have been summarized in a prior publication [1], in which calculation of fuel savings economic \$ benefit is included for each example [1].

Flue gas analysis can also be utilized during the melting or heating process, with or without chemical interaction between the furnaces gases and load, to gain insight into the process performance. One example is the rotary furnace for aluminum melting.

Flue gas analysis has been performed on several rotary aluminum melt furnaces. Flue gas CO, CO2, O2, and H2 composition, along with flue gas temperature, are recorded throughout the batch melting cycle. It has been observed that even though a reducing burner setting is employed (example lambda 0.95 or 5% reducing), in many cases, as the heat progresses, the furnace

atmosphere becomes increasingly reducing (increased CO and H2, reduced CO2). As the burner settings have not changed, these increasingly reducing conditions indicate that aluminum oxidation must be occurring, acting as a "sink" for O2, as the heat progresses. This effect is typically more pronounced when melting dross (higher surface area) than medium or heavy gauge aluminum scrap (lower surface area), which suggests, logically, that aluminum oxidation rates are higher, for higher surface area materials such as dross.

It is possible to utilize the measured flue gas concentrations to calculate the amount of aluminum oxidized during melting. In this paper, three example rotary furnace aluminum melt heats are analyzed, and calculated aluminum oxidation rates are presented and discussed.

Of course, when melting painted, coated or oily scrap, significantly reducing furnace atmosphere conditions are often encountered, especially early in the heat, owing to the additional hydrocarbon load from the scrap. In the examples considered here, only clean scrap or dross was melted, so there was no additional hydrocarbon load from the scrap.

# Definitions and Combustion Equations: for air/oxy/gas combustion

G = natural gas flow rate NM3/hr (SCFH). G =1 as basis.

Natural gas is assumed to be 100% CH4.

A = total air/gas ratio (combustion + infiltration air). A = Ac + Ai Ac = combustion air/gas ratio; and Ai = infiltration air/gas ratio X = oxygen/gas ratio (from pure O2 i.e. purchased O2)

Perfect (stoichiometric) combustion equation:

Note that for complete CH4 combustion, O2 is distributed equally between C and H.

The term Lambda (L) has been developed to quantify the total amount of combustion O2 supplied:

Lambda = 1.0: perfect stoichiometric combustion Lambda > 1.0: oxidizing conditions Lambda < 1.0: reducing conditions

For air/oxy/gas combustion, Oxygen Participation (P) expresses the amount of combustion O2 provided by pure (purchased) O2 versus air. Air is assumed to be 21% O2 and 79% N2. Relating the oxy/gas ratio X and the total air/gas ratio A to lambda (L) and O2 participation (P):

P = X / (0.21A + X) and L = (0.21A + X)/2Or, X = 2PL and A = (2L - X)/0.21

For example, with air/gas combustion, X = 0 and P = 0. With 100% oxy/gas combustion, P = 1 and A = 0 with respect to combustion air supplied by a blower Ac (A can be > 0 and P < 1 considering infiltration air Ai). For air/oxy/gas combustion, P will be between 0 and 1.

During "empty furnace" or non-reactive load conditions, the following relations apply:

For Oxidizing Conditions, Non-reactive Load (Excess O2 is Supplied):

 $1 \text{ CH4} + \text{X O2} + \text{A } (0.21 \text{ O2} + 0.79 \text{ N2}) \rightarrow 1 \text{ CO2} + 2 \text{ H2O} + 0.79 \text{ N2} + (0.21 \text{ A} + \text{X} - 2) \text{ O2}$ 

For Reducing Conditions, Non-reactive Load (Not Enough O2 is Supplied for Complete Combustion):

Incomplete products of combustion will include CO and H2 in addition to CO2 and H2O:

1 CH4 + X O2 + A (0.21O2 + 0.79N2) → d CO2 + m CO + w H2O + h H2 + 0.79A N2 + 0 O2

From these relations, one can generate equations to express dry flue gas species concentrations (O2, CO2, CO, N2, H2). For analyzing reducing conditions, it can be useful to assume an equal split of O2 between C and H. From these equations, and measured flue gas species concentrations, during empty furnace or nonreactive load conditions, one can "calibrate and confirm" the combustion control system settings, calculate infiltration air quantities, and adjust the flue damper or furnace pressure control system to minimize air infiltration [1].

Flue gas compositions are reported as dry basis (H2O removed), as gas analyzers utilize dry flue gas samples (H2O is removed from the flue gas sample via chiller/condenser unit).

# **Calculating Aluminum Oxidation from Flue Gas Analysis**

The above relations are useful when analyzing "empty furnace" or non-reactive load conditions. However, when melting aluminum in a rotary furnace, it is often observed, through flue gas analysis, that as the melt cycle progresses, furnace atmosphere conditions become more and more reducing (increasing CO and H2, decreasing CO2). This indicates that some aluminum is being oxidized. In other words, some of the total combustion oxygen supplied stays in the furnace as Al2O3 ("sink"), and less of the oxygen exits the furnace as CO, CO2 and H2O.

Oxidation of aluminum can be expressed by adding an extra term to the above non-reactive load, reducing conditions equation:

For Reducing Conditions, Including Aluminum Oxidation:

1 CH4 + X O2 + A (0.21O2 + 0.79N2) → d CO2 + m CO + w H2O + h H2 + 0.79A N2 + 0 O2 + z Al2O3 In principle, this extra aluminum oxidation term (z Al2O3) could also be added to the oxidizing conditions equation. However, from a practical standpoint, it is not desirable to melt aluminum under oxidizing atmosphere conditions, since any excess O2 supplied could increase aluminum oxidation even further. Typically, when melting aluminum in a rotary furnace, reducing conditions (zero [O2] in flue gas) are observed. (Any free/excess O2 will typically react with Al).

From the above equation, mass balances for C, H and O are:

C: d + m = 1H: w + h = 2O: X + 0.21A = d + (m/2) + (w/2) + (3z/2)

Dry flue gas volume = d + m + h + 0.79A = 1 + h + 0.79A

Measured flue gas concentrations (dry basis):

[CO] = m/(1 + h + 0.79A)[CO2] = d/(1 + h + 0.79A)[H2] = h/(1 + h + 0.79A)

And by difference,

[N2] = 1-[CO]-[CO2]-[H2] = 0.79A/(1 + h + 0.79A)

Hence, above there are 6 equations (C, H, and O mass balance equations plus 3 measured flue gas composition) and 6 unknowns (A, d, m, w, h, and z). The oxygen and natural gas flow meter readings are assumed to be reliable (known X), but A is assumed to be unknown, since air flow meter accuracy can be lower, and infiltration air can be unknown. So with 6 equations and 6 unknowns, all terms can be solved for, and aluminum oxidation rate is then determined by multiplying z by the natural gas flowrate.

#### **Rotary Aluminum Melting Furnace Data**

In a closed barrel rotary furnace, the burner fires into the horizontal barrel-shaped furnace at the open barrel end. The burner is mounted to a door structure which closes this end of the furnace, and has a flue opening positioned above the burner. The burner flue gases turn around inside the furnace and exit through this flue opening. Batch charges are made by opening the door, and charging materials in sequence, then closing the door to resume melting. At the end of the batch melt cycle, molten aluminum is tapped by tilting the furnace and pouring out the door opening.

Flue gas compositions (CO, CO2, O2, H2) were measured from a 13 ton capacity rotary aluminum melt furnace, with an air/oxy/gas burner rated for 2.93 MW (10 MMBTU/hr). Flue gases were first measured with an empty, hot furnace, to calibrate and confirm the burner control system settings. Flue gases were then measured, continuously, throughout three melting heats.

The empty furnace flue gas data are shown in Figure 1. Burner firing rate was 2.64 MW (9 MMBTU/hr) with 50% O2 participation, and lambda was varied over a wide range, to establish a "calibration V curve". The results, shown in Figure 1, indicate that for this furnace, at these firing conditions, there was

very close agreement between measured and calculated flue gas composition.

At the high fire condition, for this furnace, it appeared that the furnace (closed barrel) was under positive pressure, with little to no infiltration air. Based on the empty furnace flue gas measurements, the calculated infiltration air level was 0 to 52.6 NM3/hr (0 to 2000 SCFH), corresponding to 0-4% of the combustion air flow, so infiltration air was assumed to be zero.



Figure 1. Measured vs Calculated Flue Gas Composition For Hot Empty Rotary Furnace.

The burner was then changed to low fire (0.59 MW or 2 MMBTU/hr), at lambda = 0.95 and O2 P = 0.50. Measured flue gas compositions indicated slightly oxidizing conditions, even though lambda was set for 0.95. This suggested that there was some infiltration air being pulled into the furnace, at low fire. Calculated infiltration air was 68.4 NM3/hr (2602 SCFH), which in this case is 29% of combustion air at this low firing rate. So, at lower firing rates, or lower burner POC volumes, there can be more significant amounts of infiltration air, which is typical for these types of furnaces [1].

Continuous flue gas measurements (CO, CO2, O2, H2), along with flue gas temperature, were recorded, for three rotary furnace melting heats:

Heat 1) Clean Crushed Wheels. 2.64 MW (9 MMBTU/hr), 50% O2, lambda = 0.95

Heat 2) Dross, 2.64 MW (9 MMBTU/hr), 50% O2, lambda = 0.95

Heat 3) Dross, 2.34 MW (8 MMBTU/hr), 90% O2, lambda = 0.95

These data are shown in Figures 2, 3 and 4 for these three heats. Throughout all heats, measured flue gas [O2] concentration was zero, indicating reducing conditions throughout each heat.



Figure 2. Flue Gas Composition and Temperature For Clean Crushed Wheels







Figure 4. Flue Gas Composition and Temperature For Dross, at 90% O2

## **Observations from Rotary Furnace Flue Gas Melting Data**

# Heat 1 Clean Crushed Wheels:

As shown in Figure 2, the measured CO, H2 and CO2 levels corresponded very closely to the empty furnace data, especially early in the heat. CO and H2 levels are fairly low. As the heat progresses, there is a very slight increase in reducing atmosphere conditions (slight increase in CO and H2, slight decrease in CO2), suggesting that there could be a small amount of aluminum oxidation occurring late in the heat.

# Heat 2 Dross, 2.64 MW (9 MMBTU/hr), 50% O2:

As shown in Figure 3, at the beginning of the heat, measured CO, H2 and CO2 levels corresponded very closely to the empty furnace data. But over the last 35 minutes, CO and H2 levels increased, with CO2 decreasing, as compared to Heat 1. This suggests that there was more aluminum oxidation occurring, as compared to Heat 1.

# Heat 3 Dross, 2.34 MW (8 MMBTU/hr), 90% O2 :

As shown in Figure 4, CO and H2 levels started off slightly higher than the other two heats, and climbed to higher levels later in the heat, with CO2 levels dropping more significantly. Since at 90% O2 participation there is less N2 (air) dilution and lower total burner POC volume, all gas concentrations will be higher. However, there appears to be a more significant shift towards more reducing atmosphere conditions, as compared to the other two heats, suggesting higher aluminum oxidation rates, at the end of the heat. Note, this melt cycle ran to a higher ending temperature than the previous (707 C vs 661 C), which can also correspond to higher oxidation rates.

## **Calculated Aluminum Oxidation Rates: Discussion**

Calculated aluminum oxidation rates are shown in Table I, for the 3 melting heats considered, along with calculated total combustion air/gas ratio A and calculated infiltration air ratio Ai. The calculated fraction of total O2 reacting with aluminum is also shown.

Table I. Calculated Aluminum Oxidation Rates for Three
Rotary Furnace Melting Heats

Clean Crushed Wheels, 2.64 MW, 50% O2, L = 0.95. Burner POC = 1530 NM3/hr									
									fraction of
	Flue	meas	meas	meas	calc	calc	calc	calc Al	total O2
Time	Temp C	[CO]	[CO2]	<u>[H2]</u>	A	Ai	Ai/A	oxid kq/hr	rcting w Al
8:58	705	0.026	0.190	0.010	4.536	0.012	0.0026	-5.40	-0.0074
9:00	709	0.028	0.187	0.013	4.545	0.021	0.0046	-0.0617	0
Dross, 2.64 MW, 50% O2, L = 0.95. Burner POC = 1530 NM3/hr									
									fraction of
	Flue	meas	meas	meas	calc	calc	calc	calc Al	total O2
Time	Temp C	[CO]	[CO2]	<u>[H2]</u>	A	Ai	Ai/A	oxid kg/hr	rcting w Al
13:00	585	0.040	0.167	0.027	4.684	0.160	0.034	36.5	0.050
13:10	616	0.045	0.162	0.032	4.654	0.130	0.028	43.2	0.060
13:18	651	0.039	0.165	0.030	4.753	0.229	0.048	44.8	0.062
13:21	661	0.039	0.166	0.028	4.736	0.212	0.045	41.2	0.057
_			-						
Dross, 2.34 MW, 90% O2, L = 0.95. Burner POC = 760 NM3/hr									
									fraction of
	Flue	meas	meas	meas	calc	calc	calc	calc Al	total O2
Time	Temp C	[CO]	[CO2]	[H2]	<u>A</u>	Ai	Ai/A	oxid kg/hr	rcting w Al
8:15	639	0.061	0.454	0.022	1.138	0.233	0.205	10.0	0.016
8:42	663	0.082	0.399	0.049	1.237	0.332	0.268	35.9	0.056
8:44	670	0.101	0.382	0.063	1.190	0.285	0.239	44.0	0.068
8:48	688	0.125	0.333	0.100	1.222	0.317	0.259	72.0	0.112
8:52	702	0.136	0.272	0.133	1.424	0.519	0.364	114.9	0.178

# Heat 1 Clean Crushed Wheels:

Calculated values are shown in Table I for the two ending data points, 8:58 and 9:00. At the end of the heat, these represent the "most reducing" conditions, along with the highest temperature, and would suggest the highest aluminum oxidation rates. But the calculation shows zero aluminum oxidation – or a negative value, with less than 1% of total O2 reacting with aluminum (either way). So, within the accuracy of these measurements, this calculated Ai shows that the assumption of zero air infiltration is valid, for these combustion settings.

Note, earlier in the heat (not shown in Table 2), calculated aluminum oxidation rates were consistently negative, as high as - 65 kg/hr (-144 lb/hr), at the start of the heat, corresponding to as much as -9% of total O2 "reacting" with aluminum. Calculated aluminum oxidation rate steadily increases (less negative value) as the heat progresses, to a value of zero at heat end. These negative calculated values suggest that there may be some "offset" in the absolute calculated value for aluminum oxidation, due to absolute measurement inaccuracies.

Consider for a moment that this might be true. For example, suppose there really was 1% aluminum oxidation occurring, and offset in the calculation, due to absolute measurement inaccuracies, showed a calculated value of 0% oxidation. If this were the case, and aluminum oxidation loss was actually 1%, then by calculation it can be shown that the [CO] and [H2] concentrations would have increased by 3% (from 2% to 5%). From the flue gas data, the [CO] and [H2] concentrations did not increase by this amount, indeed the "deflection" in [CO] and [H2] concentration toward the end of the heat was 1%, not 3%.

So, based on the very small observed relative increase in [CO] and [H2] concentrations as this heat progressed, it can be concluded that the amount of aluminum oxidation occurring was very small, essentially zero. (Comparitively, the two dross heats showed a

much more significant relative increase in [CO] and [H2] concentration as the heat progressed, suggesting higher aluminum oxidation rates, and the calculations bear this out).

Typical recovery from this charge material (clean crushed wheels) is 95%+. This analysis suggests that there is essentially no additional aluminum oxidation occurring in the melt process, and overall melt losses represent the original oxide coating on the scrap as received.

#### Heat 2 Dross 2.64 MW (9 MMBTU/hr), 50% O2:

For roughly the first half of the heat, calculated aluminum oxidation was slightly negative, suggesting zero aluminum oxidation. Calculated Ai levels were also very small, negative or positive, suggesting essentially zero infiltration air.

Later in the heat, starting after 12:43, positive values for aluminum oxidation began to be calculated. Four example calculation data points are shown in Table 2, for 13:00, 13:10, 13:18, and 13:21. For the last 35 minutes of this heat, calculated aluminum oxidation rate is about 40.8 kg/hr (90 lb/hr), corresponding to 5-6% of total oxygen reacting with aluminum. (The low Ai/A ratio also indicates that there is essentially zero infiltration air).

This heat endpoint was at 661 C, corresponding to 40.8 kg/hr (90 lb/hr) aluminum oxidation rate, and 5.7% of O2 reacting with Al.

Calculated total aluminum oxidation for this heat is 24 kg (53 lbs), or about 0.5% of aluminum tap weight. This dross typically yields 65-75% recovery, so the contribution of aluminum oxidation due to the melt process appears to be fairly small.

#### Heat 3 Dross 2.34 MW (8 MMBTU/hr), 90% O2:

For roughly the first half of this heat, the calculated aluminum oxidation rate was about 9 kg/hr (20 lb/hr), corresponding to about 1-2% of total O2 reacting with aluminum. This was calculated consistently for all data points up through 8:32. The 8:15 data point is shown in Table 2 as an example. So during this first stage, corresponding to 30 minutes burner on time (factoring out delays), calculated aluminum oxidation rate is 9 kg/hr (20 lb/hr). Also, calculated air infiltration is significant, as shown by the Ai/A ratio. This is due to the reduced burner POC volume. Calculated average infiltration air level for this heat is 72.4 NM3/hr (2755 SCFH), which corresponds very well with the empty furnace Ai calculation with reduced burner POC.

Starting after 8:32, calculated aluminum oxidation rates steadily increase, from 9 kg/hr (20 lb/hr) up to 113 kg/hr (250 lb/hr). Four example data points are shown in Figure 2 (8:42. 8:44, 8:48 and 8:52). The calculated portion of total O2 reacting with A1 increases to 17.8% at the end of the heat. This corresponds to the most reducing atmosphere conditions, and the highest temperature (707 C).

At 8:42, at 663 C, the calculated aluminum oxidation rate is 35.8 kg/hr (79 lb/hr), corresponding to 5.6% of O2 reacting with Al. This is equivalent to the calculated oxidation rate for the 50% O2 dross heat, at the same temperature (endpoint for the 50% O2 dross heat). However, for this 90% O2 dross heat, the burner on-time was extended, to reach an end-of-heat temperature of 707 C.

During the last 10 minutes of this heat, as flue temperature increases from 663 to 707 C, the calculated aluminum oxidation rate significantly increases, from 44 kg/hr to 113 (97 lb/hr to 250).

Calculated total aluminum oxidation for this heat is 25 kg (56 lbs), or again about 0.5% of aluminum tap weight. For 65-75% recovery dross, this calculated 0.5% oxidation loss represents a small contribution.

Accounting for the higher end-of-heat temperature for this heat, as compared to the 50% O2 dross heat (Heat 2), and factoring in an extra 5 minute holding delay near the end of this heat, one could expect that overall total aluminum oxidation for this 90% O2 dross heat could have been less than the 50% O2 heat. This would typically be attributed to the faster melt time (lower overall exposure to the furnace atmosphere). This could be worthy of further study, by analyzing additional heats in more detail.

Figure 5 compares the calculated aluminum oxidation rates vs flue temperature, for the two dross heats studied, for 50% O2 and 90% O2, utilizing data from the latter stages of each heat. Figure 5 shows that at the same temperature, calculated oxidation rate is the same, or less, for 90% O2 vs 50% O2. For the 90% O2 heat, as burner on-time is extended to the ending 707 C temperature, the calculated aluminum oxidation rate steadily increases. Since the 50% O2 heat ended at 661 C, one cannot accurately compare oxidation rates for 50% O2 vs 90% O2 at higher tempertures, with this data set.



Figure 5. Calculated Aluminum Oxidation Rate vs Temperature For Two Dross Heats at 50% O2 and 90% O2

It would be interesting to analyze additional heats, to more accurately compare oxidation rates vs temperature, for varying %O2 burner settings.

It is interesting to note that even though the clean crushed wheels heat ran to 700 C, at end-of-heat the calculated aluminum oxidation rate was zero.

#### Conclusions

As illustrated with the 3 example rotary aluminum melt furnace heats studied, flue gas analysis can be utilized to indicate when aluminum oxidation is occurring, by shift in the furnace atmosphere to more reducing conditions as the batch melting cycle progresses. A greater relative change towards increasingly reducing conditions indicates higher rates of aluminum oxidation. Aluminum oxidation rates can be calculated, by C, H and O mass balance, with the measured flue gas CO, CO2, O2 and H2 concentrations.

These calculations, for the three heats studied, show:

- For clean crushed wheels (medium gauge, clean scrap), there was essentially zero calculated aluminum oxidation during melting, with 50% O2.
- For dross, with either 50% O2 or 90% O2 combustion settings, the calculated total aluminum oxidation during melting was 0.5% (based on aluminum tap weight), even though the end-of-heat temperature was lower for the 50% O2 heat than for the 90% O2 heat.
- At the end of the heat, calculated instantaneous aluminum oxidation rates are highest, corresponding to the highest temperature.

Accounting for the higher "end of heat" temperature, and an extra 5 minute holding delay encountered near the end of the heat, it could be expected that total aluminum oxidation could be less, for the 90% O2 dross heat, as compared to 50% O2. This would typically be attributed to the faster melt time with 90% O2 (oxy/fuel), which reduces total exposure time to the combustion atmosphere.

These data and calculations show that aluminum oxidation rate increases, as the heat progresses and temperature increases. Calculated oxidation rates are higher for dross than for clean crushed wheels. Increases in instantaeous oxidataion rate can be significant, at higher temperatures. This illustrates the importance of accurately and consistently defining end-of-heat conditions, to "not overheat the batch". At the end of the heat, to maximize recovery, it is important to cut the burner off as soon as desired final temperature is reached. Overheating can lead to significantly increased aluminum oxidation.

## References

1. Stewart Jepson, "Utilizing Flue Gas Analysis to Improve Combustion System Performance", *Industrial Heating*, October 2014, 43-46.